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Proceedings of the International Nitrogen Initiative Workshop, linking experts of the Convention on Long-range Transboundary Air Pollution and the Convention on Biological Diversity

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Preface

This volume describes the fruits of the International Expert Workshop on Nitrogen Deposition, Critical Loads and Biodiversity that was held on 16-18th November 2009, in Edinburgh, UK. The need for the workshop emerged as a result of discussion within the International Nitrogen Initiative (INI)—a joint project of the International Geosphere Biosphere Programme (IGBP) and the Scientific Committee on Problems of the Environment (SCOPE). The INI highlighted that, while there was a wealth of evidence on the magnitude, components and effects of atmospheric nitrogen deposition on floral biodiversity in Europe and North America, there was an obvious lack of information on impacts on above- and below-ground fauna and all impacts in other parts of the world, with no clear overview of how the different strands of evidence fitted together.

Building on underpinning funds from the Packard Foundation, INI therefore joined forces with several other initiatives—the COST 729 and Nitrogen in Europe (NinE) programmes of the European Science Foundation (ESF) and the European Union Integrated Project NitroEurope, together with the US Environmental Protection Agency, the Ministry of Infrastructure and the Environment (Minienm; formerly VROM), the Netherlands, the Stockholm Environment Institute (SEI), and the Centre for Ecology and Hydrology (CEH). The result was the basis to invite the world's leading experts on nitrogen deposition and its effects to Edinburgh to share experience and debate the future challenges.

It is important to recognize, however, that this could not be a purely academic endeavour. As has been shown by the Expert Workshop, atmospheric nitrogen deposition represents a major threat to the biodiversity of many of the world's most precious ecosystems. With this in mind, it was essential to place the workshop in the context of international actions to manage air pollution and biodiversity. The leading agreements of the United Nations in this regard are the Long-Range Transboundary Air Pollution (LRTAP) Convention, under the United Nations Economic Commission for Europe (UNECE), and the Convention on Biological Diversity (CBD), which has a global coverage. Although each Convention is highly relevant, they have very different ways of working, and, until the Edinburgh meeting, there had been insufficient working contacts between them. The Workshop therefore included a specific objective to bring together leading experts from both Conventions as a basis for improving cooperation and mutual understanding. At the same time, the policy drive of the Conventions would feed back to inform the future scientific agenda.

The outcome was a joint workshop between experts from both the LRTAP Convention and the CBD, together with many other leading experts globally. In total, 140 experts from 30 countries participated, representing most continents and regions of the world. The proceedings and conclusions of the Expert Workshop are reported in this volume, while selected papers (see Appendix) are further developed in a Special Section of the journal Environmental Pollution (Goodale et al. 2011). In parallel the outcomes have been reported to the LRTAP and CBD processes (UNECE 2009).

We take this opportunity to thank the members of the Organizing Committee: Albert Bleeker, Roland Bobbink, Mercedes Bustamante, Tom Clair, Frank Dentener, Nancy Dise, Jan Willem Erisman, Jean Paul Hettelingh, Duan Lei, Annika Nordin, Till Spranger, Wim de Vries, Zifa Wang and, last but not least, Jim Galloway who originally proposed the workshop. The Organizing Committee was co-chaired by Kevin Hicks and Richard Haeuber, while Mark Sutton acted as workshop host. We thank the Centre of Ecology & Hydrology (Edinburgh), and SCOPE, which together provided the secretariat prior, during and following the workshop, held at the George Hotel in Edinburgh. In this regard, we extend our special thanks to the key individuals who provided the organizational foundation for the success of the workshop: Clare Howard, Agnieszka Becher (CEH), Susan Greenwood Etienne (SCOPE) and Allison Leach (University of Virginia, USA). We would also like to thank Bill Bealey (CEH) for master-minding the electronic registration process, Richard Clay (SEI) for his work on the flyer and other materials for the workshop and Steve Johnson at the University of Virginia for his assistance with the workshop website. Special thanks are also due to Henk Strietman at Minienm in the Netherlands, Sjamsudin Chandrasa at COST 729 and Ellen Degott-Rekowski at ESF for their advice and support. The European Union kindly provided supporting funds allowing completion of this publication under the frame of the ÉCLAIRE project (FP7) and we gratefully acknowledge the encouragement of José M. Giménez Mingo of the European Commission. Finally, we would like to thank Tamara Welschot and Judith Terpos at Springer for their patience and advice.

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Acronyms and Abbreviations

ANC	Acid Neutralizing Capacity
BC	Base Cation
BNF	Biological Nitrogen Fixation.
CAD	Composition of Asian Deposition Network
CAFÉ	Clean Air for Europe
CAP	Common Agricultural Policy of the European Union
CBA	Cost Benefit Analysis—an economic tool to weigh the total expected costs against the total expected benefits of one or more actions.
CAPMoN	Canadian Air and Precipitation Monitoring Network
CASTNET	United States Clean Air Status and Trends Network
CBD	UN Convention on Biological Diversity
CLE	Critical level
CL	Critical load
DEBITS	Deposition of Biogeochemically Important Trace Species
DIN	Dissolved Inorganic Nitrogen
DON	Dissolved Organic Nitrogen
EANET	Acid Deposition Monitoring Network in East Asia
EMEP	European Monitoring and Evaluation Programme of the LRTAP Convention
GAW	Global Atmospheric Watch
GHG	Greenhouse Gas—includes carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), ozone (O_3), water vapour and various other gases.
GWP	Global Warming Potential
GPNM	Global Partnership on Nutrient Management—established under the lead of UNEP
HNO_3	Nitric acid—a reactive gas air pollutant
HONO	Nitrous acid—a reactive gas air pollutant
ICP	International Cooperative Programme of the LRTAP Convention
IDAF	DEBITS in Africa
IGAC	International Global Atmospheric Chemistry
IGBP	International Geosphere-Biosphere Programme

INI	International Nitrogen Initiative
IPBES	Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services
IPCC	Intergovernmental Panel on Climate Change
LRTAP	UNECE Long-range Transboundary Air Pollution Convention
NADP	United States National Atmospheric Deposition Program
N_2	Di-nitrogen—unreactive nitrogen gas making up 78 % of the atmosphere
N_2O	Nitrous oxide—a greenhouse gas
NEC(D)	National Emissions Ceilings (Directive) of the European Union
NH_3	Ammonia—a reactive gas air pollutant
NH_4^+	Ammonium—ion present in aerosols and precipitation
NH_x	Collective term for NH_3 and NH_4^+, inorganic reduced nitrogen
NO	Nitric oxide—a reactive gas air pollutant
NO_2	Nitrogen dioxide—a reactive gas air pollutant
NO_2^-	Nitrite—ion present in water samples
NO_3^-	Nitrate—ion present in aerosols, precipitation and water samples
NO_x	Nitrogen oxides (the sum of NO and NO_2)
NO_y	Collective term for inorganic oxidized nitrogen, including NO_x, NO_3^-, HONO, HNO_3 etc.
N_r	Reactive nitrogen—collective term for all nitrogen forms except for unreactive di-nitrogen (N_2). Includes, NH_x
O_3	Ozone—tropospheric ozone (ozone in the lowest 10–20 km of the atmosphere) unless specified in text
PAN	Peroxyacytyl nitrate ($C_2H_3O_5N$) is one constituent of photochemical smog
$PM_{2.5}$/PM_{10}	Particulate Matter. Aerosol mass contained in particles with an aerodynamic diameter below 2.5 (or 10 for PM_{10}) micrometre, measured with a reference technique
SAC	Special Area(s) of Conservation designated under the Habitats Directive of the European Union
TFRN	Task Force on Reactive Nitrogen of the LRTAP Convention
UKEAP	United Kingdom Eutrophying and Acidifying Pollutants network
UN	United Nations
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
VOCs	Volatile Organic Compounds
WGE	Working Group on Effects of the LRTAP Convention
WGSR	Working Group on Strategies and Review of the LRTAP Convention
WMO	World Meteorological Organization

Contents

Chapter 1
Nitrogen Deposition, Critical Loads and Biodiversity: Introduction

W. Kevin Hicks, Richard Haeuber and Mark A. Sutton

Abstract Human activities, related primarily to agricultural practices and the combustion of fossil fuels for energy and transport, have caused steep increases in global emissions of reactive nitrogen (N_r) over the last 50 years (e.g., Galloway et al. *Biogeochemistry, 70*(2), 153–226, 2004, *Science, 320,* 889–892, 2008). Atmospheric nitrogen (N) deposition derived from these sources represents a major threat to natural ecosystems around the world, leading to changes in structure, function and the associated biodiversity (e.g. Phoenix et al. *Global Change Biology, 12,* 470–476, 2006; Bobbink et al. *Ecological Applications, 20,* 30–59, 2010). Although substantial progress has been made in past decades, especially in Europe and North America, major uncertainties remain regarding the global perspective. In the last 30 years, Europe and North America have made great progress in assessing the problem, although the knowledge base is greater for impacts on flora than fauna; in many other parts of the world, however, the required datasets and assessments in many cases do not yet exist. This chapter summarizes the approach taken in the Workshop on Nitrogen Deposition, Critical Loads and Biodiversity and outlines the contents and structure of the book.

Keywords Nitrogen deposition • Biodiversity • Critical loads • Ecosystem services • Monitoring and modelling

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1.1 Background and Problem

Increases in nitrogen (N) deposition to sensitive ecosystems in broad areas of Europe, North America, and parts of Asia, over the last 50 years have resulted in losses of plant diversity, shifts in plant community composition, alteration of food webs and changes in ecosystem services (Bobbink et al. 2010; Sutton et al. 2011). Global scale modelling using current N emission scenarios indicates that most regions around the globe will have increased rates of atmospheric N deposition over the next decades, causing concern about significant impacts on global biodiversity (Dentener et al. 2006). Increased N emissions will also have impacts on human health (e.g. as precursors of $PM_{2.5}$ and ozone) and adversely affect crop yields though increased ozone concentrations (Sutton et al. 2011). However, not all the environmental impacts of N deposition are negative, for example, in some cases N deposition can also have beneficial effects on crop yields and also increase carbon (C) sequestration in certain vegetation types through its fertilizing effect (e.g., Butterbach-Bahl et al. 2011). This volume considers impacts on biodiversity in the context of these other important policy relevant impacts.

In some parts of the world, such as Europe and Canada, international concern over acidification and eutrophication impacts prompted the development of an effects threshold approach for assessing the impacts of acidic deposition, including N deposition, known as "critical loads" (CLs). The CLs approach has been a valuable tool to assess present and future risks of adverse effects of N deposition on biodiversity. Critical load exceedance for N has been used as an indicator by the Streamlining European 2010 Biodiversity Indicators (EEA 2007; SEBI 2010) for assessing, reporting on and communicating achievement of the 2010 target to halt biodiversity loss under the CBD. However, it is unclear if CLs and their exceedance can be adopted usefully for global application under the CBD.

In addition to Europe and North America, N deposition is above or approaching critical loads in parts of Asia, Africa and Latin America. However, insufficient studies exist on the effects of N deposition in these regions to provide a basis for comprehensive application of the CLs approach. Other shortcomings in several areas currently hamper adoption of the critical thresholds approach and assessment of N impacts in general:

- Significant uncertainty in total deposition estimates around the globe, particularly for dry deposition;
- Uncertainty about the relationship between biodiversity loss and N dynamics and the translation into critical loads;
- Uncertainty in the global transferability of critical level values for ammonia and nitrogen oxides concentrations developed in Europe;
- Need for more field-based evidence for biodiversity effects, where plant studies are often lacking in many regions and studies on animals and other groups are even scarcer;
- More persuasive indicators of biodiversity loss in areas that have exceeded critical N loads are required on a global scale;

- Further development of tools/indicators for N induced biodiversity loss should ideally take account of impacts of N addition on valuable ecosystem services such as C sequestration and regulating services related to soil and water quality, in interaction with climate change.

1.2 Workshop Approach

The Expert Workshop considered five key topic areas in plenary and breakout sessions. Overarching themes included the exchange of information between different regions and disciplines and how measurements and approaches for assessing N deposition and biodiversity loss can be harmonized at a global scale. Key topic areas, serving as the focus for plenary and Working Group sessions included:

i. Progress in monitoring and modelling estimates of N deposition at local, regional and global scales;
ii. Factors affecting N deposition impacts on terrestrial and aquatic ecosystem biodiversity;
iii. Development of the critical loads concept and its application to different regions of the world;
iv. Importance of N deposition effects on ecosystem services and interactions with other pollutants and climate change;
v. Implications of current knowledge of N deposition and its impacts pertaining to policy, management and capacity building needs.

1.3 Structure and Purpose of Book

This introduction is followed by a series of sections based on the five key topic areas that served as the focal points for plenary and Working Group sessions. Each section contains an updated version of the background document that was written before the workshop to inform the discussions in each session, followed by the papers submitted by the speakers of the workshop on the key topics. Topics (iv) and (v) have been combined into one section. The final section reports the conclusions and recommendations from the breakout groups and ends with a synthesis and summary for policy makers.

This book is intended to serve as a resource for:

- Scientists involved from both air pollution and biodiversity fields;
- Policy makers in many countries globally, including especially those with an interest in the UN Convention on Biological Diversity and the UNECE Convention on Long-range Transboundary Air Pollution;
- Agencies responsible for conservation, land management, and natural resources;

- Environment and pollution control agencies;
- Environmental managers;
- Post graduates and undergraduates.

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Part I
Monitoring and Modelling Atmospheric Nitrogen Deposition

Chapter 2
Progress in Monitoring and Modelling Estimates of Nitrogen Deposition at Local, Regional and Global Scales

Frank Dentener, Robert Vet, Robin L. Dennis, Enzai Du, Umesh C. Kulshrestha and Corinne Galy-Lacaux

Abstract This chapter discusses the status and progress of activities around the world to measure and model dry and wet deposition of reactive nitrogen (N_r), i.e. the final removal processes from the atmosphere, at the local, regional and global scales. It gives an overview of present status and developments in networks and techniques for measuring deposition of N_r. We describe recent developments in the modelling of emissions and deposition, and finish by giving research and policy recommendations regarding N-deposition measurement and modelling, including the need for;

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- an increase in the number of regional-scale, long-term monitoring sites for the routine measurement/estimation of wet and particularly dry deposition worldwide;
- an increase in the number of N species routinely measured, especially dissolved organic N (DON), ammonia (NH_3) and nitrogen dioxide (NO_2);
- global and regional models to improve their estimation of dry deposition and their resolution, especially in situations with complex topography.

Keywords Atmospheric deposition • Emissions • Measurement • Modelling • Oxidized and reduced deposition • Wet and dry deposition

2.1 Introduction

Reactive nitrogen (N_r) compounds in the oxidized form (NO_y) and the reduced form (NH_x) play a central role in the chemistry of the atmosphere as well as in the functioning of marine, freshwater and terrestrial ecosystems. There is ample evidence that increasing human activities seriously disturb the natural nitrogen (N) cycle. Reactive nitrogen enters the environment through a number of processes related to fertilization, waste discharge and atmospheric emissions, transport and deposition.

Here we discuss progress pertinent to measurement and modelling of dry and wet deposition of N_r, i.e. the final removal processes from the atmosphere, at the local, regional and global scales. We cover (a) present status and developments in networks and techniques for measuring deposition of N_r, (b) recent developments in the modelling of emissions and deposition, and (c) research and policy recommendations regarding N-deposition.

2.2 Measurements

2.2.1 Introduction

The term dry deposition applies to all removal processes of gases and aerosols at the earth's surfaces; this process does not necessarily have to be 'dry', in fact the removal of gases like SO_2 is rather efficient to wetted surfaces or ocean water. The research of dry deposition processes has been stimulated by the acid rain problem in the USA, Europe and Asia. Many different techniques have been used to measure dry deposition fluxes such as gradient methods, eddy correlation techniques, chambers or the use of artificial surfaces. Whereas these measurements provided new insights into the processes playing a role for removal of air pollutants by dry deposition, they were by no means routine determinations, and required a large effort in terms of equipment, labor and interpretation. The accuracy of the measurements was in the best case of the order of ±30%. The validity of the measured fluxes for a larger region (the so called 'fetch') was in most cases rather limited. Aircraft measurements provided a new method for estimating dry deposition fluxes, mainly by means of eddy correlation techniques. However these measurements are generally very expensive, and the sampling period limited. The geographical coverage was obviously much better than the 'local' measurements mentioned previously and in addition showed the complex behavior of boundary layer dynamics and the resulting effect on dry deposition. Measurements are generally presented as dry deposition velocities [cm/s] or as surface resistances, which is approximately reciprocal of the dry deposition velocity.

Wet deposition refers to the removal of gases and aerosols by scavenging in clouds (uptake in cloud droplets/ice crystals, formation and sedimentation of rain) and precipitation scavenging (falling rain droplets and frozen hydrometeors interacting with particles and gases). Measurements of wet deposition are almost entirely made by collection and analysis of rain and snow samples. Whereas in the past frequently bulk samplers were utilized, which measured a substantial and largely unquantified amount of dry deposition, nowadays mostly wet-only samplers are employed, opening and closing the sampler at the beginning and end of rainfall events.

2.2.2 Worldwide Networks of Wet Deposition

Continuous large-scale measurements of wet deposition have been made since the 1970s. Since then, many international, national, and sub-national monitoring networks/programs have been operated and, in some cases, expanded, reduced and/or closed. The major long-term, large scale, regionally-representative monitoring networks that exist at this time include the Canadian Air and Precipitation Monitoring Network (CAPMoN) and related Canadian provincial networks, the Acid Deposition Monitoring Network in East Asia (EANET), the European Monitoring and Evaluation Program (EMEP), the International Global Atmospheric Chemistry (IGAC) Program's Deposition of Biogeochemically Important Trace Species Project (DEBITS) in Africa (IDAF), Asia (CAD and EANET) and South America (LBA), the United States National Atmospheric Deposition Program (NADP), and the World Meteorological Organization Global Atmosphere Watch Precipitation Chemistry Program (GAW). A number of other national and sub-national networks also operate in countries such as Russia, China, Korea, Taiwan, and India. These networks typically measure the concentrations of the following major anions and cations in precipitation: SO_4^{2-}, NO_3^-, Cl^-, H^+, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+ and K^+(and in some cases, organic acids and phosphorus) as well as precipitation amounts. Figure 2.1 shows the regional sites of the aforementioned major networks that reported data in 2005.

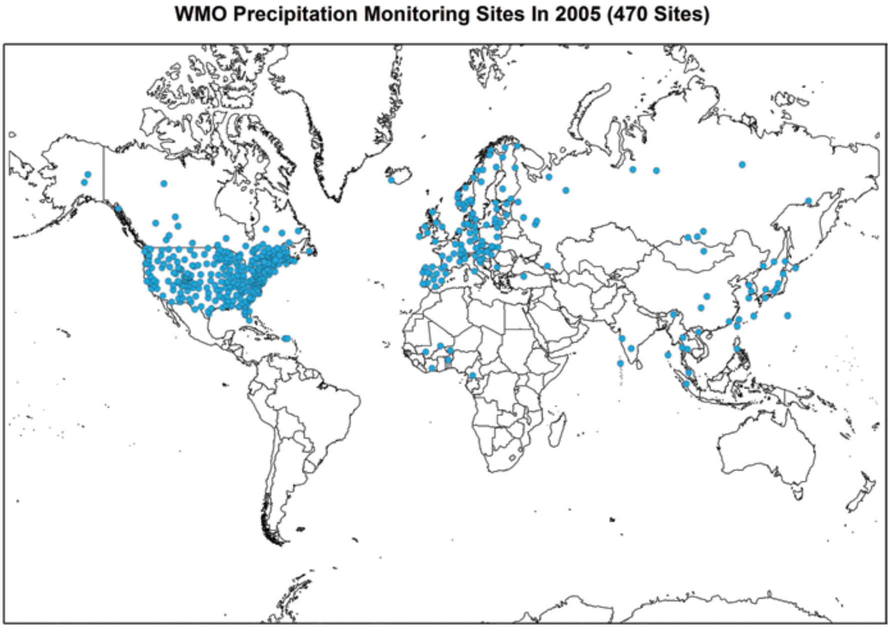

Fig. 2.1 Regional-scale wet deposition monitoring sites that reported data in 2005

The scientific objectives of wet deposition monitoring networks vary depending on the country and/or the specific scientific program, but most networks focus on the following: defining the spatial patterns of ion wet deposition, investigating the long term trends of ions in precipitation, evaluating chemical transport models, calculating critical loads, and investigating atmospheric processes. The World Meteorological Organization (WMO), through its Scientific Advisory Group for Precipitation Chemistry is currently preparing a scientific assessment of global deposition and, to that end, has integrated and synthesized data from most of the foregoing networks. An example of that effort, a preliminary global pattern of N-NO_3^- wet deposition in 2005, is shown in Fig. 2.2.

Over the last decade, the number of wet deposition monitoring sites has generally increased in Asia, Eastern Europe and the USA. Unfortunately, large areas of the world still have few if any measurements, namely, South America, Africa, Australia, Oceania, western/northern Canada, the oceans, and the polar regions.

The major problems with wet deposition measurements, beyond the paucity of measurement sites, are poor laboratory performance and inaccurate field measurements. The World Meteorological Organization is addressing these problems through the long-term operation of semi-annual laboratory inter-comparison studies and the publication of a manual for the proper measurement of wet deposition (WMO 2004). Nevertheless, these problems persist in many countries.

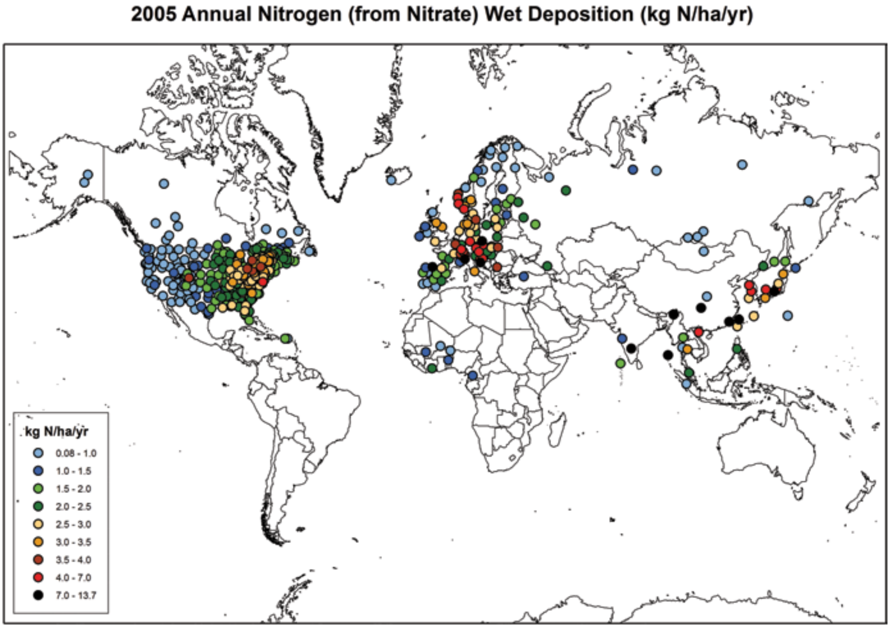

Fig. 2.2 Preliminary 3-year average annual deposition of wet deposition of NO_3^- as N (in kg N ha^{-1} $year^{-1}$) for the period 2005. Some sites do not have all 3 years of data

2.2.3 Dry Deposition Measurement Networks

Dry deposition is not measured directly by large-scale monitoring networks because of the requirement for sophisticated instrumentation and methods. Instead, networks measure ambient gas and particle concentrations and model the associated dry deposition velocities. This method, which ultimately requires multiplying the ambient concentrations by the modelled dry deposition velocities, is called the *inferential technique*. Only two major networks currently make regionally-representative routine inferential estimates of dry deposition fluxes, namely, the United States Clean Air Status and Trends Network (CASTNET) and the Canadian Air and Precipitation Monitoring Network (CAPMoN)Canadian Air and Precipitation Monitoring Network (CAPMoN). The former currently comprises 86 sites in the USA (www.epa.gov/castnet/docs/CASTNET_factsheet_2007.pdf) and the latter 15 sites in Canada (www.msc.ec.gc.ca/capmon/index_e.cfm). An inferential model is currently under development for Africa under the IDAF (**I**GAC/**D**EBITS/**AF**rica) project of the International Global Atmospheric Chemistry/Deposition of Biogeochemically Important Trace Species (IGAC/DEBITS) program (http://medias.obs-mip.fr/idaf).

Unfortunately, neither the US nor Canadian networks measure all of the major oxidized and N_r species needed to estimate the total atmospheric loading of N. Both

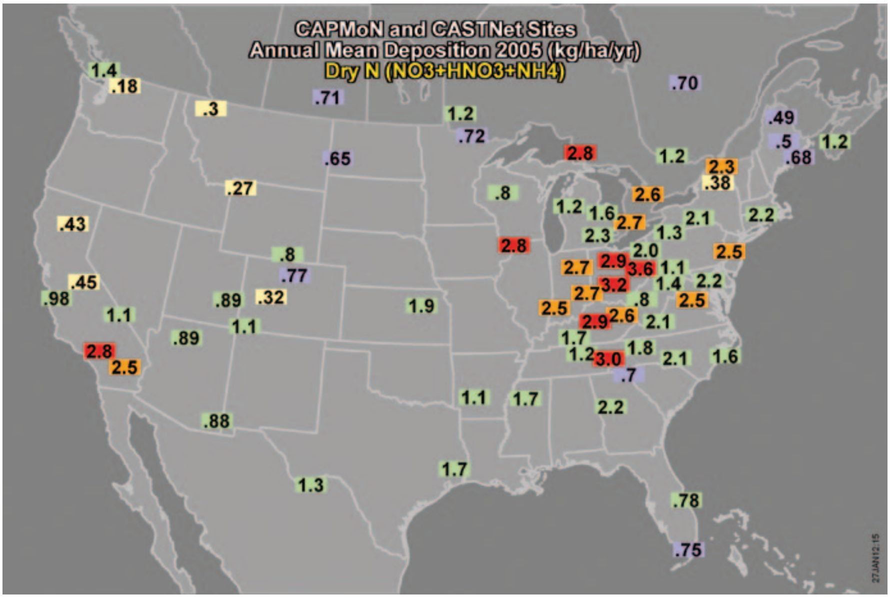

Fig. 2.3 Estimated 3-year-average dry deposition fluxes of nitrogen (N $ha^{-1}year^{-1}$) from particle-NO_3^-, particle-NH_4^+, and gaseous HNO_3 based on data from the United States Clean Air Status and Trends Network and the Canadian Air and Precipitation Monitoring Network

networks measure particle-NO_3^-, particle-NH_4^+, and gaseous HNO_3, but not NO, NO_2, PAN, NH_3 or organo-nitrates—some of which are important contributors to dry deposition. Thus, the dry deposition fluxes (and wet + dry deposition fluxes) of N estimated by these two networks are thought to be quite conservative.

An illustration of the CASTNET and CAPMoN dry deposition monitoring sites and their estimated 2005–2007 annual average dry deposition fluxes of N is shown in Fig. 2.3. As mentioned above, these estimates are based only on particle-NO_3^-, particle-NH_4^+, and gaseous HNO_3 fluxes and are missing the other potentially-important nitrogen species, most notably NH_3 and NO_2. From Fig. 2.3, one can see that dry deposition fluxes are higher in eastern North America than in western North America (with the exception of southern California), which is a reflection of the spatial distribution of NO_x emissions in North America.

Globally, the number of sites that provide inferential dry deposition estimates is insufficient, with few estimates in South America, Africa, Australia, Oceania, northern Canada, Asia, the oceans and the polar regions. Additionally, most ambient air monitoring networks do not measure all of the N compounds necessary to determine the total atmospheric loading of N. Even the two existing North American inferential dry deposition networks, CASTNET and CAPMoN, have known measurement uncertainties due to the volatilization of particle-NH_4NO_3, and large uncertainties in the flux estimates due to differences in their respective inferential models. As a result, dry deposition monitoring on a global basis is inadequate.

There needs to be a commitment in the measurement community to developing routine network measurement systems that provide the data required to assess dry deposition on a regional and global basis.

In the appendix to this chapter we give a short overview of some of the networks, Table 2.1 lists some of the issues that were identified for these networks.

2.2.4 Use of Deposition Measurements

How are the network measurements being used? Using statistical techniques like Kriging or Optimal Interpolation, the measurements can be directly interpolated to larger geographical regions. The applicability of such methods depends on the presence of sufficient data that are at a short-enough-distance to be correlated with each other. They can be combined with meteorological modelling, for instance to derive dry deposition fluxes. They can be used as independent data sets to verify atmospheric models, as will be elaborated in Sect. 2.3 (this chapter), the measurements can be assimilated in models to achieve an optimized agreement between model and measurements space- a process known as data-assimilation. An overarching theme in all techniques is the representativeness of point measurements for larger scales.

2.3 Modelling

2.3.1 Models

There is a large range of models available to describe air pollution chemistry and transport. These models range from describing near-point source dispersion to global transport processes- the choice of model depends on the issue and the availability of input data.

Many processes are parameterized in models, and consequently the models can only provide a limited representation of reality. The models in use to describe N emissions, chemistry and transport, can be typically separated into plume models, useful at say farm-scale, Lagrangian and trajectory models tracking long range transport of pollution plumes, and Eulerian grid-point models. While plume models continue to be useful in a regulatory framework, today overwhelmingly Eulerian models are used to describe ozone and aerosol chemistry, and are also providing estimates of the deposition of N components. Global models are increasingly used for providing maps of reduced and oxidized N. Resolutions of global models are currently ranging from $1° \times 1°$ to $4° \times 5°$ lat-lon, and expected to improve to $0.5° \times 0.5°$ in the coming years. The global models obviously cannot cover many of the regional deposition details; nevertheless a recent comparison of Dentener et al. (2006) showed good comparison of 21 global models with measurements in North America and

Table 2.1 Issues associated with regional nitrogen deposition monitoring networks

North America: CASTNET/ NADP/CAPMoN	Europe (EMEP)	South Asia (CAD)	South East/East Asia (EANET)	Africa (DEBITS/IDAF)
Wet deposition: Incomplete closure of N budget; no DON Too few measurement sites in certain areas	Measurements performed on country basis, differences in measurement quality and sampling protocols?	Data quality: delay in analysis leading to underestimate of NH_4 and NO_3	Currently focus on acid deposition rather than N deposition. DON is not measured. Insufficient sites in China	Eight stations covering continental scale; representing major ecosystems Wet deposition budget incomplete (no DON)
Dry deposition: Not all gases being measured routinely e.g. NH_3; NO_x, PAN and organo-nitrates are missing Too few measurement sites	In some regions very few measurements (Southern Europe)	Lack of rural sites, and long term measurements Lack of quality controlled data	Organic nitrogen species (e.g. PAN and organo-nitrates) are missing In some sites especially in China, dry N deposition data is missing Insufficient sites in rural and remote places. More sites needed in China	Dry deposition complete $NO_2 + HNO_3 + NH_3 + pNO_3^- + pNH_4$. Dry deposition of gases combining long-term passive samplers measurements and site-specific deposition velocities: large uncertainty. Bulk measurements for particles
Siting criteria require placement of the sites away from large sources. Thus, the network will miss hot spots and estimates of deposition budgets based on interpolation of sparse sites will be biased low At some sites, violation of theoretical siting requirements for dry deposition monitoring, e.g., locating sites in complex terrain	Measurements for N budget incomplete	Difficulties estimating deposition of NO_x and NH_3 gases	Regional specific models need to estimate the rates of dry deposition	All the African Sites are located in non perturbed rural regions Lack of urban sites to measure hot spots sources and associated deposition (planned)
Lack of comparability between the US and Canadian inferential dry deposition estimates		High ammonia specific for India	Nitrogen deposition in coastal areas should be emphasized especially in east China	Development of an inferential model for African ecosystems

Europe, reasonable performance in South East Asia, but larger problems in Africa, South Asia, and South America.

The spatial domain and resolution of regional models has been steadily improving. In the USA and Europe the typical resolution of continental models has decreased from 36 km to 12 km grid sizes. However, 12 km is still too coarse for critical load modelling in complex terrain (hills, valleys), where much of the critical load work in e.g. the USA is focused. Throughfall measurements suggest that there is a high degree of deposition variability within a grid in complex terrain that is important to critical loads (Weathers et al. 2006). These problems are associated with the inability of models to capture orographic effects on rainfall amounts, or effects of terrain and land cover type on dry deposition. Parameterizations for this subgrid variability would be helpful.

Also, even in flat terrain, dry deposition will depend on land cover type. It is essential that methods be developed to account for this variability rather than use a single number per grid. Efforts are being made to make dry deposition land-use specific within a grid.

A similar problem occurs in Europe, and probably also elsewhere, where patches of natural land are included in farmland. Current global and regional models should address this sub-grid phenomenon.

It is worth mentioning here, that models describing NO_x and NH_x chemistry and deposition, are almost always part of larger models describing photochemistry and aerosol dispersion processes in general, and not necessarily focusing on correctly describing deposition processes. Increasingly, models now combine their aerosol and photochemistry modules.

2.3.2 Land Use Databases

As mentioned above models use land cover databases to describe a number physical processes (e.g. albedo, surface roughness), but also the parameters needed to perform calculations of dry deposition. These databases are provided on a relatively detailed resolution by the USGS and the updated NLCD (National Land Cover Data base) in the USA, or CORINE (Coordination of information on the environment) in Europe. Examples of relatively high resolution global land cover database include the GLC2000 land cover database, MODIS land cover, and the IGBP. A recent comparison of 3 global land cover databases (Herold et al. 2008) shows large differences in these databases arising from the use of different remote sensing instruments, interpretation methods, and perhaps most importantly different classification methods, that may regionally differ. Especially among classes of mixed vegetation there are large differences. These uncertainties are propagated into atmospheric models, and often it is not clear what land-cover database is actually included in the various model results. Very recently, a global land-cover database from the MERIS (Envisat's Medium Resolution Imaging Spectrometer) at 300 m resolution has become available. The high spatial resolution should help to more unambiguously attribute land-cover classes—with less need to define 'mixed' classes. A recurring theme in the land-cover and land-use databases is the adequacy of the chosen classification to accurately address the users need. We mention here that many atmospheric models work with often outdated landcover databases, possibly leading to large inconsistencies.

2.3.3 Emissions

Because photochemistry and aerosol physics are involved, description of N deposition, emissions for local, regional and global models requires inclusion of NO_x, VOC, NH_3 and SO_x emissions at a minimum. Except for power plant SO_2 and NO_x emissions, which can be measured at the stack, emissions are estimated using models and emission factors multiplied by activity indicators. Then these emissions must be geographically located, which introduces additional uncertainty. SO_x emissions are mostly from power plants, and industry. NO_x emissions involve many sectors, including on-road and off-road vehicles, area sources, and industrial and power plant stacks. NH_3 emissions are mostly from animal operations and fertilizer application (agriculture). Assessments of emission uncertainty for the USA suggest SO_x emissions are the most certain, due to the use of stack Continuous Emissions Monitors (CEMs). NO_x emissions have an intermediate level of uncertainty and NH_x emissions are the least certain (Dennis et al. 2008). This ranking is corroborated by comparisons of the regional models in the USA against NADP wet deposition data. Similarly, in Europe country total emissions are relatively well known, and detailed spatial desegregation (gridding) is available for some countries. EMEP interprets national reports on emissions, and provides an expert based emission inventory on a 50 km scale. Elsewhere in the world inventories have been created on a project-basis (i.e. TRACE-P), but there are generally no officially endorsed gridded emission databases available. There are attempts to provide compilations of gridded datasets on global and regional scales by the IGAC endorsed GEIA (Global Emissions Inventory Activity; http://www.geiacenter.org). Consistent inventories of pollutant and greenhouse gas emissions are provided by the EDGAR team (edgar.jrc.ec.europa.eu/index.php). EDGAR4 will contain global high resolution 10 km by 10 km data for the major pollutant emissions.

Emission projections (e.g. the new projections in the context of the IPCC AR5 report) indicate that air pollution control strategies may lead to stabilization or even a decrease of NO_y depositions worldwide. Mitigation strategies addressing climate change may also lead to reduced NO_y deposition. Much less attention is given to NH_3 emissions, and most scenarios indicate further growth of NH_3 emissions.

2.4 Key Recent Developments

Key recent developments are attempts to bring together datasets on wet and dry deposition at the global scale that are endorsed by international programs (e.g., IGBP and WMO). Deposition data availability in Asia is rapidly improving due to the operation of the EANET network and many national networks. First steps to set-up consolidated measurement capacity in Africa are encouraging. From the analytical point of view, the recent measurements of organic N components have triggered research to determine the origin and importance of these components, with literature estimates as high as 30 % of the wet N deposition budget.

Models are improving. There is a tendency for global models to go to finer resolutions, and regional models are expanding their model domain, as well as improving resolutions. This development is fostered by a continuing increase of computing capacity, and improved skills of numerical weather prediction models, from the global to the regional scale. Nevertheless, errors in emission inventories and in the meteorological model predictions are still a significant issue for modelling of N deposition and critical loads. Improvements of the physics in meteorological models are still needed. For instance careful analysis of throughfall measurements suggest cloud deposition can be very important above certain elevations. The models typically do not include cloud droplet deposition (also known as 'occult' deposition).

Regional models in the USA have been used successfully to establish top down constraints on NH_3 emissions and estimate the seasonality of the NH_3 emissions (Gilliland et al. 2003, 2006). With the top down estimates the model predictions of the gas-particle partitioning of the inorganic species significantly improved. Of course, the inverse results subsume and are influenced by any model errors. Konovalov et al. (2006) used satellite information to derive NO emissions over Europe, and similarly. Kurokawa et al. (2009) obtain NO emissions over East China.

Models are increasingly using the possibility to ingest large sets of observations, a process called data assimilation, and adapted from the numerical weather prediction community. Relevant for N, the suite of NO_2 measurements available from GOME, Sciamachy, OMI, GOME-2 satellites, is increasingly used. Important information on trends can be obtained from satellite information (Richter et al. 2005). While the process understanding does not necessarily improve by data assimilation, it certainly improves the model predictions of the related NO_y deposition. Very recently, also the first satellite based NH_3 measurements were reported, but it is unlikely that the current IR satellite instruments will provide reliable measurements globally.

Finally, more detailed emission inventories are being compiled, either by combining national level detailed inventories, but also high resolution bottom-up inventories like EDGAR4, targeting at global resolutions of $0.1° \times 0.1°$.

2.5 Recommendations

- **Measurement gaps**
  - The deposition measurement community has long recognized that there are too few wet and dry deposition measurement sites operating worldwide (WMO 2008). Those monitoring sites that do exist generally do not measure the complete suite of N species needed to close the atmospheric N budget. The problem is worse in substantial parts of the developing world.
- **Measurement recommendations**
  - Increase the number of regional-scale, long-term monitoring sites for the routine measurement/estimation of wet and dry deposition worldwide.
  - Continue and increase capacity building for measuring wet and dry deposition in the developing world.
  - Increase the number of N species routinely measured in wet and dry deposition monitoring networks to close the atmospheric N budget, most notably DON, NH_3 and NO_2.
- **Modelling gaps**
  - Regional and global model representation of wet deposition is reasonable in Europe and the USA but still very uncertain in other parts of the world. Modelled dry deposition fluxes are very uncertain, and can seldom be compared to measurements, due to many factors including incompleteness of observations, uncertainties in chemistry schemes, and sparseness of measurements.
- **Modelling recommendations**
  - Global as well as regional models need to improve their resolutions, especially in situations with complex orography. All models still have substantial uncertainties in their representation of the hydrological cycle (rain, snow). It is recommended that models closely follow improvements in model parameterization coming from the meteorological community.
  - Relatively little attention is given to model representations of dry deposition. Use of the best available land-use datasets, and closer linkage to meteorological model predictions of critical parameters and to observations of parameters to estimate dry deposition fluxes is important. More measurements are essential to improve the models, including carefully designed special field campaigns.
  - Deposition processes vary on several timescales: from daily fluctuations to seasonal and inter-annual variations. The models' performance should be tested on all timescales- e.g. at least the seasonal changes with variations in landcover (e.g. snow, vegetation) and hydrology (monsoon) should be represented well in the models.
  - Since there is a serious lack of wet and dry deposition measurements, models need to be verified and improved using as much as possible alternative datasets, such as ambient concentrations, dedicated field study data and model intercomparisons. Promising datasets are becoming available from satellites,

but more work needs to be done to consistently combine the model and measurement frameworks.

- New emission data sets are becoming available; and should be used. However, these datasets should be checked as much as possible using knowledge in countries and regions under consideration ('ground-truthing'), as well as with top-down techniques.

For further recommendations on the monitoring and modeling of N deposition see the working group report (Aas et al. 2014, Chap. 48, this volume).

Appendix: Overview of Networks

DEBITS/IDAF (http://medias.obs-mip.fr)

Under the auspices of the international DEBITS program, with about 25 stations in the tropical belt, the objective of the African IDAF project is to measure wet- and dry-deposition fluxes and identify the relative contribution of natural and anthropogenic source of a number of components. The IDAF project implemented 8 monitoring sites covering the major African ecosystems over West and Central Africa: dry savanna (Niger, Mali, South Africa), wet savanna (Côte d'Ivoire and Benin) and equatorial forest (Cameroon, Congo). Wet deposition is measured by precipitation collectors specially designed for the IDAF network, and all the analysis are quality controlled by the quality assurance and quality control (known as 'QA/QC') intercomparison WMO programme. Typical values for wet deposition of N components range from 0.9 kg N-NO_3^- ha^{-1} $year^{-1}$ and 1.5 kg N-NH_4^+ ha^{-1} $year^{-1}$ in dry savannas, 1.3 kg N-NO_3^- ha^{-1} $year^{-1}$ and 2.9 kg N-NH_4^+ ha^{-1} $year^{-1}$ in wet savannas and 2 kg N-NO_3^- ha^{-1} $year^{-1}$ and 3 kg N-NH_4^+ ha^{-1} $year^{-1}$ in forests. Dry deposition is estimated using measurements of gaseous and particulate species based on continuous measurements of gaseous concentrations through passive gas sampling (NO_2, NH_3, HNO_3), and on bulk air sampling (ammonium and nitrate particulate content). These concentrations are multiplied by site and species specific dry deposition velocities. A detailed overview of the IDAF network can be made available by C. Galy-Lacaux.

EANET (www.eanet.cc)

The Acid Deposition Monitoring Network in East Asia (EANET) was established in 1998 and the regular phase activities were started in 2001, with the UNEP Regional Resource Centre of Asia and the Pacific (UNEP RRC.AP) in Thailand as the secretariat, and the Acid Deposition and Oxidant Research Center (ADORC) in

Japan as the Network Center. The objectives of the EANET are to create a common understanding on the state of acid deposition problems in East Asia, provide useful inputs for decision making at various levels with the aim of preventing or reducing the adverse impacts on the environment, and promote cooperation among countries (http://www.eanet.cc/eanet/outline.html). EANET monitors four environmental items—wet deposition, dry deposition, soil and vegetation, and inland aquatic environment. Currently there are 56/47 wet/dry deposition monitoring sites and 19 ecological monitoring sites from fourteen countries in East Asia. Using common methods, wet acid deposition is estimated by analyzing the rainwater's concentrations of sulphate (SO_4^{2-}) and nitrate (NO_3^-), and dry acid deposition by calculating measured concentrations of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and particulate components (for more details see http://www.eanet.cc/index.html).

South Asian Network: Composition of Asian Deposition

Several initiatives like the CAD (Composition of Asian Deposition) associated with DEBITS, and the Malé Declaration provides a framework for the measurement of rain chemistry and gaseous concentrations. Nevertheless, in India, for example, there is no national deposition network, although there are several individual measurement activities. Recently, Kuhlshrestha et al. (2005) compiled a data set of about 100 stations, of which 50 stations which can be characterized as "rural" and "sub-urban." Only a few stations operated wet-only measurements.

In the South Asian region, specific studies to monitor N deposition have not been carried out. As part of individual efforts or through limited networks, wet and dry deposition of N has been reported, unfortunately most results are not reliable due to the delay in chemical analysis and improper sample storage. Estimation of nitrate or ammonium needs to be done immediate after sample collection. Moreover, very few publications reveal their quality assurance (QA) procedures, and clearly future network activities will have to address these QA/QC issues. It is worth mentioning here that through CAD, a few groups working on wet and dry deposition studies have been trained for good quality analysis. Good results in a recent EANET inter- comparison exercise are encouraging. More encouragement for QA/QC in measurements in the South Asian region will strengthen the data reliability. More information can be obtained from Umesh C. Kulshrestha.

European EMEP network

The framework for EMEP (European Monitoring and Evaluation Programme) is provided by the Convention on Long-range Transboundary Air Pollution), ratified by 50 countries. The network (tarantula.nilu.no/projects/ccc/network/index.html) consists of some 100 operating stations, which cover measurements of acidifying/

eutrophying components, ozone, heavy metals, POPs, VOCs and PM. The stations are not equally distributed over Europe, with very few stations in Southern Europe. Likewise, the quality and completeness of the measurements may differ from country to county. Given the large heterogeneity of land-use and emissions in Europe, it is sometimes difficult to classify stations as truly background, rural, or urban. More information can be obtained from Wenche Aas.

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Chapter 3
Gaseous Nitrogen Emissions from Australian Cattle Feedlots

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Abstract At any one time, close to 700,000 beef cattle are raised intensively in Australian feedlots. This chapter describes measurements of emissions of the

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greenhouse gas N_2O and the reactive nitrogen gases NH_3 and NO_x from two Australian beef cattle feedlots made over two years with open- and closed-path concentration measurement systems and backward Lagrangian stochastic dispersion modelling. Emissions of all three gases exhibited marked diurnal cycles with maxima close to mid-day and minima over night. The average emission rate for N_2O was 1.3 ± 1.65 (s.d) kg N ha^{-1} d^{-1}, that for NH_3 was 95 ± 36 kg N ha^{-1} d^{-1}, and for NO_x 1.20 ± 0.58 kg N ha^{-1} d^{-1}. Extrapolating these figures to all the feedlots in the country and accepting the estimate by Mosier et al. (1998) that 1 % of the NH_3 and NO_x would be converted to N_2O after eventual deposition, the direct emissions of N_2O from feedlots amount to 241 kt CO_2-e $year^{-1}$ and those from NH_3 plus NO_x to 181 kt CO_2-e $year^{-1}$, or 43 % of the total N_2O emissions. These direct and indirect emissions are substantial, amounting to 60 % in terms of CO_2-e of the CH_4 emissions measured in the project.

Keywords Ammonia • Direct and indirect nitrogen greenhouse gases • Micrometeorological bLs measurement technique • Nitrous oxide • Oxides of nitrogen

3.1 Introduction

Agriculture ranks second to stationary energy as a source of greenhouse gas emissions in Australia, accounting for 16.3 % of the national total. It is the main contributor of methane (CH_4) and nitrous oxide (N_2O). The national inventory notes that the present growth in N_2O emissions in Australia is driven in part by increased emissions from the manure of intensively managed livestock. Beef cattle account for 48 % of agricultural greenhouse gas emissions and 7 % of national emissions. There are 28.8 million beef cattle in the country and at any one time, close to 700,000 of them are raised intensively in feedlots. The authors have recently completed a detailed study of greenhouse gas emissions from beef cattle feedlots in the north and south of the country extending over two years and employing open- and closed–path concentration measurements and atmospheric dispersion modelling to estimate emission rates. Reports of various aspects of the study including rates of emission of methane (CH_4), ammonia (NH_3), nitrous oxide (N_2O), carbon dioxide (CO_2) and the odd oxides of nitrogen (N), NO and NO_2 (known collectively as NO_x), dietary aspects and comparison with published biophysical models, and environmental aspects are in course of preparation. Here, we give a preliminary report of measurements of emissions of the direct greenhouse gas N_2O and the indirect greenhouse gases, NH_3 and NO_x. Mosier et al. (1998) suggest that about 1 % of the NH_3 and NO_x released into the atmosphere is eventually converted to N_2O after deposition. We have used that figure and our emission estimates to calculate the relative N_2O contributions of each gas.

3.2 Sites and Methods

The feedlots were located in Victoria in the south of Australia and Queensland in the north. Cattle numbers during the studies varied from around 18,000 to around 13,000. Line-averaged concentrations of NH_3 and N_2O in the feedlots were measured continuously, circumstances permitting, in campaigns of approximately 10 days in summer and winter, commencing in the winter of 2006 and extending into 2008. Upwind and downwind concentrations of NH_3 at a height of 1.5 m were measured with two open–path laser systems and concentrations of both NH_3 and N_2O were measured at the same height with an open-path Fourier transform infrared (FTIR) spectrometer. In 2008, the summer campaign at the southern feedlot was extended for a further 6 months through autumn and winter by using a closed-path chemiluminescence analyser to measure concentrations of NH_3 and NO_x. Unlike the open-path instruments employed in campaign mode, the analyser is closed-path, providing concentration measurements at a point in space rather than as line-averages. Thus the air samples they analysed were subject to emissions from a smaller part of the feedlot than those analysed by the open-path instruments whose paths of measurement were hundreds of m long. For the analyser, air was drawn from intakes at heights of 1.5 and 3 m above the ground at a location within or beside the feedlot and the two air streams were switched at 7½ min intervals. All data were processed as 15 min means.

Emissions of the various gases were inferred from the concentration measurements by a use of a backward Lagrangian stochastic (bLs) dispersion model. Implentation of the model was achieved through a computer package, WindTrax (Thunder Beach Scientific), which simulated trajectories of “particles” backwards from the sensor. Fluxes were calculated from the numbers of particle touchdowns inside and outside the source area. The basis of the method is described by Flesch and Wilson (2005) and its application to feedlots by Flesch et al. (2007). Required inputs for the model calculations are the geometry of the source area, the location and type of sensor, the background gas concentrations, wind speed and direction, atmospheric stability and statistics of the turbulence. The atmospheric inputs were obtained with a 3-D sonic anemometer and the background concentrations from gas measurements in periods when winds blew from unfavourable directions with very little or no coverage of occupied cattle pens.

The available data were filtered for: unfavourable wind directions; the number of touchdowns in the feedlot in the footprint of the gas sensors, cut-off coverages of 10% of the feedlot area for the open-path measurements and alternative cut-offs of 1 and 2% of the area for the closed-path measurements; low turbulence levels, with a cut-off for the friction velocity of 0.15 m s^{-1} for the open-path measurements and 0.1 m s^{-1} for the closed-path; and periods of intense atmospheric stability and instability affecting the turbulence, with cut-offs for Monin-Obukhov stability indices between 10 and −10 m. The results reported here are a conglomerate of the open- and closed-path measurements.

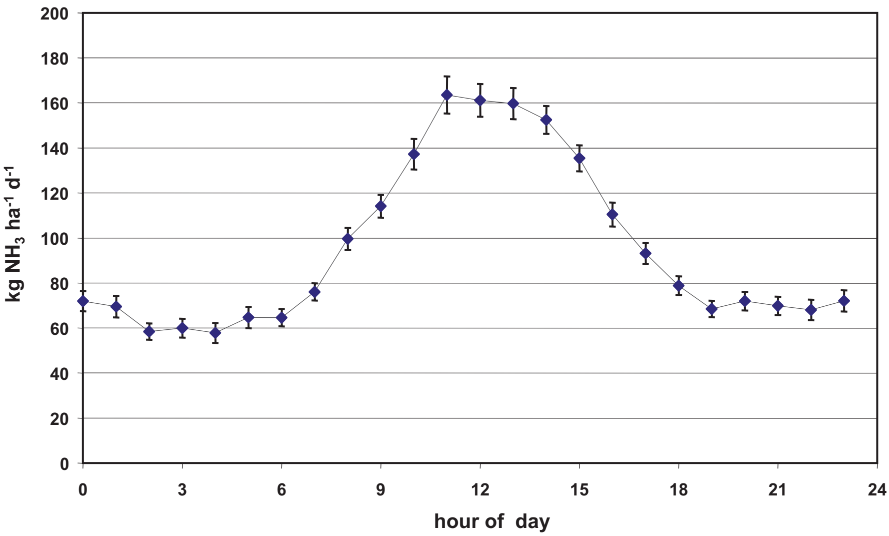

Fig. 3.1 Hourly ensemble-means of NH_3 emissions measured with three open-path systems in campaigns in summer and winter between 2006 and 2008. Error bars indicate the standard errors of the ensemble-means

3.3 Results and Discussion

3.3.1 Ammonia Emissions

Feedlot ammonia emissions exhibit a diurnal cycle. Hourly ensemble means measured with the three open-path systems during the summer and winter campaigns from 2006 to 2008 are shown in Fig. 3.1. The highest emissions occurred in the afternoon and the lowest values just prior to sunrise as observed in previous studies by Flesch et al. (2007) in the USA and by Loh et al. (2008) and Denmead et al. (2008) in Australia. Undoubtedly, the cycle is linked to temperature which has been shown to have a large effect on ammonia volatilisation because of its effect on NH_3 vapour pressure at the surface, but other factors such as surface wetness, wind speeds and diet are probably involved.

The average rate of NH_3 emission during the campaigns was 107 kg ha^{-1} d^{-1}, while that measured with the closed-path system over 6 months during autumn and winter in 2008 was 124 kg ha^{-1} d^{-1}. These rates are considerably higher than predicted by the IPCC Tier II methodology (IPCC 2006), which appear to be based on diet rather than environmental effects. In turn, the higher rates observed in our studies appear to be associated with lower than predicted N_2O emission rates, as discussed in another section of the chapter, due perhaps to the lower soil supply of NH_3 for nitrification and N_2O production.

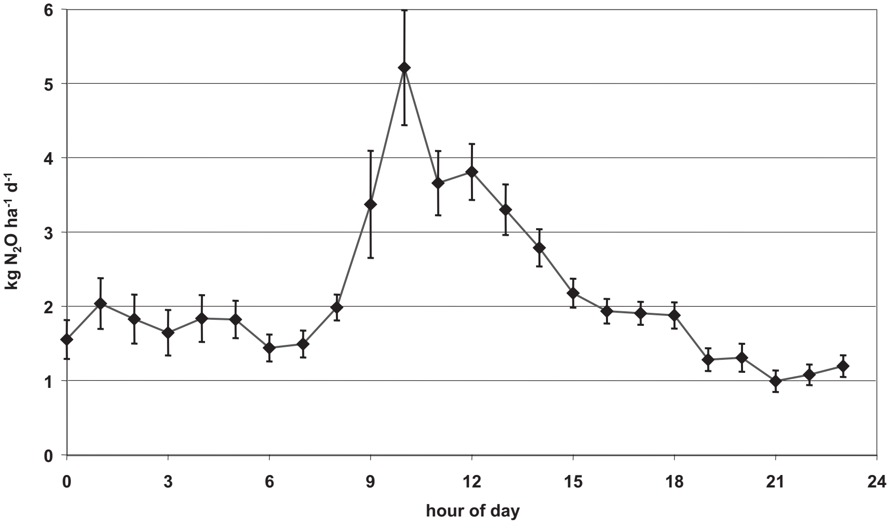

Fig. 3.2 Hourly ensemble-means of N_2O emissions measured in campaigns in summer and winter between 2006 and 2008. Error bars indicate the standard errors of the ensemble-means

3.3.2 Nitrous Oxide Emissions

Hourly ensemble-means measured with FTIR spectrometry in the summer and winter campaigns are shown in Fig. 3.2.

Like ammonia, N_2O emissions exhibited a diurnal cycle, although with a somewhat different time course. Maximum emissions occurred earlier in the day, between 09:00 and 13:00. Also, the error bars were relatively larger than for NH_3, indicating greater variability. Feedlot N_2O emissions averaged 2.0 kg ha^{-1} d^{-1} which is about half that suggested by IPCC (2006), while as mentioned in the previous section, the average NH_3 emission was several times higher than that modelled by IPCC (2006). We suggest that the greater than expected NH_3 volatilisation resulted in a smaller than expected source of ammonium in the soil and manure for nitrification and N_2O production.

3.3.3 NO_x Emissions

These were measured continuously for 6 months with the closed-path system, but only during the autumn and winter of 2008. However, there were still close to 5,000 determinations of NO_x flux available after filtering. The typical time-courses and magnitudes of the flux are exemplified in Fig. 3.3, which shows results from measurements during a week when there were favourable wind directions.

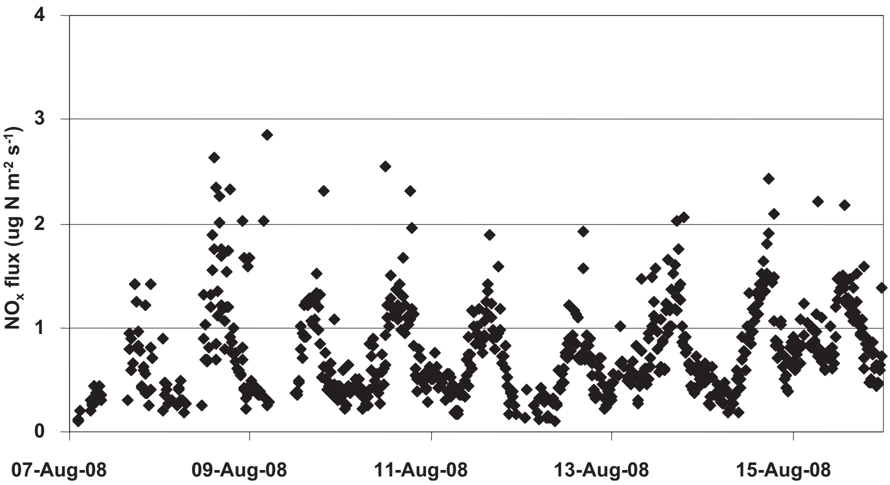

Fig. 3.3 Diurnal cycles of NO_x emissions during a week with favourable wind directions

Table 3.1 Measured and estimated national N emissions from Australian beef cattle feedlots

Gas	Measured emission rate kg N ha^{-1} d^{-1} ± s.d.	Estimated national total N emissions t N $year^{-1}$	Greenhouse equivalents kt CO_2-e $year^{-1}$
N_2O	1.30 ± 1.65	527	241
NH_3	95 ± 36	38,489	179
NO_x	1.20 ± 0.58	486	2

NO_x emissions also exhibited a diurnal cycle (noted previously by Denmead et al. 2008) although the cycle appears to be not quite as well defined as that of NH_3 emission, probably because the concentrations of the gas were smaller and more difficult to measure. Unlike emissions of NH_3, those of NO_x did not appear to show any seasonal dependence. NO_x formation is known to be temperature dependent, but is affected strongly by other factors that influence nitrification and denitrification such as N supply, moisture status and aeration.

3.3.4 Environmental Impacts of Nitrogen Gas Emissions

The emissions of NH_3 were large. For feedlots the size of those reported on here (ca. 22 ha), the daily NH_3 emissions amount to 2.5 t d^{-1}. Without considering pollution aspects, we can estimate the possible greenhouse effects by using the Mosier et al. (1998) figure of 1 % conversion of NH_3 and NO_x to N_2O after eventual deposition, and the measured emission rates for all three gases. The latter are given for the study sites and, by extrapolation, for all cattle feedlots in the country in the second and third columns of Table 3.1.

From these rates and the global warming potential of N_2O of 298, we estimate a net annual contribution of N_2O to the atmosphere from Australian cattle feedlots through emissions of NH_3, NO_x and N_2O itself of 422 kt CO_2-e (the sum of the items in column 4 of Table 3.1), 43 % of which comes from the indirect greenhouse gases NH_3 and NO_x. These direct and indirect N_2O emissions are substantial, more than half as large in terms of CO_2-e as the emissions of CH_4 from feedlots (722 kt year^{-1}). A further programme of continuous measurement for a whole year is needed. As well, the ecological impact of the 99 % of the deposited N remaining after emission as NH_3 and NO_x requires investigation. Much of the deposition is likely to occur within a few km of the feedlot at rates of tens of kg N ha^{-1} year^{-1} (Loubet et al. 2009).

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Chapter 4
Ammonia Emissions in the US: Assessing the Role of Bi-directional Ammonia Transport Using the Community Multi-scale Air Quality (CMAQ) Model

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Abstract A pilot study assessing bi-directional ammonia (NH_3) transport using the Community Multi-scale Air Quality (CMAQ) Model for the Eastern United States (US) is underway. The study develops and tests bi-directional flux algorithms, explores methods of providing agricultural fertilizer information into CMAQ, and clarifies possible NH_3, and overall one-atmosphere, chemical budget changes with the full implementation of the bi-directional flux option planned for the 2011 CMAQ release. One focus area is the adjustment of the current CMAQ bi-directional flux module to include a dynamic soil emission potential component. The soil emission potential (Γ_g) is calculated offline using commercial fertilizer application survey data from the National Nutrient Loss & Soil Carbon (NNLSC) Database and is then input to CMAQ for computation of the NH_3 air-soil compensation point and subsequent NH_3 flux. A full 2002 year model run over the standard CMAQ (v. 4.7) Eastern US domain incorporating the revised bi-directional flux module is planned.

Keywords Agricultural soils • Ammonia emissions • Bi-directional flux • CMAQ • Fertilizer emissions

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4.1 Introduction

Given its role in the formation of atmospheric aerosols and adverse impacts on terrestrial and aquatic ecosystems, interest in improving the understanding of the emissions, transformation, transport, and deposition of ammonia (NH_3) has remained strong, despite the lack of federal regulations. Based on the current emissions inventory, approximately 85 % of total US NH_3 emissions are from agricultural sources, with about two-thirds due to animal husbandry and the remaining one-third due to volatilization from commercial nitrogen (N) fertilizer application. Low concentrations of reduced nitrogen (NH_x), defined as the sum of NH_3 and ammonium (NH_4^+), are beneficial to plant growth, but elevated levels can lead to soil and water acidification, eutrophication, and forest damage (Aneja et al. 2001). In the atmosphere, NH_3 acts as a neutralizing agent, reacting with oxides of nitrogen (NO_x) and sulphur (SO_x) to form ammonium nitrate and ammonium sulphate, major constituents of fine particulate matter (PM_{fine}) (Asman et al. 1998).

Large uncertainties still exist in developing NH_3 emissions inventories and modelling environmental processes. Recent research has focused on adjusting and improving existing US inventories through inverse and process-based modelling (Pinder et al. 2006). Additionally, work is being done to represent more accurately NH_3 atmospheric processes in air quality models, most recently with the incorporation of bi-directional NH_3 surface exchange using a resistance and compensation point approach based on studies by Sutton et al. (1998) and Nemitz et al. (2001). With fertilizer use expected to increase (Erisman et al. 2008), and the potential shifts in NH_3 emissions patterns due to an increased focus on bio-fuels production, accurate representation of NH_3 emissions and processes will be essential to assessing regulation needs and abatement strategies in the coming years.

The focus of the current study is the adjustment of the bi-directional NH_3 flux option in CMAQ (v. 4.7) with the addition of a soil emission potential (Γ_g) component calculated offline using commercial fertilizer survey data and a box model representing nitrification processes. Implementation of the bi-directional flux option in CMAQ involves the replacement of the current National Emissions Inventory (NEI) fertilizer emissions data, derived from fertilizer sales and emission factors (Goebes et al. 2003), with dynamic parameterizations of soil and canopy processes.

4.2 Methodology

Determining the soil emission potential for input into the CMAQ bi-directional flux module consisted of two steps: the first determined the crop distribution and fertilizer application for regions of similar crop mix, and the second calculated a daily Γ_g time series for each identified region.

4.2.1 Crop Distribution and Fertilizer Application by Region

Crop and fertilizer application data used to calculate the soil emission potential inventory for the current study was obtained from the National Nutrient Loss & Soil Carbon (NNLSC) Database. The NNLSC is a catalog of databases and tools designed to evaluate relationships between agricultural practices and resulting impacts on carbon, nitrogen, and phosphorus fluxes over 298 million cropland acres, representing 79 % of the total US acreage. The Environmental Policy Integrated Climate (EPIC) model was utilized to create the NNLSC database in conjunction with farm management and site characteristic data derived from farmer surveys and various national level databases. Commercial fertilizer application data available in the database includes the timing and method of application and the amount applied for a select set of crops including corn, soybeans, wheat, cotton, barley, sorghum, rice, potatoes, oats, peanuts, legume hay, and grass hay, under both dry and irrigated conditions. Probabilities of occurrence were assigned to the timing and rate of nutrient application by state and crop based on the frequency of each nutrient management option reported in the survey data. Limitations of the NNLSC database include only partial crop representation, assumption of no change in cropland characteristics and management, e.g., land use change, over a 40-year time period, and no adjustment for double cropping. A detailed description of the NNLSC database can be found in Potter et al. (2006).

Using the NNLSC crop and N fertilizer application data, sub-regions with relatively distinct crop mixes were identified within the larger US regions of the Northern Great Plains, Southern Great Plains, Midwest, Southeast and Northeast, and fertilizer application timing profiles were determined for each crop by state. Sub-regions were identified by aggregating survey data to the county level to determine the crop distribution in each county, and then by grouping counties of similar crop mix, with a median annual N application rate computed for each crop in a sub-region. Crops representing a relatively small fraction of the total N applied were omitted. An example of the crop distribution and median N application rate for west-central Texas, i.e. sub-region B, in the Southern Great Plains is shown in Tables 4.1 and 4.2. State fertilizer application timing profiles were computed by crop and state by determining the probability of a crop acre in a state receiving fertilizer in each of ten application timing scenarios, e.g., fall (autumn), at plant, and after plant. The crop distribution and fertilizer application data was used both in calculating and weighting the soil emission potential in each sub-region, with each county in the sub-region assumed to have the same crop mix, N application rate by crop, and subsequent soil emission potential.

4.2.2 Soil Emission Potential

CMAQ (v. 4.7) includes a bi-directional ammonia flux option utilizing a temperature dependent parameterization of canopy and soil compensation points that relies on fixed values for emission potential and uniform bias adjustment factors to

Table 4.1 Crop distribution for the Southern Great Plains. Table 4.2 gives further details on sub-region B

Crop	Southern Great Plains sub-region								
	A	*B*	C	D	E	F	G	H	I
Corn—dry				X	X	X	X		X
Corn—irrigated	X	*X*			X	X	X		X
Cotton—dry		*X*					X	X	
Cotton—irrigated		*X*						X	
Grass hay						X			
Legume hay						X			
Oats				X					
Rice							X		
Sorghum	X	*X*		X	X	X	X	X	X
Soybeans					X	X			
Winter wheat—dry	X	*X*	X	X	X	X			X
Winter wheat—irrigated	X								
% of total crops represented	95%	*92%*	93%	89%	91%	96%	95%	96%	88%

Table 4.2 Crop distribution and fertilizer application for the Southern Great Plains sub-region B

Southern Great Plains sub-region B		
Crop	% of nitrogen (N) applied	Median N applied (kg/ha)
Corn—irrigated	7.4	150.7
Cotton—dry	20.7	31.5
Cotton—irrigated	32.3	76.4
Sorghum	10.6	93.2
Winter wheat—dry	20.9	44.0

calculate emission and deposition. A revised, resistance-based bi-directional flux module under development, discussed in detail in Cooter et al. (2010), allows for a process-based dynamic parameterization of NH_3 soil compensation point, which is then used to calculate the flux. Parameterization for the canopy compensation point is discussed in Bash et al. (2010).

In the revised CMAQ bi-directional flux module, the concentration of NH_3 at the air-soil interface can be related to the NH_4^+ concentration in the soil by assuming an equilibrium exists between NH_3 and NH_4^+ (Nemitz et al. 2001), such that (Eq. 4.1):

$$X_g = \frac{A}{T_S} \exp^{-B/T_s} \Gamma_g \tag{4.1}$$

where X_g is the compensation point based NH_3 air concentration (mol m^{-3}) at the air-soil interface, T_s is the soil temperature (K), A and B are Henry's Law coefficient constants, and Γ_g is the dimensionless NH_3 soil emission potential, (Eq. 4.2):

$$\Gamma_g = \frac{\left[NH_4^+\right]}{\left[H^+\right]} \tag{4.2}$$

where $[NH_4^+]$ and $[H^+]$ are the respective NH_4^+ and H^+ ion concentrations in the soil water. If the NH_3 concentration just above the soil surface is less than X_g, NH_3 will volatilize.

The daily Γ_g time series for each crop and application timing scenario in each sub-region in the current study was calculated offline using a box model constructed from EPIC model algorithms representing the nitrification process. Box model inputs include the physical properties of the ambient soil profile, meteorology, and fertilizer management practices. Crop and N fertilizer application data was obtained from the NNLSC database, and meteorology and soil moisture from the CMAQ Meteorology-Chemistry Interface Processor (MCIP). The daily Γ_g values calculated by the box model were limited by simplifying measures including the assumption of representative MCIP meteorology and a single, typical agricultural soil for the entire sub-region. With the exception of hay crops and post-planting applications that are placed on the soil surface, all fertilizer was assumed to be applied at a depth of 5 cm. Once the initial Γ_g time series for each sub-region had been calculated for each crop and application timing scenario, weights were applied to adjust for crop distribution and probability of fertilizer application timing. The adjusted daily Γ_g time series can then be assigned to the 12 km grid cells that lie within each sub-region for direct input via an I/O API file to CMAQ. Full implementation of the revised bi-directional flux module, planned for the 2011 CMAQ release, will allow for the internal calculation of Γ_g for each grid cell, with only fertilizer application calculated offline. A detailed description and validation of the box model can be found in Cooter et al. (2010).

4.3 Results

Considerable variation exists in the magnitude and temporal distribution of Γ_g across the Eastern US, largely due to regional differences in crop mix and planting schedules. An example of the daily Γ_g time series at various stages in the weighting process is provided in Figs. 4.1, 4.2, 4.3 for sub-region B of the Southern Great Plains. Nitrogen fertilizer for cotton is applied in sub-region B under dry conditions in three possible windows, representing winter, before plant, and after plant applications. The daily Γ_g time series calculated by the box model for each dry land cotton application timing scenario is shown in Fig. 4.1. The distribution for each of the three scenarios is characterized by a sharp increase in emission potential at the onset of N application that tapers off gradually over time. A sensitivity analysis was performed to evaluate the influence of variations in meteorology across each sub-region, also shown in Fig. 4.1 by including the results for two different representative MCIP grid cells contained within the region. In cases where the difference in the magnitude or temporal variation of Γ_g was notable, the sub-region was further divided. The temporal variation in N application was accounted for by multiplying the Γ_g time series for each crop by the fraction of crop acres in a state and the probability of the application timing scenario. Summed across all application

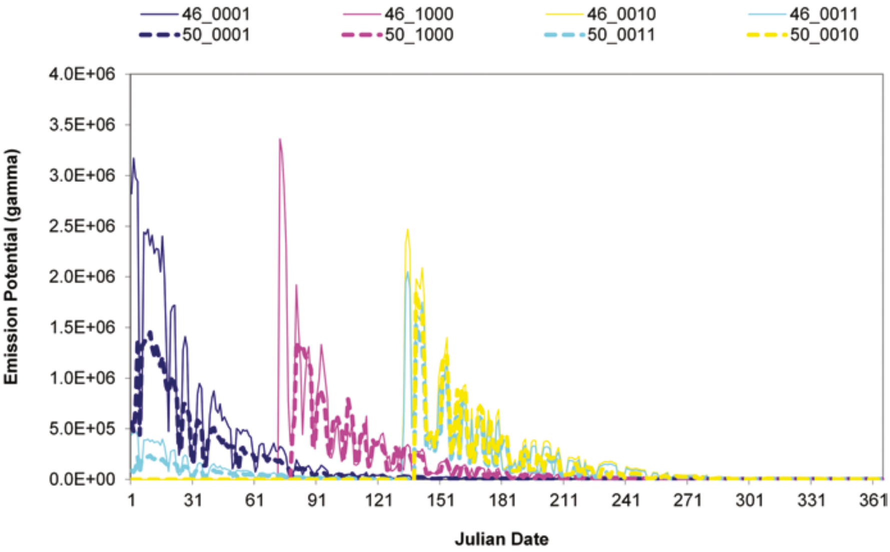

Fig. 4.1 Daily soil emission potential (Γ_g) for the Southern Great Plains sub-region B for dry land cotton. Variable meteorology across the sub-region is represented by two MCIP grid cells (46 = *solid*, 50 = *dashed*). All cotton acres in sub-region B are assumed to receive 31.5 kg/ha annual nitrogen fertilizer application. The application schedule is defined as: 0001 = 1 application on January 1st, 1000 = 1 application 30 days prior to planting, 0010 = 1 application 30 days after planting and 0011 = 2 applications assumed to be 15 % of annual on January 1st and 85 % of annual 30 days after planting

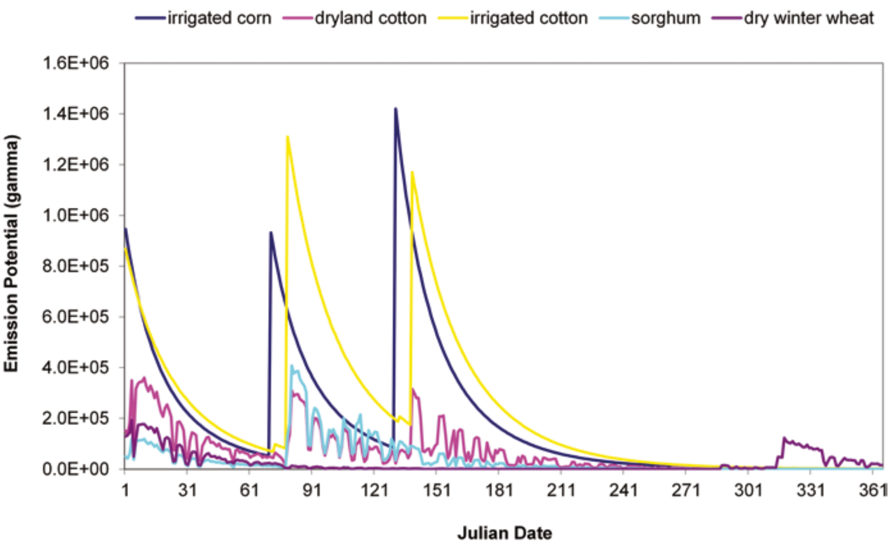

Fig. 4.2 Daily soil emission potential (Γ_g) for the Southern Great Plains sub-region B weighted across all application schedules for all selected crops including: irrigated corn, dry land cotton, irrigated cotton, sorghum, and winter wheat

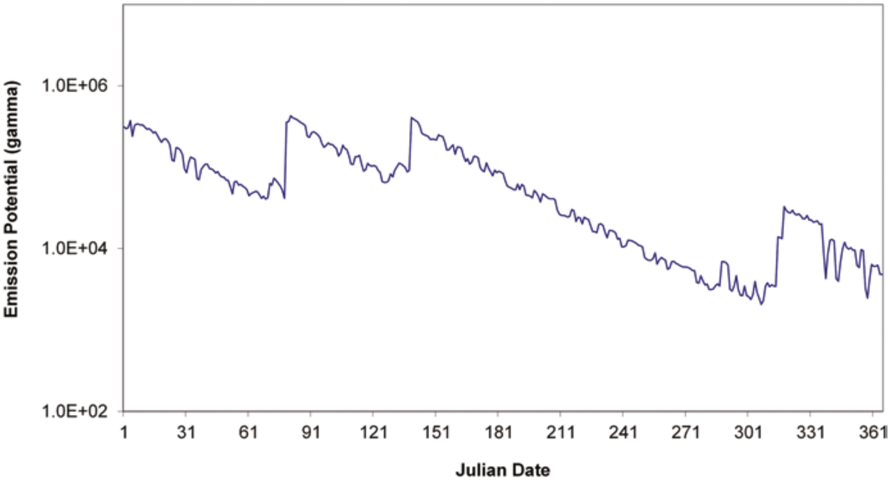

Fig. 4.3 Daily soil emission potential (Γg) for the Southern Great Plains sub-region B weighted across all crops and fertilizer application schedules

timing scenarios and states in the sub-region, the result is a single Γ_g time series for each crop in that sub-region, shown in Fig. 4.2. In this particular region, fertilizer emissions will be dominated by N applied to irrigated corn and cotton crops in the spring, with a much smaller contribution from winter wheat in the fall. The Γ_g time series is then multiplied by the fraction of crop acres in the sub-region and summed across all crops. The result is a single Γ_g time series for the entire sub-region, shown in Fig. 4.3. The greatest emissions potential for sub-region B exists from January 1st through late spring, with a secondary peak in the fall; however, given the temperature dependence of NH_3 volatilization, the Γ_g time series suggests a bi-modal NH_3 emissions distribution with the largest peak occurring in the spring followed by a secondary peak in the fall, similar to fertilizer emissions patterns in the current NEI.

4.4 Conclusions and Future Work

A full year run for 2002 over the standard CMAQ (v. 4.7) Eastern US domain using the daily Γ_g time series and revised bi-directional flux module is planned, with test runs for select months currently underway. Once testing is complete, output from the full model run will be compared to a base 2002 CMAQ run, using the default uni-directional flux configuration and NEI fertilizer emissions, to examine potential impacts of bi-directional transport on the NH_3 and PM_{fine} budgets. The expectation is to see shifts in the magnitude and seasonality of NH_3 emissions and subsequent atmospheric concentration, as well as an increase in wet and decrease in dry deposition.

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Chapter 5
Regional Scale Modelling of the Concentration and Deposition of Oxidised and Reduced Nitrogen in the UK

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Abstract The Fine Resolution Atmospheric Multi-pollutant Exchange model (FRAME) was applied to model the spatial distribution of air concentration and deposition of nitrogen (N) compounds between 1990 and 2005. Modelled wet deposition of N was found to decrease more slowly than the emissions reductions rate. This is attributed to a number of factors including increases in NO_x emissions from international shipping and changing rates of atmospheric oxidation. The modelled deposition of NO_y and NH_x to the United Kingdom (UK) was estimated to fall by 52 % and 25 % between 1970 and 2020. The percentage of the UK surface area for which critical loads for sensitive ecosystems are exceeded was estimated to fall from 73–49 % for nutrient N deposition. Comparison with model simulations at 1 km and 5 km resolution demonstrated that fine scale simulations are important in order to spatially separate agricultural source regions from sink areas (nature reserves) for ammonia dry deposition.

Keywords Ammonia • Chemical transport model • Critical load exceedance • FRAME • Nitrogen deposition

5.1 Introduction

The application of atmospheric transport models is an important technique to simulate the fate of nitrogen (N) released into the atmosphere, its transport, chemical transformation and deposition to vegetation. Models allow calculation of N deposition to a greater number of model grid cells than can be covered by national monitoring networks. In addition, models may be applied to run historic emissions scenarios, which are important in order for assessing the correlation between monitored change in ecosystem health and biodiversity and changes in N inputs. The ability of models to assess the response of N deposition to future emissions scenarios is of importance for policy makers to assess the benefits of implementing controls on atmospheric N emissions. The European Monitoring and Evaluation Programme (EMEP) model (Simpson et al. 2003) has been applied on a European scale to assess spatial patterns of N deposition. Here we apply a relatively simple Lagrangian model, the Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME) to estimate the spatial distribution of N deposition in the UK, past and estimated future changes and the exceedance of critical loads.

5.2 Model Description

The main features of the FRAME model can be summarised as:

- 5×5 km^2 or 1×1 km^2 resolution over the British Isles (incorporating the Republic of Ireland); grid dimensions: 244×172.

- Input gas and aerosol concentrations at the edge of the model domain are calculated with FRAME-Europe, using European emissions and run on the EMEP 50 km scale grid.
- Air column divided into 33 layers moving along straight-line trajectories in a Lagrangian framework with a 1° angular resolution. The air column advection speed and frequency for a given wind direction is statistically derived from radiosonde measurements (Dore et al. 2006). Variable layer thickness from 1 m at the surface to 100 m at the top of the mixing layer.
- Emissions are gridded separately by SNAP (Selected Nomeclature for Air Pollutants) sector for SO_2 and NO_x and by agricultural sector for NH_3 and injected into vertical model layers which depend on the sector.
- Vertical diffusion in the air column is calculated using K-theory eddy diffusivity and solved with the Finite Volume Method.
- Wet deposition is calculated using a diurnally varying scavenging coefficient depending on chemical species and mixing layer depth and a 'constant drizzle' approximation driven by an annual rainfall map. A precipitation model is used to calculate wind-direction-dependent orographic enhancement of wet deposition (Fournier et al. 2005)
- Five land classes: forest, moorland, grassland, arable, urban and water are considered. A vegetation specific canopy resistance parameterisation is employed to calculate dry deposition of SO_2, NO_x and NH_3.
- The model chemistry includes gas phase and aqueous phase reactions of oxidised sulphur and oxidised nitrogen and conversion of NH_3 to ammonium sulphate and ammonium nitrate aerosol.

5.3 Results and Discussion

The model was found to give a good representation of aerosol and gas concentrations of N compounds as well as wet deposition when compared with measurements from the UK national monitoring networks (Dore et al. 2007). From Fig. 5.1 it is apparent that modelled NO_2 concentrations agree well with measurements as the spatial distribution of emissions (principally from vehicles) is well mapped.

More scatter is evident in the correlation of modelled NH_3 concentrations with measurements due to greater uncertainty in mapping emissions and the highly localised and spatially variable nature of NH_3 emissions. The model was better able to represent the spatial variability of ammonium and nitrate aerosol concentrations due to the fact that these particulate concentrations are a product of chemical reactions in the atmosphere and long range transport. Consequently they are not subject to such high spatially variable concentrations as ammonia gas. The correlation for ammonium aerosol is illustrated here. Correlation with nitrate (shown in Fig. 5.1) and ammonium wet deposition shows that, whilst there is generally greater scatter than for air concentrations, the model obtained satisfactory agreement with the measurements.

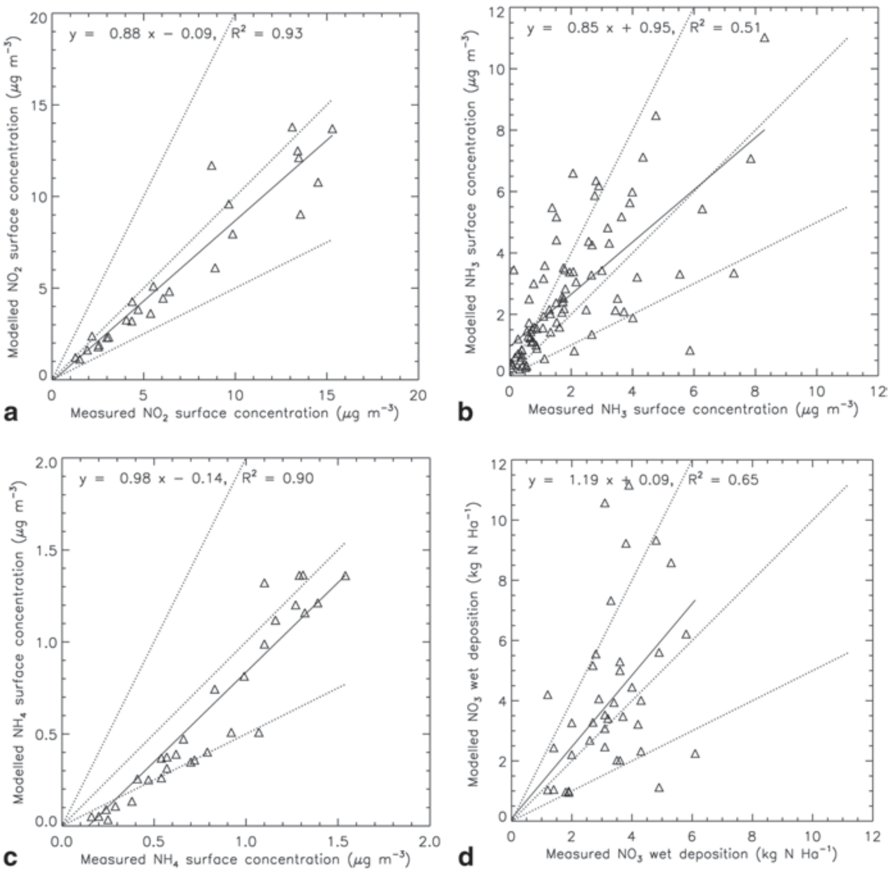

Fig. 5.1 Correlation of model with annually averaged measurements from the national monitoring networks for the year 2007: NO_2 concentration (**a**); NH_3 concentration (**b**); NH_4^+ aerosol concentration (**c**); NO_3^- wet deposition (**d**)

NO_x emissions in the UK (illustrated in Fig. 5.2) were at a maximum of 951 Gg N in 1970 and fell to 378 by 2005, with a further decrease to 243 Gg N forecast by 2020. The significant reduction (of 46 %) in NO_x emissions occurred, in particular from passenger cars due to the introduction of three-way-catalysts as well as a number of increasingly stringent emissions standards. Emissions from power generation have also reduced due to the increased use of gas over coal fired stations. These large decreases in emissions have not been matched by similar changes for NH_3 which only decreased from 315 Gg N in 1990 to 259 in 2005 and is forecast to barely fall, to 222 Gg by 2020. For reduced nitrogen, the smaller reduction in emissions (of 18 %) has been driven primarily by a decrease in livestock numbers in the UK, changes to animal diet and improvements to manure management.

The model was applied to make 16 simulations of annual deposition using meteorological data and emissions for each of the years 1990–2005. These results

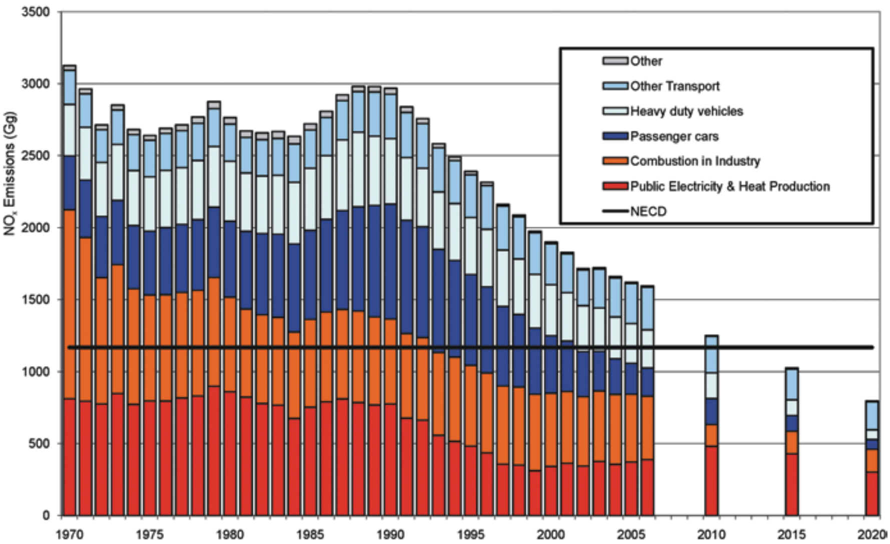

Fig. 5.2 Trend in emissions of NO_x from the UK and future projections (1970–2020). NECD = National Emissions Ceiling Directive

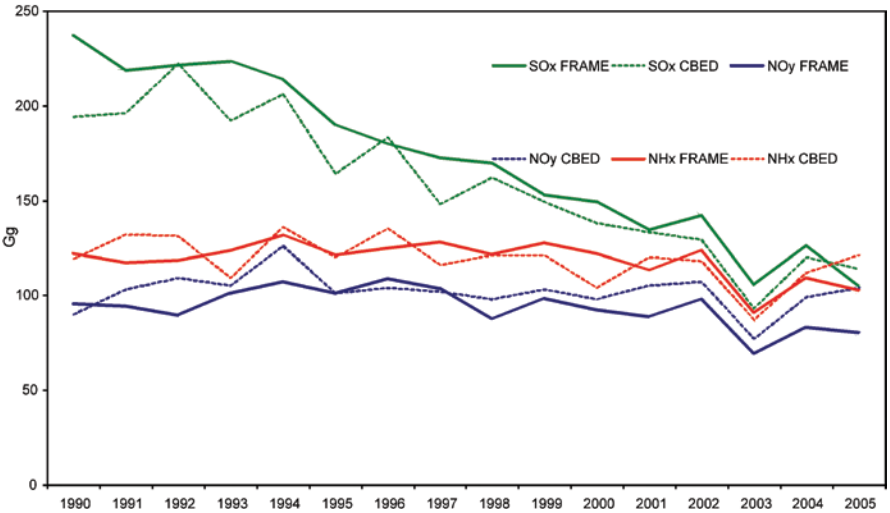

Fig. 5.3 Trend in total UK nitrogen and sulphur wet deposition in between 1990 and 2005 calculated by FRAME and by CBED

were used to calculate the trend in total deposition of N and sulphur to the UK. In Fig. 5.3, the modelled national wet deposition budgets are compared with those from the Concentration Based Estimated Deposition (CBED; Fowler et al. 2005) which combines measured concentrations of ions in precipitation from 38 national monitoring sites with a map of annual precipitation to generate interpolated maps of wet deposition for the UK and budgets of total national deposition. The CBED data shows that significant inter-annual variability in total national deposition occurs due to variable precipitation and changing circulation patterns importing differing amounts of polluted air from the European continent. Due to its simple representation of meteorology, the FRAME model is less sensitive to meteorological changes than is apparent with CBED. Wet deposition of sulphur shows a clear downwards trend during the 15 year time period driven by major decreases in national emissions of approximately 80 % during this time period. Wet deposition of both oxidised and reduced nitrogen however show only minor downward trends which are partially masked by inter-annual meteorological variability.

The EMEP source-receptor matrices correlate national deposition to emissions source amongst the nations of European. For the year 2005, these calculations show that reduced nitrogen deposition in the UK is dominated by the contribution (73 %) from national emissions sources. For oxidised nitrogen deposition, the contributions were: international shipping (18 %), UK (42 %), Europe and long range transport (40 %). In this case it is apparent that deposition is not controlled predominantly by UK emissions. Increases in emissions from international shipping during this period are thought to partially off-set the reductions in UK emissions. Secondly, atmospheric chemical reaction rates are known not to respond linearly to emissions changes (Fowler et al. 2007; Matejko et al. 2009). The major decreases in SO_2 concentrations during this period are believed to have resulted in less depletion of atmospheric oxidants, maintaining the rate of nitrate aerosol production despite lower NO_x emissions. These non-linearities are thought to be present particularly in 'source' countries such as the UK which generally export more pollutants than they import as well as coastal countries with a pollution climate influenced by international shipping emissions.

The spatial distribution of modelled deposition of reduced nitrogen in the UK is illustrated in Fig. 5.4. Dry deposition is high in the cattle farming regions of western England and Wales as well as in localised hot spots of intensive poultry and pig farming in East Anglia and north-east England. A very different pattern is evident for wet deposition of reduced nitrogen which is greatest in the high rainfall hill areas of Wales and northern England. This is associated with the long range transport of N aerosol.

The model was run using historical emissions for the year 1970 as well as forecasting emissions for the year 2020. The deposition data was used to calculate the exceedance of critical loads for N deposition in the UK, using the methods described by Hall et al. (2003). Maps of the estimated exceedance of critical loads for the past, recent and future years are illustrated in Fig. 5.5.

Emissions reductions during the 50 year time period are shown to decrease both the magnitude and area of ecosystems with exceedance of the critical load for N deposition.

However, it is estimated that in 2020 49 % of the total area of sensitive habitats in the UK will still be subject to exceedance of deposition (compared to 73 % for 1970). For unmanaged forest, this figure is 95 %, due to the efficiency of deposition of ammonia to tall vegetation.

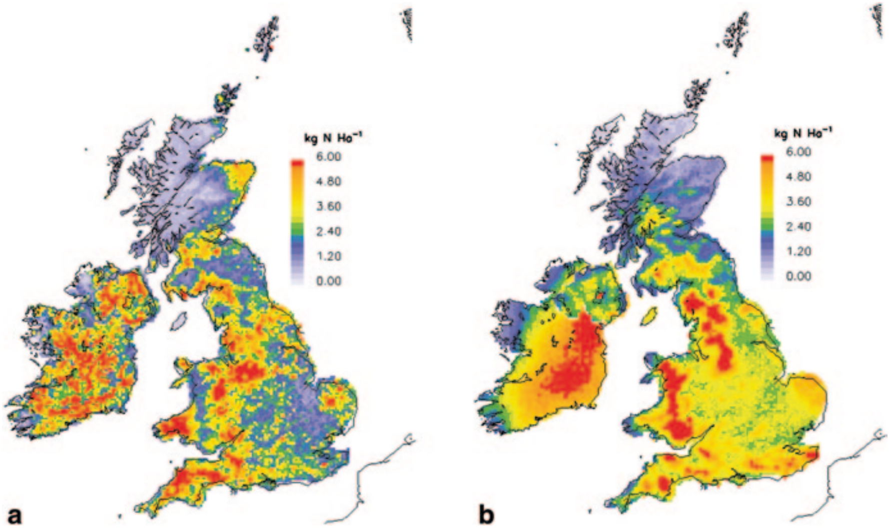

Fig. 5.4 Modelled dry deposition (**a**) and wet deposition (**b**) of NH_x for the year 2007

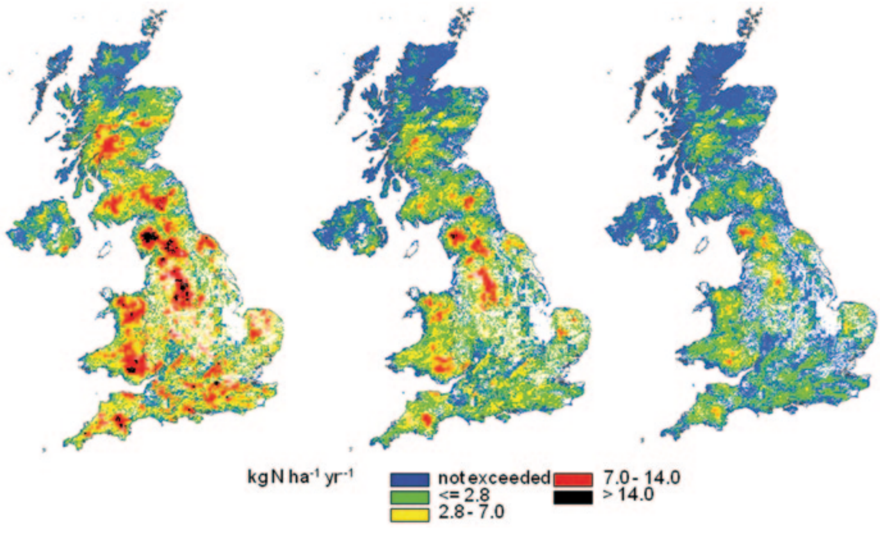

Fig. 5.5 Exceedance of critical loads for nitrogen deposition (kequiv ha^{-1} year^{-1}) for 1970 (*left*); 2005 (*middle*) and 2020 (*right*)

FRAME was also run using a 1 km resolution for both the mapped emissions data and the model grid. The spatial distribution of ammonia concentrations and spatial separation of agricultural source regions from Natura 2000 sites was significantly improved at the finer resolution. An improved correlation with measurements of ammonia concentrations at Natura sites and reduced overestimate resulting from the

Table 5.1 Percentage area of UK Natura 2000 Special Area of Conservation network exceeding the 1 and 3 μg NH_3 m^{-3} critical levels and correlation with measurements of ammonia concentrations from nature reserves (y: modelled concentrations; x: measured concentrations) for model simulations with 5 km and 1 km grid resolutions

Model resolution	5 km	1 km
% area exceedance of 1 μg m^{-3} critical level	40%	21%
% area exceedance of 3 μg m^{-3} critical level	2.2%	0.9%
Line of best fit	y = 1.58 x + 0.31	y = 1.39 x + 0.21
R^2 correlation	0.72	0.83

1 km simulation (illustrated in Table 5.1) as compared to the 5 km simulation was evident. An assessment of the exceedance of the critical level for ammonia concentration (1 μg m^{-3} for bryophytes and lichens, 3 μg m^{-3} for other vegetation, Sutton et al. 2009) was undertaken. The results (Table 5.1) suggest that a fine resolution for both the model grid and mapped emissions data is necessary to assess critical level exceedance. With the 5 km resolution data, there was a tendency for the agricultural source regions and the sensitive Natura sites to be mixed into the same model grid square, resulting in over-estimate of the area exceeding the critical level. It can be expected that calculations of the exceedance of critical loads will also be sensitive to model grid resolution. This will be the subject of future work.

5.4 Conclusion

The Fine Resolution Atmospheric Multi-pollutant Exchange model (FRAME) has been applied to model the spatial distribution of N deposition over the United Kingdom. The model, despite its relatively simple parameterisation, was found to obtain reasonable agreement with measurements of NO_x and N aerosol concentrations in air as well as wet deposition of ammonium and nitrate. Considerable scatter was evident in the correlation with measurements of ammonia gas concentrations due to the highly localised distribution of ammonia emissions.

- NO_x emissions in the UK were at a maximum of 951 Gg N in 1970 and fell to 378 by 2005 with a further decrease to 243 Gg N forecast by 2020.
- The large changes in NO_x emissions have not been matched by emissions changes for NH_3 which decreased from 315 Gg N in 1990 to 259 in 2005 and are forecast to fall to 222 by 2020.
- Modelled wet deposition of N during this 50 year time period was found to decrease more slowly than the emissions reductions rate. This is attributed to a number of factors including increases in NO_x emissions from international shipping and changing rates of atmospheric oxidation. The modelled deposition of NO_y and NH_x to the UK was found to fall by 52% and 25% during this period.
- The percentage of the United Kingdom surface area for which critical loads for sensitive ecosystems are exceeded was estimated to fall from 73 to 49% for nutrient N deposition.

- Comparison with model simulations at 1 km and 5 km resolution demonstrated that fine scale simulations are important in order to spatially separate agricultural source regions from sink areas (nature reserves) for ammonia dry deposition.
- In addition to existing policies to restrict emissions from road vehicles, future policies to control emissions of ammonia from agriculture and NO_x from international shipping will be required to effect further significant reductions in N deposition.

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Chapter 6
High Rates of Wet Nitrogen Deposition in China: A Synthesis

Enzai Du and Xuejun Liu

Abstract Anthropogenic reactive nitrogen emissions (especially NH_3 and NO_x) have been increasing rapidly since the late 1970s in China and may lead to increased atmospheric input of reactive nitrogen to the Earth's surface through wet and dry deposition. Analyzing the temporal and spatial patterns of nitrogen (N) deposition is a high priority in order to assess environmental impacts of N deposition on a national scale. To this end, we have established a database for China, based on wet N deposition measured between 1995 and 2007. High rates of wet N deposition have been observed in large areas, particularly in central and eastern China. Average rates of wet deposition for dissolved inorganic nitrogen (DIN), NH_4^+-N and NO_x^--N were 17.36 ± 10.53, 10.66 ± 6.54 and 6.57 ± 4.93 kg N ha^{-1} $year^{-1}$. The average ratios of NH_4^+-N/NO_x^--N in wet deposition were as high as 1.96 ± 1.27 and showed no significant difference among urban, rural and remote sites. Average wet deposition for DON was 4.84 ± 2.80 kg N ha^{-1} $year^{-1}$ accounting for 25.4 ± 13.5 % of the total dissolved nitrogen (TDN) deposition. Wet N deposition exceeded 15 kg N ha^{-1} $year^{-1}$ at 52 % of the rural sites. The high rates of wet N deposition in central and eastern China suggest heavy atmospheric reactive nitrogen pollution and substantial negative effects on the terrestrial and aquatic ecosystems of China.

Keywords Air pollution • China • Nitrogen deposition

6.1 Introduction

Increasing industrial activities (e.g. energy production and consumption, chemical nitrogen (N) fertilizer production) and agricultural activities (e.g. application of chemical N fertilizers, livestock and poultry breeding), have led to rapid increases in anthropogenic reactive nitrogen emissions (especially NH_3 and NO_x) since the

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late 1970s in China (Tian et al. 2001; Ohara et al. 2007; FRCGC 2007; Wang et al. 2009). Elevated reactive nitrogen emissions to the atmosphere have raised the concentrations of nitrogen dioxide in the troposphere over China (e.g. Richter et al. 2005) and increased reactive nitrogen input to the earth surface through wet and dry deposition. Eastern and southern Asia (especially China and India) has become the third N deposition 'hotspot' after Europe and North America (Holland et al. 1999). Reactive nitrogen deposition has aroused concerns about the negative impacts on ecosystem health and services, such as biodiversity loss (Sala et al. 2000; Bobbink et al. 2010), eutrophication and nitrogen saturation (Aber et al.1998), soil acidification (Bergkvist and Folkeson 1992; Richter and Markewitz 2001), and increased susceptibility to secondary stress (Green et al. 1994; Nilsen 1995; Witzell and Shevtsova 2004; Aerts and Bobbink 1999).

In Europe and North America long-term monitoring networks have been running for decades including the European Monitoring and Evaluation Program (EMEP), the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the United States National Atmospheric Deposition Program (NADP). Nitrogen deposition in Europe and North America has been relatively well documented (Erisman et al. 2003; Holland et al. 2005). However, synthesis of the national patterns and characteristics of N deposition in China is lacking. The objectives of this chapter are to: 1) assess the patterns of wet deposition of dissolved inorganic nitrogen (DIN = NH_4^+-N + NO_3^--N) averaged during the period 1995 to 2007; and 2) evaluate the rates of wet N deposition onto urban, rural and remote areas using observed data from the published literature and online reports. Furthermore, wet deposition of dissolved organic nitrogen (DON) is also summarized in this paper because it has been found to be directly taken up by boreal forest plants (Näsholm et al. 1998) and phytoplankton (Peierls and Paerl 1997) and may play a considerable role in increasing primary productivity in forest (Näsholm et al. 1998) and marine (Duce et al. 2008) ecosystems. Due to the limited measurements of dry deposition and its large uncertainty, dry deposition was not considered in this chapter.

6.2 Data Collection and Statistical Analysis

There are several related networks monitoring wet nitrogen deposition in China including the sub-network of Acid Deposition Monitoring Network in East Asia (EANET) in China (http://www.eanet.cc), the Integrated Monitoring Program on Acidification of Chinese Terrestrial Ecosystems (IMPACT) (Tang et al. 2001), the World Meteorological Organization Global Atmosphere Watch Precipitation Chemistry Program (WMO/GAW) of China (http://cdc.cma.gov.cn/index.jsp) and the China Agricultural University Network (CAU network) (Zhang et al. 2006, 2008a, b). There also are some other individual observation sites (e.g. Hu et al. 2007; Xie et al. 2008). Measurements of wet deposition are made by collection of wet only rainwater and snow samples and analysis of the concentrations of NH_4^+-N, NO_x^--N, and

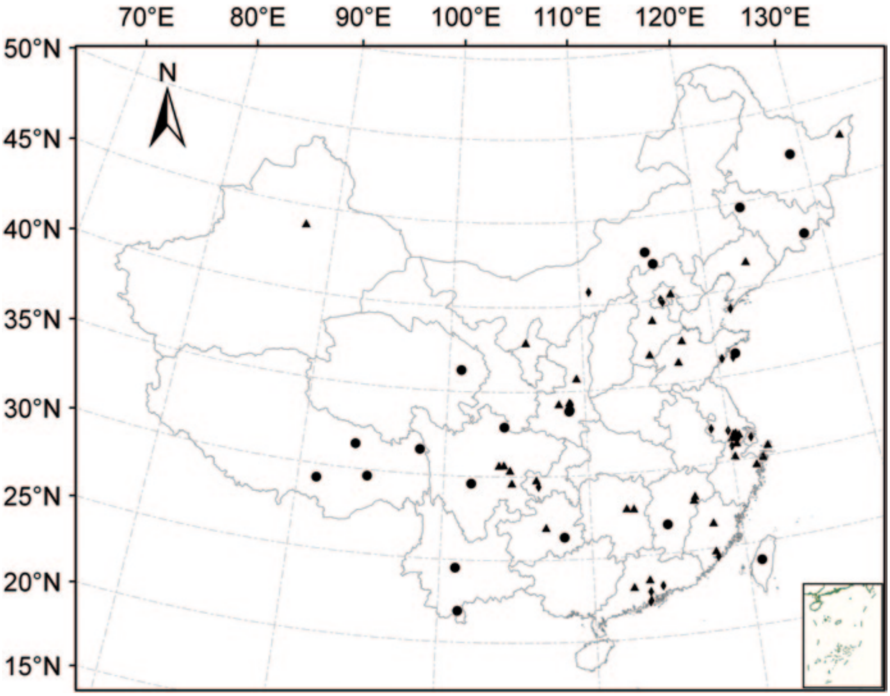

Fig. 6.1 Distribution of the 74 monitoring sites in this study. ● Remote, ▲Rural, ♦ Urban

total dissolved nitrogen (TDN). DON is estimated by subtracting DIN from TDN. Samples are stored at 4 °C before analysis or else the preservative (mostly CH_3Cl) is used. Quality control is carried out by evaluation of the ion balance of the samples. The rates of annual wet N deposition are calculated as follows:

$$\mathrm{R_i} = \sum C_i \times P_i \times 0.01 \qquad \text{(Eq. 6.1)}$$

in which $\mathrm{R_i}$(unit: kg N ha^{-1} year^{-1}) is the rate of annual wet N deposition, $\mathrm{C_i}$ (unit: mg N L^{-1}) is the average concentration of the samples for each precipitation event and $\mathrm{P_i}$ (unit: mm) is the precipitation for each event. We collected data from the published literature and online reports and established a database of wet deposition measured during the period 1995 to 2007, currently including 74 sites from 24 of the 34 provinces in China (Fig. 6.1). Data on wet deposition of DON were available at only 35 sites from 13 provinces. If data were observed for more than one year at a site, precipitation-weighted mean deposition rates were calculated as follows:

$$\overline{\mathrm{R}} = \frac{\sum \mathrm{R_i} \times \mathrm{P_i}}{\sum \mathrm{P_i}} \qquad \text{(Eq. 6.2)}$$

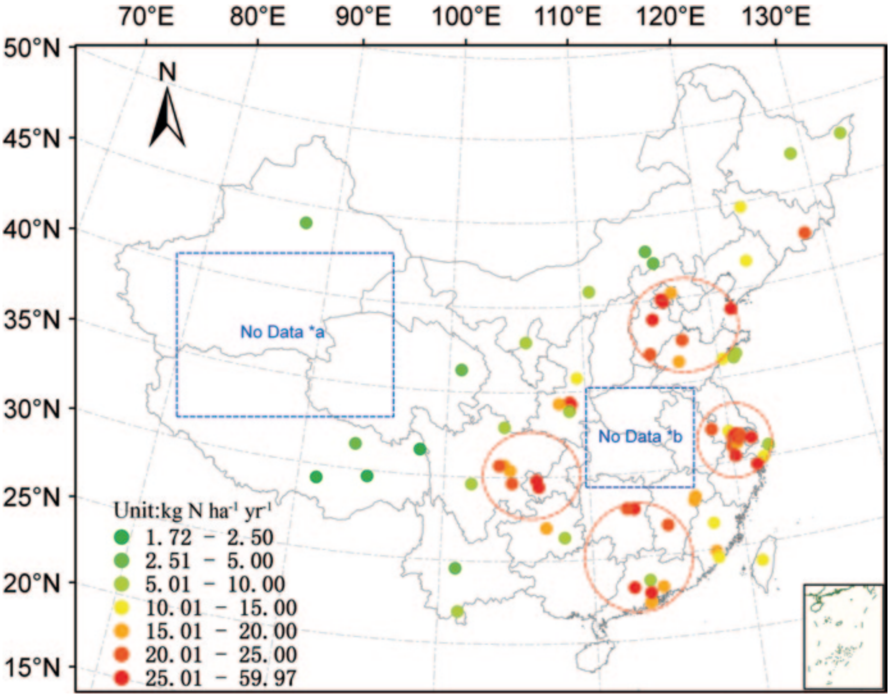

Fig. 6.2 Wet deposition of dissolved inorganic nitrogen deposition in China. Unit: kg N ha^{-1}year^{-1}. There are two blank areas with no data and *a is supposed to be with low rates of nitrogen deposition whereas *b is supposed to be with high rates of nitrogen deposition

in which $\overline{R}$ (unit: kg N ha^{-1} year^{-1}) is the average rate of annual wet deposition, R_i (unit: kg N ha^{-1} year^{-1}) is the total rate of wet N deposition for each year, and P_i (unit: mm) is the annual precipitation.

The spatial pattern of wet DIN deposition was illustrated using ArcGIS Desktop Version 9.1 (ESRI, Inc., USA). All the sites were divided into three groups—urban, rural and remote areas. The average rates of wet deposition onto these groups were assessed and compared with each other using independent-samples t-test in SPSS 13.0 for Windows (SPSS, Inc., USA).

6.3 Results and Discussion

6.3.1 Patterns of Wet DIN Deposition in China

Rates of wet DIN deposition showed large variation ranging from 1.72 kg N ha^{-1} year^{-1} at Shannan site in Tibet (Jia 2008) to 59.97 kg N ha^{-1} year^{-1} in Shanghai (Mei and Zhang 2007). Figure 6.2 shows that wet deposition is substantial in

Table 6.1 Summary of statistical results of wet inorganic nitrogen deposition. Unit: kg N $ha^{-1}year^{-1}$

	DIN[a]		NH_4^+-N		NO_x^--N		NH_4^+-N/ NO_x^--N ratio		No.
	Mean ± SD	Median	Mean ± SD	Median	Mean ± SD	Median	Mean ± SD	Median	
Urban	23.04 ± 12.63	23.27	14.18 ± 6.69	13.21	8.91 ± 6.58	8.06	1.96 ± 1.28	1.56	20
Rural	18.95 ± 7.64	19.15	11.22 ± 5.15	11.88	7.14 ± 3.62	6.83	1.73 ± 0.79	1.85	34
Remote	8.99 ± 7.26	8.01	4.80 ± 5.62	3.22	2.22 ± 1.45	2.21	2.50 ± 1.94	1.54	20
All	17.36 ± 10.53	16.79	10.66 ± 6.54	10.65	6.57 ± 4.93	5.68	1.96 ± 1.27	1.77	74

[a] DIN is sum of NH_4^+ -N and NO_x^- -N.

central, southern and eastern China. There appear to be four hotspots, namely the North China Plain or Jing-Jin-Ji region, the Yangtze River Delta, Sichuan Basin, and the Pearl River Delta. A similar deposition pattern was reported by Lü and Tian (2007), who appeared to have underestimated the rates of wet nitrogen deposition on the North China Plain compared with the results from Liu et al. (2006) and Zhang et al. (2008b). The national average wet DIN deposition is 17.36 (SD = 10.53) kg N ha^{-1} $year^{-1}$ which is much higher than that in Europe (6.8 kg N ha^{-1} $year^{-1}$) or in the United States (3.0 kg N ha^{-1} $year^{-1}$) (Holland et al. 2005). The national value during the 1990s and 2000s is also higher than that reported for China in the 1980's (Zhu et al. 1997). The NH_4^+-N/NO_x^--N ratios in wet deposition average 1.96 (SD = 1.27) which is similar to the ratio in Europe (1.64), but higher than that in the United States (0.84) (Holland et al. 2005). The average ratios of NH_4^+-N/NO_x^--N in wet deposition showed no significant difference between urban, rural and remote sites ($p = 0.430$, 0.174 and 0.335 respectively). NH_4^+-N still seems to dominate wet DIN deposition in China, indicating a substantial agricultural contribution to atmospheric N deposition.

Table 6.1 shows decreasing gradients of wet deposition for DIN, NH_4^+-N and NO_x^--N from urban to rural areas and then remote areas, but there is no significant difference between urban and rural sites in DIN ($p = 0.143$), NH_4^+-N ($p = 0.083$) or NO_x^--N ($p = 0.219$). Intensive agricultural activities in rural areas combined with the short-range transportation of N emissions (e.g., NO_x) from urban areas to rural areas are supposed to have elevated the rates of wet deposition in rural areas in China. At 52 % of these 54 rural sites, deposition rates exceeded 15 kg N ha^{-1} $year^{-1}$ and reached the critical loads for all types of ecosystems according to Bobbink et al. (2010). This suggests that negative effects of N deposition on ecosystems are likely to occur in large areas of China, particularly in the centre and eastern parts.

6.3.2 Wet Deposition of DON in China

Most of the wet DON deposition ranged from 1.1 kg N ha^{-1} $year^{-1}$at Biru site in Tibet (Jia 2008) to 11.7 kg N ha^{-1} $year^{-1}$ at Taihu site in Jiangsu province (Song et al. 2005). The average rate of DON deposition is 4.84 (SD = 2.80) kg N ha^{-1} $year^{-1}$, which is higher than 3.1 (SD = 2.8) kg N ha^{-1} $year^{-1}$ averaged data mainly in Europe

Table 6.2 Summary of statistical results of wet DON deposition

	Wet deposition of DON (kg N $ha^{-1}yr^{-1}$)		Ratio of DON/TDN(%)		No.
	Mean ± SD	Median	Mean ± SD	Median	
Urban	7.34 ± 2.16	6.15	24.8 ± 4.3	26.4	7
Rural	4.68 ± 2.78	4.25	19.5 ± 7.5	16.7	20
Remote	3.05 ± 1.71	2.90	41.0 ± 18.6	39.2	8
All	4.84 ± 2.80	4.29	25.4 ± 13.5	22.8	35

and the United States (Neff et al. 2002). DON contributed 25.4 % (SD = 13.5 %) to wet TDN deposition in China, which was slightly lower than the reported DON/TDN ratio of 30–35 % in other regions worldwide (Neff et al. 2002; Cornell et al. 2003; Duce et al. 2008). The rates of DON in wet deposition showed decreasing trends from urban areas to rural areas and then remote areas (Table 6.2) and the differences between rural and remote sites were not significant ($p = 0.135$). The DON/TDN ratios showed significantly increasing trends from rural and urban areas to remote areas ($p < 0.05$). These results indicate that DON makes an important contribution to the overall N deposition and its influence becomes increasingly more important from urban to remote areas in China.

6.4 Conclusions and Outlook

High rates of wet N deposition have been observed in large areas, particularly in central and eastern China. Average rates of wet DIN deposition have substantially exceeded those in Europe and North America. Average rates of wet deposition of DON were as high as 4.84 kg N ha^{-1} $year^{-1}$ and contributed about one quarter of the TDN deposition. Rates of wet N deposition have exceeded 15 kg N ha^{-1} $year^{-1}$ in large parts of the non-urban areas. These results suggest that in large areas of central and eastern China elevated nitrogen deposition is likely to exert negative effects on the natural and semi-natural ecosystems. Wet N deposition in rural and urban areas was much higher than that in remote areas. No significant difference in wet deposition has been found between rural and urban areas, suggesting that both agricultural sources and urban sources contribute to elevated N deposition. Uncertainties exist when synthesizing observed data from different networks and individual monitoring sites because the methods of sample collection and chemical analysis are not always fully consistent.

A long-term national monitoring network needs to be integrated with sufficient sites for the routine measurement of N deposition using standard collection and measurement methods. Specific models for China are also urgently needed to simulate the patterns and projections of N deposition. In addition, the environmental impacts of the elevated N deposition should be assessed systematically and scientific recommendations or strategies for policy makers to reduce anthropogenic reactive N emissions and negative effects of N deposition on sensitive ecosystems should be acted on.

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Chapter 7
Enrichment of Atmospheric Ammonia and Ammonium in the North China Plain

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Abstract Atmospheric ammonia and ammonium in PM_{10} were measured at six sites (two suburban sites and four rural sites) in the North China Plain (NCP) between August 2006 and September 2009, i.e. for 3 years. The annual mean concentrations of ammonia and ammonium were 7.3–19.9 μg N m^{-3} with an average of 12.8 μg N m^{-3} and 5.6–13.1 μg N m^{-3} with an average of 9.6 μg N m^{-3} respectively, at the sampling sites. Both ammonia and ammonium concentrations were higher at the rural sites than at the suburban sites, highlighting the importance of agricultural sources for atmospheric ammonia and ammonium. Higher ammonia concentrations were observed in the nitrogen (N) fertilization seasons, indicating that ammonia emission from N fertilizer application was an important source of atmospheric ammonia in the NCP. Based on the measured ammonia and ammonium concentrations and their deposition velocities taken from literatures, the annual mean NH_x (NH_3 plus NH_4^+) dry deposition rate was 25.6 kg N ha^{-1} $year^{-1}$ among the six sampling sites. The high NH_x concentrations and dry deposition rates in the NCP indicated agricultural sources were a large contributor to air pollution, and should be taken into account in the control of regional air pollution.

Keywords Ammonia • Dry deposition • Nitrogen deposition • Particulate ammonium

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7.1 Introduction

Ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. Once it has entered the atmosphere, it can deposit to land surface directly in gas form or react with acidic gases (e.g., H_2SO_4, HNO_3 and HCl) to form secondary ammonium particles, aerosols which can then be removed by dry and wet deposition, or be transported long distances (Sutton et al. 1993; Asman et al. 1998). The formation of ammonium particles can affect air quality, human health and solar radiation (Erisman and Schaap 2004; Pinder and Adams 2007; Adams and Seinfeld 2001), while the deposition of ammonia and particulate ammonium can cause eutrophication, acidification and loss of biodiversity in natural and semi-natural ecosystems (Bergström and Jansson 2006; Bouwman et al. 2002; Stevens et al. 2004).

The North China Plain (NCP) is a region with intensive crop and animal production. The overuse of nitrogen (N) fertilizer and inappropriate treatment of animal faeces have led to large NH_3 emissions in recent years. For example, Zhang et al. (2010) estimated NH_3 emissions from dense areas of agricultural sources exceeded 100 kg N ha^{-1} in 2004 in the NCP. High NH_3 emission density in this region suggests a very high NH_x (NH_3 + wet NH_4^+) deposition. Wet deposition monitoring in this region partly supports this trend (Zhang et al. 2008). Dry NH_x deposition monitoring in this region has been hindered by a shortage of monitoring instruments. The objectives of this study were to: (1) monitor concentration dynamics of ammonia and particulate ammonium and reveal the transformation from ammonia to particulate ammonium in the NCP; and (2) infer the dry deposition of NH_x, which mainly originates from agricultural sources, in the NCP.

7.2 Materials and Methods

7.2.1 Sampling Sites

Sampling was conducted at six agricultural sites in the North China Plain. The six sites include Dongbeiwang (DBW), Shangzhuang (SZ), Quzhou (QZ), Huimin (HM), Wuqiao (WQ) and Shouguang (SG). Their locations are shown in Fig. 7.1. DBW and SZ are suburban sites surrounded by small-scale cultivated lands mainly growing winter wheat and summer maize in rotation. QZ, WQ and HM are rural sites surrounded by large-scale cultivated lands for winter wheat, summer maize and cotton production, while SG is the rural site surrounded by large-scale greenhouse vegetable fields.

7.2.2 Sampling Methods and Chemical Analysis

Both passive and particle samplers were used to collect atmospheric NH_3 and particulate NH_4^+ respectively at all the sampling sites. Monthly NH_3 and particulate

Fig. 7.1 Locations of sampling sites in the North China Plain

NH_4^+ concentrations were monitored at DBW (from August 2006 to July 2007), SZ (October 2007 to September 2009) and QZ (from August 2006 to September 2009), while typically seasonal NH_3 and particulate NH_4^+ concentrations were monitored at WQ, HM (from August 2006 to July 2007) and SG (from September 2008 to August 2009). Detailed information about the sampling methods and chemical analysis are reported in Shen et al. (2009).

7.2.3 Estimation of Dry Deposition

Dry deposition (DD) of NH_3 and particulate NH_4^+ were inferred from the measured concentrations (C) and cited deposition velocities (V_d) based on the following function:

$$DD = (C - C_0) \times V_d \qquad \text{(Eq. 7.1)}$$

where C_0 is the compensation point. A compensation point of 5 μg N m^{-3}, which is a common value for a variety of crops (Denmead et al. 2008) was used for estimating the dry deposition of NH_3. The compensation point of NH_4^+ was considered to be 0 μg N m^{-3}.

7.3 Results and Discussion

7.3.1 NH_3 Concentrations

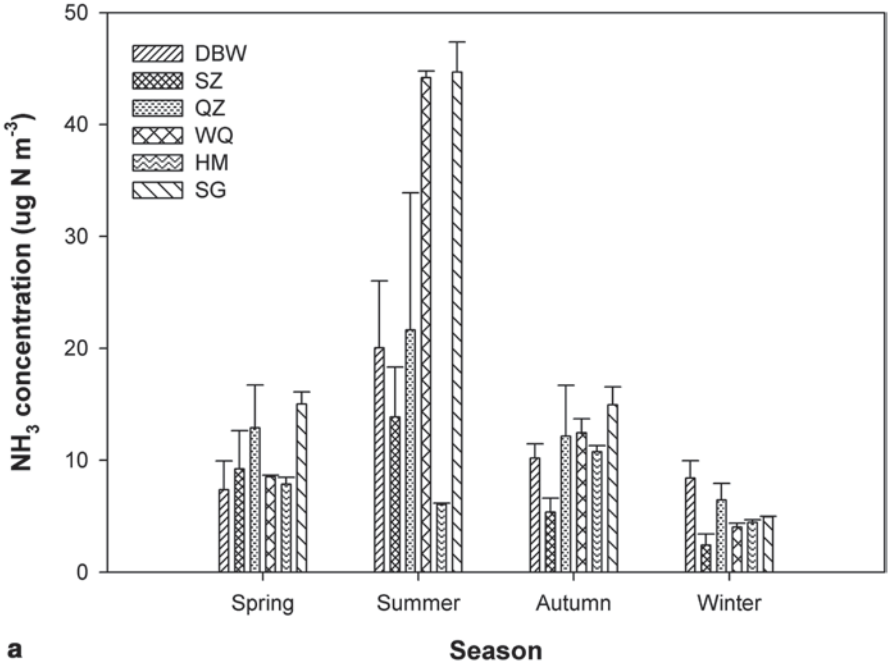
Annual mean NH_3 concentrations ranged between 7.3 and19.9 μg N m^{-3} with an average of 12.8 μg N m^{-3} at the sampling sites (Tab. 7.1). NH_3 concentrations at the rural sites (QZ, WQ, HM and SG) exceeded those at the suburban sites (DBW and SZ), with the exception of much lower NH_3 concentration at HM caused by rainfall scavenging during the summer sampling. As the area of cultivated land in rural areas is much larger than that in suburban sites in the NCP (ca.75 % *vs* ca.30 %), NH_3 emission intensities from N fertilizer application for crop production are also higher in those rural areas than in suburban areas. Thus greater NH_3 emission rates led to high NH_3 concentrations at rural sites. The NH_3 concentration was highest at SG (Tab. 7.1), where extremely large amounts of N fertilizers (e.g. >2,000 kg N ha^{-1} $year^{-1}$) were used to attain high yields of greenhouse vegetables (Guo et al. 2010).

Ammonia concentrations showed distinct seasonal variation at the six sampling sites (Fig. 7.2). The seasonally averaged NH_3 concentrations across the six sampling sites were 10.1, 25.1, 11.0 and 5.1 μg N m^{-3} respectively, in spring, summer, autumn and winter. Summer NH_3 concentrations were 3.9, 2.5 and 1.3 times higher than NH_3 concentrations in winter, spring and autumn, respectively. Nitrogen fertilizer application and high temperature most likely caused the highest NH_3 emission rates and subsequently higher NH_3 concentrations in the summer. In contrast, the winter temperatures were very low and almost no fertilizers were used, conditions that are not conducive to NH_3 formation. Consequently NH_3 emissions were low at all the sampling sites.

Table 7.1 Estimates of NH_3 and particulate NH_4^+ dry depositions at sampling sites

Site	NH_3 μg N m^{-3}	NH_4^+ μg N m^{-3}	DD_{NH3} kg N ha^{-1} year^{-1}	DD_{NH4+} kg N ha^{-1} year^{-1}	DD_{NHx} kg N ha^{-1} year^{-1}
DBW	11.5	8.0	15.2	6.1	21.3
SZ	7.7	5.6	6.3	4.2	10.5
QZ	13.3	11.7	19.4	8.9	28.3
WQ	17.3	13.1	28.7	9.9	38.6
HM	7.3	11.3	5.4	8.6	14.0
SG	19.9	8.0	34.8	6.1	40.9
Average	12.8	9.6	18.3	7.3	25.6

Dry deposition velocities are 0.74 and 0.24 cm s^{-1} for NH_3 and NH_4^+ respectively according to Hanson and Lindberg 1991
Compensation point for NH_3 is 5 μg N m^{-3} based on Denmead et al. 2008, while that for NH_4^+ is zero



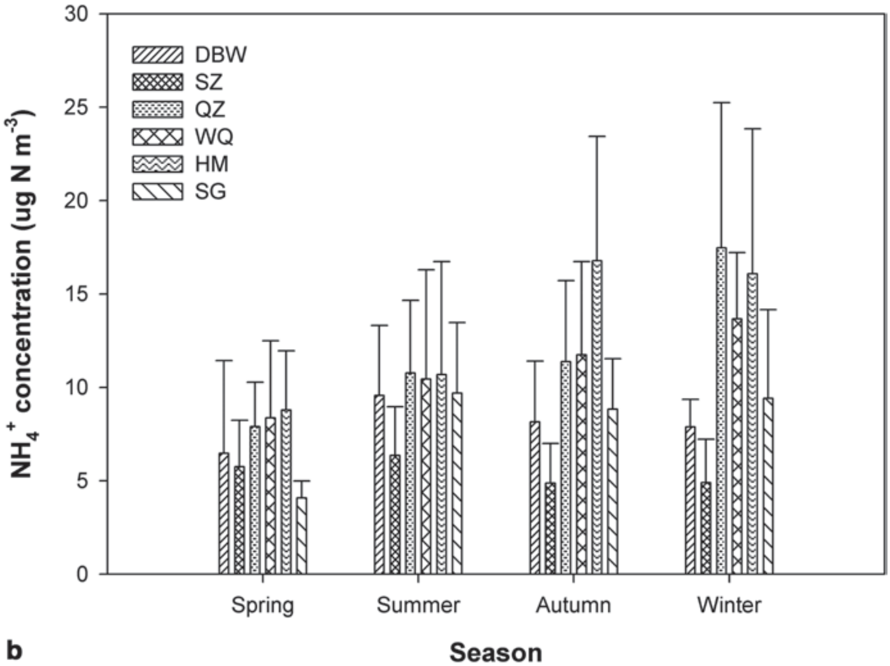


Fig. 7.2 Average concentrations and the standard deviations (mean square errors) of NH_3 (**a**) and particulate NH_4^+ (**b**) in the four seasons at the sampling sites

7.3.2 Particulate NH_4^+ Concentrations

Mean particulate NH_4^+ concentrations ranged from 5.6 to 13.1 µg N m^{-3} with an average of 9.6 µg N m^{-3} at the six sampling sites. NH_4^+ concentrations were also higher at rural sites than at suburban sites. This is likely to be caused by higher NH_3 concentrations at rural sites. The seasonal trends for NH_4^+ concentrations at the sampling sites were different from those for NH_3. As shown in Fig. 7.2, higher NH_4^+ concentration occurred in the summer at the rural sites, compared with autumn and winter at the suburban sites. Different seasonal variation patterns of particulate NH_4^+ at the sampling sites can be ascribed to a number of factors i.e. factors affecting gas to particle conversion, meteorological conditions and rainfall washout, which can influence particulate NH_4^+ concentrations.

A previous study showed that particulate NH_4^+ occurred mainly in the form of fine secondary particles, e.g. $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, at two sites in the NCP (Shen et al. 2009). In this study, we found higher particulate NH_4^+ concentrations at six sampling sites in the NCP, indicating that particulate SO_4^{2-} and NO_3^- concentrations would also be higher at these sampling sites. The occurrence of high concentrations of secondary particles in the NCP has implications for human health, air quality and solar radiation in this region. For example, heavy PM_{10} pollution has caused high rates of mortality and morbidity in Beijing in recent years (Zhang et al. 2007). In order to reduce the damage caused by these ammonium related particles, it is very important to control NH_3 emissions from agricultural sources (e.g., N fertilization and animal husbandry) in the NCP.

7.3.3 Dry Deposition of NH_3 and NH_4^+.

At the sampling sites, dry deposition rates were inferred based on the measured concentrations and deposition velocities taken from the literature. This enabled estimation of the atmospheric deposition of reduced nitrogen (NH_x) to croplands and its potential impacts on natural and semi-natural ecosystems. As shown in Tab. 7.1, the average NH_x dry deposition was 25.6 kg N ha^{-1} year^{-1}. Considering high NH_x wet deposition in the NCP (18 kg N ha^{-1} year^{-1}, according to Zhang et al. 2008), the total mean deposition (wet plus dry) of NH_x can be as high as 44 kg N ha^{-1} year^{-1} at the sampling sites. Such levels of NH_x deposition should be considered in N fertilizer management for crop production to improve N fertilizer use efficiency as well as reducing N loss to environment (e.g. atmosphere, groundwater and rivers) in the NCP. The high NH_x deposition may have contributed to eutrophication of lakes (Song et al. 2005) and cropland acidification (Guo et al. 2010) in China. Such negative effects have been documented by many monitoring and modelling experiments worldwide (Bergström and Jansson 2006; Bouwman et al. 2002; Stevens et al. 2004).

7.4 Conclusions

Atmospheric NH_3 and NH_4^+ concentrations (7.3–19.9 μg N m^{-3}) and their dry and wet deposition (average 43.6 kg N ha^{-1} $year^{-1}$) were very high across six monitoring sites in the NCP, reflecting large NH_3 emission from N fertilizer application and intensive domestic livestock production in the region. There were significant spatio-temporal variations of atmospheric NH_3 and NH_4^+ concentrations due to different NH_3 emission intensities and meteorological conditions at different seasons and locations. A number of negative effects originating from high atmospheric ammonium particles and NH_x deposition indicate NH_3 emissions, induced mainly from agricultural sources, should be reduced substantially in the NCP. Further study will be focused on developing more precise NH_x flux measurement techniques as well as reliable measures for controlling NH_3 emission from agricultural production in the NCP.

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Chapter 8
Nitrogen Deposition within the Littoral-Highlands County of Croatia Between 1996 and 2008

Ana Alebic-Juretic

Abstract Temporal trends in bulk nitrogen ($NH_4^+ + NO_3^-$) deposition at four sites within the Littoral-highlands County of Croatia are discussed. The selected sites included: the remote island Site 1, an urban and industrial coastal Site 2 (Rijeka), Site 3 which is a settlement and Site 4 a hunting resort located in the highlands area, claimed to suffer from acidic deposition. The lowest deposition of nitrogen (N) was measured at the remote Site 1 (5.6–11.2 kg N ha^{-1} $year^{-1}$), while higher values were obtained at the urban Site 2 (7.6–17.9 kg N ha^{-1} $year^{-1}$) due to the local washout of the atmosphere, and at the highlands Sites, 3 (10.3–32.1 kg N ha^{-1} $year^{-1}$) and 4 (5.6–24.9 kg N ha^{-1} $year^{-1}$) because of higher precipitation. The bulk nitrogen (N) deposition at the highlands Sites 3 and 4 is below the critical load for the corresponding soil-vegetation type (CL = 64.4 kg N ha^{-1} $year^{-1}$). In the period 1996–2003 NH_4-N made up 66 % of the N deposition at all sites, but since 2004 this ratio has diminished to 50 %, due to the increase in NO_3-N deposition. Overall there has been almost no change in N deposition at all except Site 4, where N deposition has increased, reflecting an increase in NO_3-N deposition but no significant decline in NH_4-N.

Keywords Bulk deposition • Inorganic nitrogen • NH_4^+/N-tot ratio

8.1 Introduction

As a result of human activities the input of reactive nitrogen (N_r) to terrestrial ecosystems worldwide has more than doubled (Smil 1990). Most of this input was confined to the developed regions of the world, due to fertilizer use, fossil fuel combustion and biomass burning, but is now rapidly increasing in the developing regions (Galloway and Cowling 2002). The observed responses of terrestrial systems to nitrogen (N) deposition can be understood within the context of the so called "nitrogen saturation" model developed from temperate–forest ecosystems

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(Aber et al. 1989). This model predicts that N limited systems will initially retain anthropogenic N, using it for plant and microbial growth, as well as accumulation in biomass and soil organic matter; then at the point when inputs of N begin to exceed the biotic (and possibly abiotic) demands for N within the ecosystem, the system is predicted to lose its N retention capacity. As a consequence, the excess of N can be lost in solution or via gaseous emissions. Furthermore, the model predicts a decrease in production in response to: cation losses, nutrient imbalances or increased susceptibility to stress such as frost, ozone or insect attack.

Increased N availability due to atmospheric N deposition leads to enhanced growth and dominance of fast growing, nutrient demanding species, over slow-growing nutrient economical ones, with a decline in species richness. Also alteration of plant tissue chemistry and timing of growth is likely to change the interaction between plants and herbivores (Matson et al. 2002).

Reduced biodiversity due to long-term N deposition has been observed in grasslands across Great Britain (5–35 kg N ha^{-1} $year^{-1}$), even at quite low annual nitrogen deposition. Species adapted to infertile conditions were systematically reduced at high nitrogen deposition. At the mean chronic N deposition rate of Central Europe (17 kg N ha^{-1} $year^{-1}$) there was a 23% reduction in species compared to grasslands receiving the lowest levels (5 kg N ha^{-1} $year^{-1}$) of N deposition (Stevens et al. 2004). According to Hautier et al. (2009), competition for light is a major mechanism of plant diversity loss in response to eutrophication.

Though analysis of precipitation chemistry within the Littoral-highlands County started in 1984 (Alebic-Juretic 1994) with the determination of sulphates and nitrates, the analyses were only extended to include ammonium in 1996. As NO_3^- and NH_4^+ form approximately 85% of the nitrogen species in precipitation (Kieber et al. 2005), their sum may be used as an indicator of reactive N deposition. Wet deposition (1,200–2,000 mm of rain annually) dominates in this area. Here we present temporal trends in bulk total nitrogen ($NH_4^+ + NO_3^-$) deposition at four sites within the Littoral-highlands County of Croatia. The contribution of dry deposition was not measured. The major source of oxidized nitrogen is industrial combustion (power plant, petroleum refinery) and traffic at the urban Site 2, the latter being the only source at highlands town Site 3. Refrigerating units in the harbour and petroleum refinery were industrial sources (with unknown emission) of ammonia at urban Site 2, while humans as ammonia sources can be considered in Sites 2 (Alebic-Juretic 2008) and 3. Due to the infertile nature of the soil and orography, agriculture is not an important economic activity and ammonia source in this area. Sites 1 and 4 are uninhabited remote locations.

8.2 Materials and Methods

8.2.1 Location of Sampling Sites

The locations of the sampling sites are given in Fig. 8.1.

Site 1 (Vrana) is a remote island site, approximately 100 km south from Rijeka, 250 m above sea level (a.s.l.) Site 2 (Rijeka) is an urban site (approximately 145,000

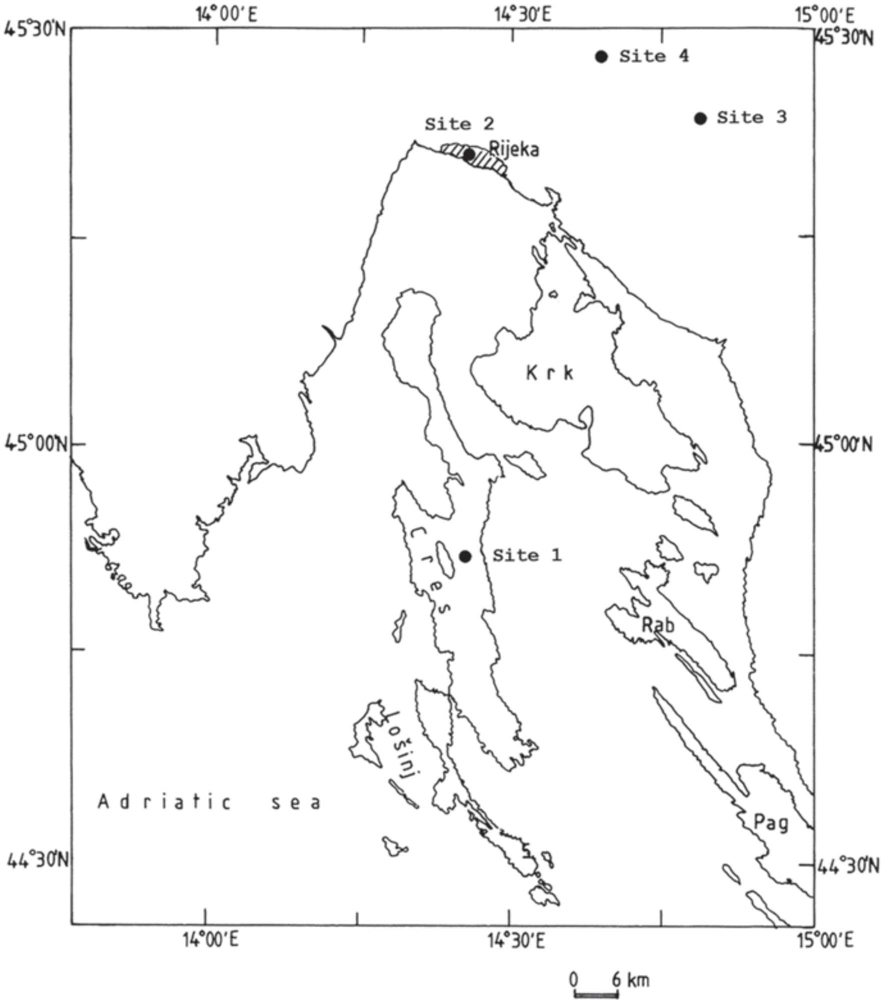

Fig. 8.1 Location of sampling sites

inhabitants), based at the Institute building in the wider city centre, 20 m above street level, at the divide between the harbour and residential area. Site 3 (Delnice) is a small settlement (approximately 6,200 inhabitants) in a mountainous area, 700 m a.s.l., approximately 40 km east of the city. Site 4 (Lividraga) is an uninhabited hunting resort in a mountainous area 930 m a.s.l., approximately 25 km north-east from Rijeka.

8.2.2 Methods of Analyses

Daily bulk rainwater samples were collected in open polyethylene buckets having 12 cm diameter and 15 cm height. The buckets were supported in aluminium

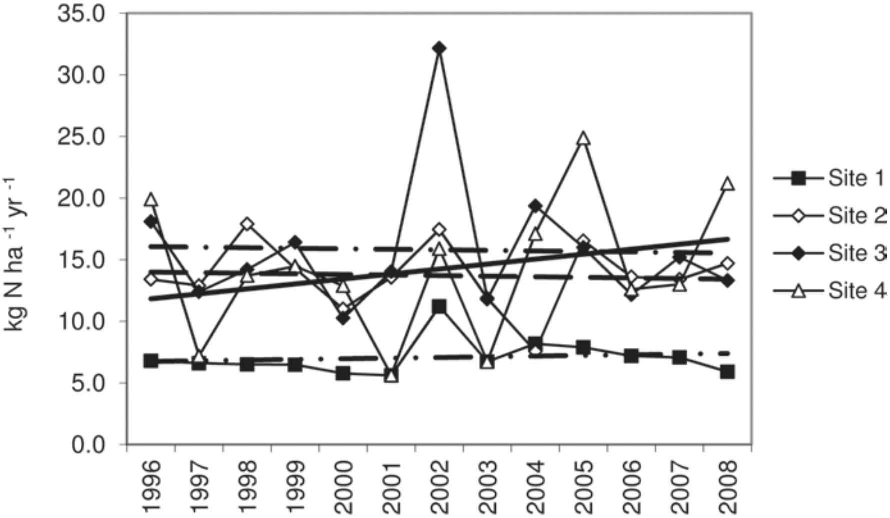

Fig. 8.2 Bulk total-N ($NO_3^- + NH_4^+$) deposition at four selected sites (kg N ha^{-1} year^{-1}) showing a particularly large Saharan dust episode in 2002

brackets 2 m above the ground. The buckets were replaced with clean ones once a day to avoid uncontrolled contamination by dry deposition.

The rainwater acidity was determined by measuring pH with pH-meter. Concentrations of ammonium and nitrate were determined by UV-VIS spectrometry (WHO 1976; APHA 1985). The respective lower detection limits (LDL) were: 0.1 mg/l for ammonium and 0.2 mg/l for nitrates. Annual deposition rates were obtained from the concentration of N species and the rainwater volumes collected over the year. The annual depositions of N were compared with critical loads for corresponding soil-vegetation type, where available. Irregular precipitation patterns during the seasons led to different deposition rates of N (and other species).

8.3 Results and Discussion

In an earlier examination of the precipitation data it was clear that orography was playing an important role in the deposition of acidic species: local wash out of the atmosphere in the wider urban area of Rijeka, an industrialized city within the Rijeka bay (Alebic-Juretic 1994), and greater precipitation in the background Highlands District (Alebic-Juretic 2008). The Highlands District was claimed to suffer from acidic deposition (Coz-Rakovac et al. 1995), though the first precipitation analyses started only in 1996, by which time SO_2 emissions had decreased by ~70% and NO_x emissions had fallen by ~40% relative to the mid-eighties in the Rijeka Bay area (Matkovic and Alebic-Juretic 1998). Such trends were similar to those observed in Europe (Toerseth et al. 2001). These lower emissions resulted in a decline

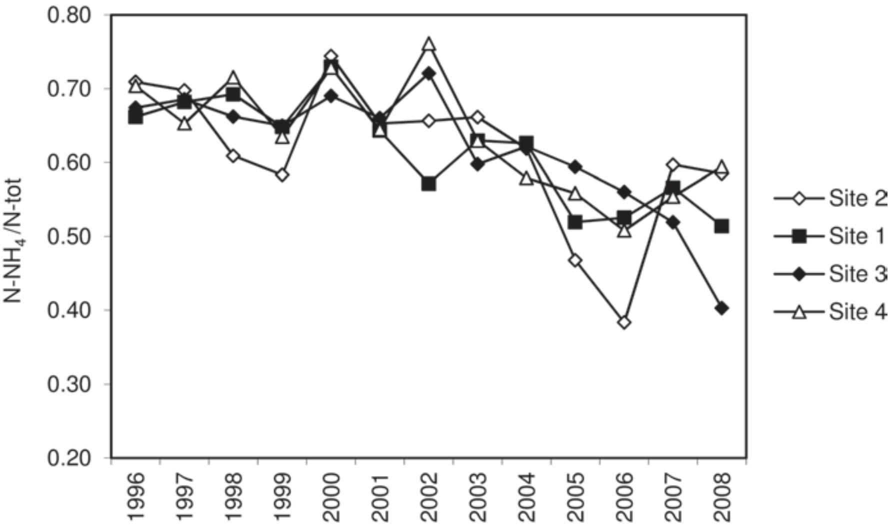

Fig. 8.3 Proportion of reduced NH_4-N at four selected sites

in the background air pollution for both SO_4-S and to a lesser degree NO_3-N deposition within the Rijeka Bay area (Alebic-Juretic 2008).

Deposition of total-N at the selected sites is given in Fig. 8.2. The lowest N deposition was obtained at the remote Site 1 (5.6–11.2 kg N ha^{-1} year^{-1}), while higher values were obtained at urban Site 2 (7.6–17.9 kg N ha^{-1} year^{-1}) due to the local washout of the atmosphere and at the highlands Sites, 3 (10.3–32.1 kg N ha^{-1} year^{-1}) and 4 (5.6–24.9 kg N ha^{-1} year^{-1}) reflecting the enhanced precipitation. Bulk N depositions at the highlands Sites 3 and 4 are below the critical loads (CLs) for the corresponding soil-vegetation type (*Abietatum dolomiticum/Calcic cambisol with redzina*) with $CL_{tot\text{-}N}=64.4$ kg N ha^{-1} year^{-1} (Jelavic et al. 1998). Such a high CL reflects the buffering capacity of the alkaline composition of the underlying geology. However, exceedance might have been possible at the most sensitive area within the Highlands District (*Querco-Carpinetum orientalis/Chromic cambisols*) with $CL_{tot\text{-}N}=24.4$ kg N ha^{-1} year^{-1} (Jelavic et al. 1998) in 2002, when a severe Saharan sand episode led to unusually high N and sulphur (S) deposition. Saharan sand episodes, the so called 'yellow rain' are characterized by high pH and high deposition of sulphates, nitrates, ammonium, and also calcium and iron. The quantity of Saharan sand deposited during an exceptionally severe episode of 'yellow rain' on April 12th 2002 was estimated to 11,000 t for the whole County area (1,320 km^2) bearing 1,239 kg of sulphates, 206 kg of nitrates and 159 kg of ammonium (Alebic-Juretic 2005).

In the period 1996–2003 NH_4-N made up 67 % of total-N deposition at all sites, but since 2004 this ratio has fallen down to 50 % reflecting the increase in nitrate-N (Fig. 8.3) from increased traffic in the wider region. The increase in nitrate-N offset the decline in ammonium-N so that overall there was no change in reactive N deposition at all Sites, except Site 4 (Fig. 8.4). This remote forest site showed no significant

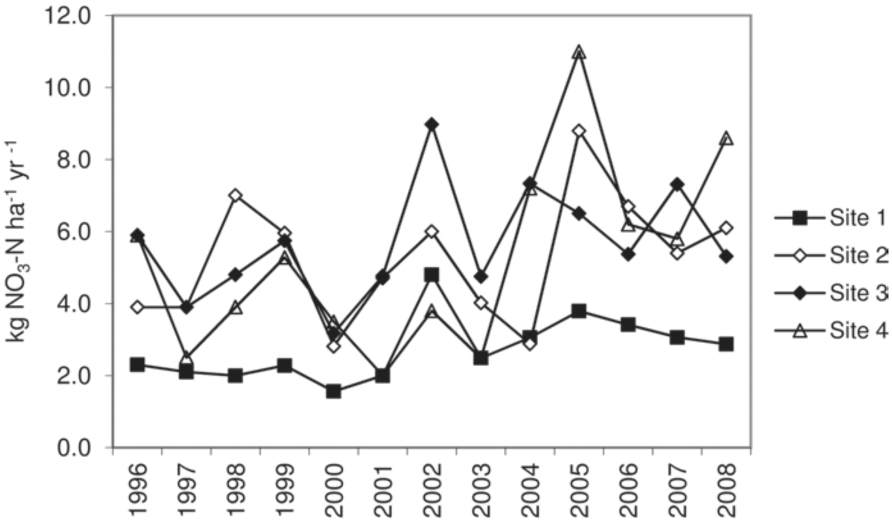

Fig. 8.4 Deposition of NO_3-N^- at four selected sites (kg NO_3-N ha^{-1} $year^{-1}$)

decline in ammonium-N, since the natural vegetation and the underlying soil are both ammonia sources (Langford and Fehsenfeld 1992; Bouwman et al. 1997).

8.4 Conclusion

The 12-year survey of bulk N deposition (wet + dry excluding occult) shows no exceedances of CLs for reactive N deposition in the area studied. These findings therefore contrast with the decline in forests observed in the mountainous Highlands District (Gorski kotar). This suggests that the observed forest decline was caused by factors other than N, or that the CL is too high to protect the ecosystem. Recent studies in boreal forests, where background N deposition is extremely low, suggest this might be the case (Nordin et al. 2005). An increase in vehicular use in the wider region appears to account for the increase in nitrate deposition since 2004.

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Chapter 9
Atmospheric Deposition of Reactive Nitrogen in India

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Abstract The increasing demand of food and energy of the global population is contributing excess reactive nitrogen (N_r) in the atmosphere primarily in the form of ammonium and nitrate compounds. Subsequently, through wet and dry deposition processes, these compounds are deposited onto the ground, vegetation, soils, water bodies etc. enriching these systems with excess nitrogen (N). Knowledge about N deposition in North America and Europe is quite advanced because of systematic studies. But the present knowledge about N deposition in India and the south Asian region is very limited due to a lack of systematic measurements dedicated to nitrogenous compounds. Though a number of wet deposition studies have been reported by various groups for different sites and years in India, only a few of these are considered as having good quality data. This chapter reports quality controlled wet deposition fluxes of N_r at rural (2006–2008) and urban (2005–2008) sites in south India as part of the RAPIDC-CAD programme. The rural site Hudegadde is located in the reserve forest area of Western Ghats by the south-west coast of India while the urban site Hyderabad, the capital of Andhra Pradesh State is located in south-central India. In general, at both the sites, wet deposition of N through NH_4^+ was observed to be higher than NO_3^-. Fluxes of NH_4^+ showed an increasing pattern

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at Hudegadde, while those of NO_3^- showed an increasing pattern at Hyderabad. The possible reason for increasing NH_4^+ at Hudegadde may be an increase in biomass burning and vegetation decay in the forest areas, which contribute higher ammonia to the atmosphere, together with transboundary pollution due to air-masses from nearby continental areas. The increasing pattern of NO_3^- fluxes at Hyderabad might be due to an increase in population, vehicular density and other urban activities. Projections using the MATCH model coupled with rain chemistry measurements showed that the Indo-Gangetic region experiences very high wet deposition of NH_4^+ which might be due to a prevailing higher density of ammonia sources in the region. This chapter also highlights the importance of dry deposition of N_r species for the Indian region.

Keywords Ammonium fluxes • Dry deposition rates • Indian region • Reactive nitrogen • Wet deposition

9.1 Introduction

The primary reactive nitrogen (N_r) species are NH_3 and NO_x, which react further to produce other N_r species such as HNO_3, NH_4^+ and NO_3^- in the atmosphere. The major sources of NH_3 are cattle, agricultural activities, fertilizer applications, fertilizer manufacturing, biomass burning, human excretion, and anaerobic activities in the soil system. The major sources of NO_x are vehicular exhaust, industrial combustion processes, and biomass burning. Emissions of NO_x result in the formation of nitric acid in the atmosphere. Ammonia (NH_3) reacts with nitric acid or sulphuric acid forming ammonium sulphate and ammonium nitrate compounds. The presence of various phases of reactive nitrogen depends upon meteorological conditions, atmospheric acidity, temperature, humidity, and the scavenging processes.

In many countries, global emissions of nitrogen (N) and sulphur species are increasing due to the enhanced energy demands of a rapidly growing population. In the Indian region also, an upward trend of energy consumption has been recorded during the past two decades. Considering their importance, studies of wet and dry deposition have been carried out systematically in North America, Canada, Europe and East Asia. But in the Indian region, deposition fluxes have not been reported through a comprehensive and systematic network. The 'Composition of the Atmospheric Deposition' (CAD) program was an effort to study wet and dry deposition in Asia focusing upon quality of data (www.sei-international.org/rapidc/networks-cad.htm).

This chapter presents some of the CAD findings, highlighting the wet deposition of nitrate and ammonium at a rural and an urban site in south India. At Hudegadde a rural site in south-west India, 3 years of data on wet deposition fluxes of nitrate and ammonium are discussed, while at Hyderabad, an urban site in south-central India, 4 years data are discussed. The deposition of NH_4^+ and NO_3^- at other Indian sites is also based on the compilations of Kulshrestha et al. (2003, 2005). The comparison of dry and wet deposition is also highlighted with reference to the Indian region.

9.2 Methods

9.2.1 Sampling Sites

As a part of the CAD program, samples of rain water were collected at two contrasting sites. The details of the sites are given below. Apart from this, data from about 100 locations as synthesized by Kulshrestha et al. (2003, 2005) are used to provide wet deposition flux estimates of NO_3^- and NH_4^+.

9.2.1.1 Hudegadde—A Rural Site

Hudegadde is a rural site located at 14.36° N and 74.54° E in Western Ghats by the south-west coast of India, in the Kannada district of Karnataka state (near the border of Kerala state). The site is located in a reserve forest in mountain ranges having dense green surroundings with thick forest and waterfalls. There are no residential houses nearby within a radius of 6 km. The site is located at 915 m above mean sea level (msl), and 145 km away from the coast of the Arabian Sea. The samples were collected using bottle and funnel on a rainfall event basis. The collector was installed just before the rain event to avoid any dustfall before the rain. The collector assembly was kept on the terrace of a house (~5 m above ground level), and at a height of 1 m from the base of the roof.

9.2.1.2 Hyderabad—An Urban Site

Hyderabad (17.5° N, 78.5° E) is the capital of Andhra Pradesh state of India. It is the fifth largest city in India with an area of 260 km^2. The land use is almost 93% urban (including industrial). The samples were collected at the terrace of the main building of our institute at a height of around 11 m above ground using a switch controlled rain water collector to avoid any contamination during sampling. The collector is opened whenever rain occurs and gets closed after the rain event with the help of a remote switch installed in the laboratory.

9.2.2 Sample Collection and Analysis

The samples were transferred into 60 ml polypropylene bottles and preserved by using a small quantity of thymol. The samples were kept in a refrigerator until they could be further analysed. The pH and electrical conductivity (EC) of these samples were measured by using a pH meter (Elico LI 612) and a conductivity meter (Elico CM 183), respectively. Both instruments were calibrated with a certified reference solution traceable to NIST. Determination of NO_3^- and NH_4^+ used ion chromatography (Metrohm 792 basic IC system). Separation of NO_3^- was performed with a Metrosep A supp 5-100 column, using a mixture of 3.2 mM

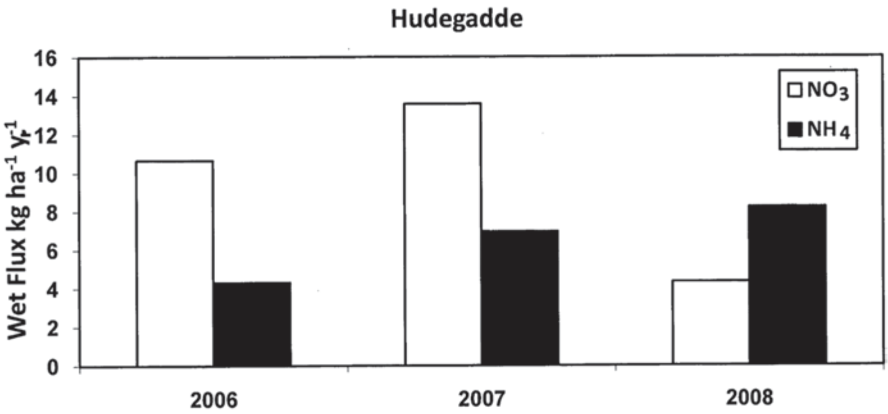

Fig. 9.1 Wet fluxes of NO_3^- and NH_4^+ at rural site Hudegadde, in India

Na_2CO_3 and $NaHCO_3$ as eluent at a flow rate of 0.7 ml/min. Separation of NH_4^+ was attempted by using a mixture of 4 mM tartaric acid (TA) and 0.75 mM of 2, 6-pyridine dicarboxylic acid (PDC) as eluent at a flow rate of 1.0 ml/min with the Metrosep C2-100 column.

9.3 Results and Discussion

9.3.1 Increasing Patterns of NO_3^- and NH_4^+

Wet deposition fluxes of NO_3^- and NH_4^+ at Hudegadde are shown in Fig. 9.1. These fluxes have been calculated for annual rainfall based on monsoon data, combined with the measured precipitation amount. It should be noted that non-monsoonal rains have higher concentrations of NO_3^- and NH_4^+ in samples and hence, the fluxes in this chapter represent conservative estimates.

Wet deposition fluxes of NO_3^- at Hudegadde were observed to be 11, 14 and 4 kg ha^{-1} year^{-1} during 2006, 2007 and 2008 respectively. At Hudegadde, average NH_4^+ fluxes were estimated as 4, 7 and 8 kg ha^{-1} year^{-1} during 2006, 2007 and 2008 respectively. While at Hyderabad, NH_4^+ deposition fluxes were estimated as 6, 14, 36 and 15 kg ha^{-1} year^{-1} and that of NO_3^- fluxes were estimated as 18, 44, 52 and 63 kg ha^{-1} year^{-1} during 2005, 2006, 2007 and 2008, respectively (Fig. 9.2).

Although the short-term data of the present study are not sufficient to predict any trends, these results suggest that NH_4^+ fluxes have an increasing pattern at Hudegadde, while NO_3^- fluxes have an increasing pattern at Hyderabad. The possible reason for increasing NH_4^+ at Hudegadde may be due to an increase in biomass burning and vegetation decay in the forest areas, which contribute higher ammonia to the atmosphere. In addition, moving air-masses from nearby continental areas

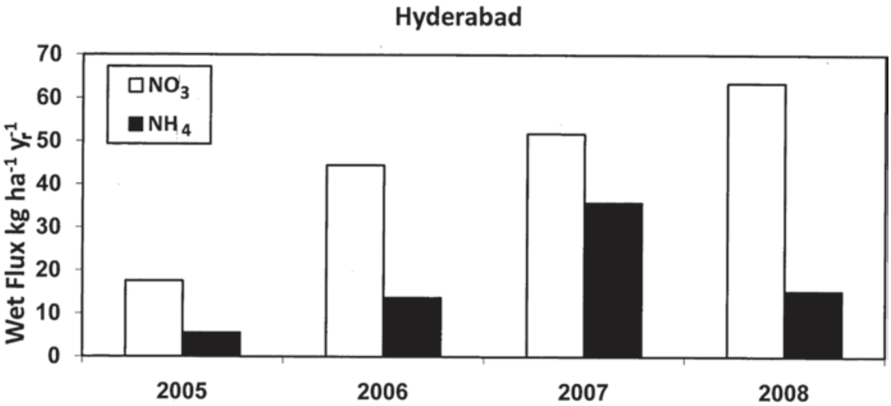

Fig. 9.2 Wet fluxes of NO_3^- and NH_4^+ at the urban site Hyderabad, India

also transport these fluxes to Hudegadde (Satyanarayana et al. 2010). The reason for the increasing pattern of NO_3^- fluxes at Hyderabad might be due to the growing size of the city, with an increase in population, vehicular density and industries etc. which contribute precursors of NO_3^- to the atmosphere. The decrease of NO_3^- at Hudegadde during 2008 and the decrease of NH_4^+ at Hyderabad during 2008 needs to be investigated in terms of source strength and trajectory analysis for these sites and years. This also suggests a need to carry out long-term N deposition measurements in the Indian region to quantify the trends and to reduce uncertainties in the measurements.

9.3.2 Wet Deposition Concentration and Rates for Different Categories of Sites in India

In a developing country like India, deposition measurements are carried out sporadically. Recently, Kulshrestha et al. (2003, 2005) have synthesized the data reported by various workers for about 100 locations in 35 research papers throughout the country. This review indicated poor data quality associated with NO_3^- and NH_4^+ values. In most of the studies, samples were not preserved properly. Also, delay in chemical analysis was found to be an important factor which is responsible for the decay of NO_3^- and NH_4^+ in samples.

Based on the rain chemistry data, the sites have been classified into five categories, i.e. rural, suburban, rural and suburban, urban and industrial (Kulshrestha et al. 2003). Average wet deposition fluxes of NO_3^- and NH_4^+ have been calculated for these categories which are presented in Table 9.1.

Table 9.1 shows that fluxes of NO_3^- are always higher than NH_4^+ at all categories of sites. Highest concentrations of NO_3^- are recorded for urban sites, which is obvious due to more vehicular emissions (contributing more NO_x as a precursor of NO_3^-). A similar feature has been observed at Hyderabad as reported in the

Table 9.1 Wet deposition flux of NO_3^- and NH_4^+ for different categories of sites in India as reported by Kulshrestha et al. (2003)

Site category	NO_3^- kg ha^{-1} year^{-1}	NH_4^+ kg ha^{-1} year^{-1}
Rural	18	3
Suburban	9	3
Rural and suburban	15	3
Urban	20	3
Industrial	17	6

Table 9.2 NH_4^+ and NO_3^- deposition at different sites (meq m^2 year^{-1})

Site	Category	Type of deposition	NH_4^+	NO_3^-	Reference
Delhi	Urban	Wet	19	26	Khemani et al. (1989)
		Dustfall	4	4	Parashar et al. (1996)
		DD aerosol	2	17	
		DD gases	115	3	
Pune	Suburban	Wet	17	18	Pillai et al. (2001)
		Dustfall	1	12	Pillai et al. (2001)
		DD aerosol	2	6	
		DD gases	16	2	
Bhubaneshwar /NK	Rural forest	Wet	22	13	Granat et al. (2001)
		Dustfall	–	2	Granat et al. (2001)
Silent Valley	Rural forest	Wet	11	74	Rao et al. (1995)
		Dustfall			
		DD aerosol	3	6	
		DD gases	2	1	
Sinhagad	Rural forest	Wet	16	8	Pillai et al. (2001)
		Dustfall			
		DD aerosol	1	3	
		DD gases	2	2	
Agra, Dayalbagh	Suburban	Wet	30	4	Saxena et al. (1991)
		Dustfall	3	6	Kulshrestha (1993)
		DD aerosol		27	
		DD gases			

DD dry deposition

previous section, where increasing fluxes of NO_3^- have been noticed. The highest NH_4^+ fluxes at industrial sites indicate that industrial areas also experience significant deposition of ammonia in India. Interestingly, suburban sites show minimum levels for both NO_3^- and NH_4^+ deposition, indicating minimum influence of nitrogenous sources. It should be noted that higher NO_3^- fluxes at rural sites might be due to soil resuspension. Projections using the MATCH model coupled with rain chemistry measurements in India show that wet deposition of NH_4^+ is the highest in the Indo-Gangetic region, which might be due to the prevailing higher density of ammonia sources in the region.

9.3.3 Importance of Wet and Dry Deposition in the Indian Region

In India, most of the rainfall occurs during the monsoon period (June–September) and the remaining period is dominated by dry weather conditions. Even during monsoons, there are gaps of several days when it does not rain. This highlights the importance of dry deposition of atmospheric constituents in the Indian region. According to Kulshrestha et al. (2003), dry deposition of gaseous ammonia is more significant than its wet deposition in India. Unfortunately, not many reports are available on dry deposition in India. Among the limited studies available, most of these consider dustfall as dry deposition without differentiating dry deposition of gases and particles. Table 9.2 shows estimated dry deposition of gas phase NH_3, NH_4^+ aerosols and NH_4^+ dustfall based on the reported studies as referred to in the table. In an estimate based upon EMEP dry deposition velocities, Singh et al. (2001) found that dry deposition of NH_4^+ was 9 times more significant than wet deposition at Agra. Wet deposition of NH_4^+ has been reported as 3.4 kg ha^{-1} year^{-1} as compared with 39 kg ha^{-1} year^{-1} of dry deposition.

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Chapter 10
Dry and Wet Atmospheric Nitrogen Deposition in West Central Africa

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Abstract This work is part of the IDAF (IGAC/DEBITS/AFrica) programme which started in 1995 with the establishment of 10 measurement sites representative of major African ecosystems. The objectives of the programme are to study wet and dry deposition fluxes, to identify the relative contribution of natural and anthropogenic sources and factors regulating these fluxes. This study presents an estimation of the atmospheric nitrogen (N) deposition budget in Africa based on a long term monitoring measurements database including gaseous, precipitation and aerosols chemical composition. Annual nitrogen fluxes including wet and dry processes are estimated to be around 6 kg N ha^{-1} year^{-1}, 6.5 kg N ha^{-1} year^{-1} and

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13 kg N ha^{-1} year^{-1} respectively over dry savanna, humid savanna and over the forest.

Keywords African ecosystems • Atmospheric deposition budget • Nitrogen • Wet and dry deposition

10.1 Introduction

The international program DEBITS (Deposition of Biogeochemically Important Trace Species) started in 1990 as part of the IGAC/IGBP (International Global Atmospheric Chemistry/International Geosphere-Biosphere Programme) " Core Project ". It is to study wet- and dry- atmospheric deposition in tropical regions (Lacaux et al. 2003). The DEBITS network includes 25 measuring stations well distributed within the tropical belt. DEBITS activities have been positively reviewed and are thus continuing within the new IGAC structure or DEBITS II (Pienaar et al. 2005; Bates et al. 2006). For tropical Africa, the IDAF (IGAC/DEBITS/AFRICA) Project started in 1994. Since IDAF has been recognized by the Institut National des Sciences de l'Univers (INSU) and the Centre National de la Recherche Scientifique (CNRS) as a part of the Environmental Research Observatory (ORE) network. ORE/IDAF has the mission of establishing a long-term measuring network to study the atmospheric composition and wet- and dry- atmospheric processes and fluxes.

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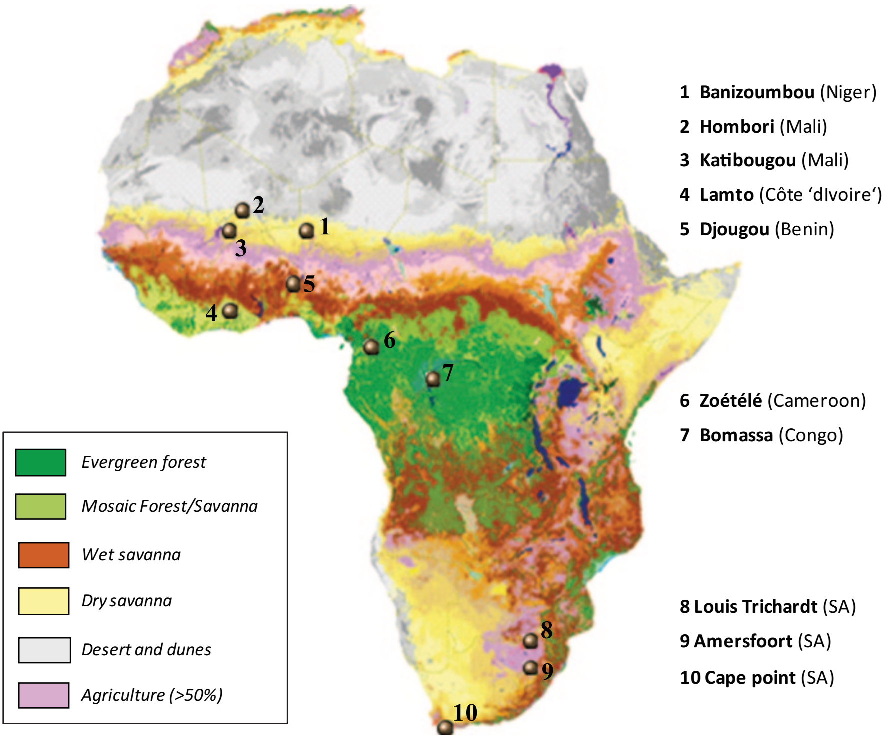


Fig. 10.1 Vegetation and location map of the 10 measurement stations of the IDAF network. Reused from Adon et al. 2010 (© Authors 2010. CC Attribution 3.0 License)

The IDAF program is associated with the African Monsoon Multidisciplinary Analyses/Long Observation Program (AMMA/LOP, Lebel et al. 2010) over West/Central Africa and with the South African Climate Change Air Pollution-PICS (SACCLAP) Program. The main objectives of IDAF were to measure wet- and dry- deposition fluxes and identify the relative contribution of natural and anthropogenic source. In this way, the IDAF activity is based on high quality measurements of atmospheric chemical data (gaseous, precipitation and aerosols chemical composition) on the basis of a multi-year monitoring. The IDAF project implemented 8 monitoring sites covering the major African ecosystems over West and Central Africa: dry savanna (Niger, Mali, South Africa), wet savanna (Côte D'Ivoire and Benin) and equatorial forest (Cameroon, Congo) (Fig. 10.1).

10.2 Regional Wet and Dry Nitrogen Deposition

The objective is to present a first estimation of the atmospheric nitrogen (N) deposition budget in West and Central Africa based on experimental measurements. To estimate atmospheric nitrogen (N) deposition, including both wet and dry processes, we compiled the IDAF N data (gas, particles, rain) obtained from the network presented above. We studied a transect going from dry savanna to humid savanna and forest. Presenting the different component of the N atmospheric deposition on these sites, i.e., dry deposition in gaseous and particulate forms associated with wet deposition, this study allows the relative contribution of dry and wet deposition processes to the total N deposition to be given.

10.3 Wet and Dry Deposition

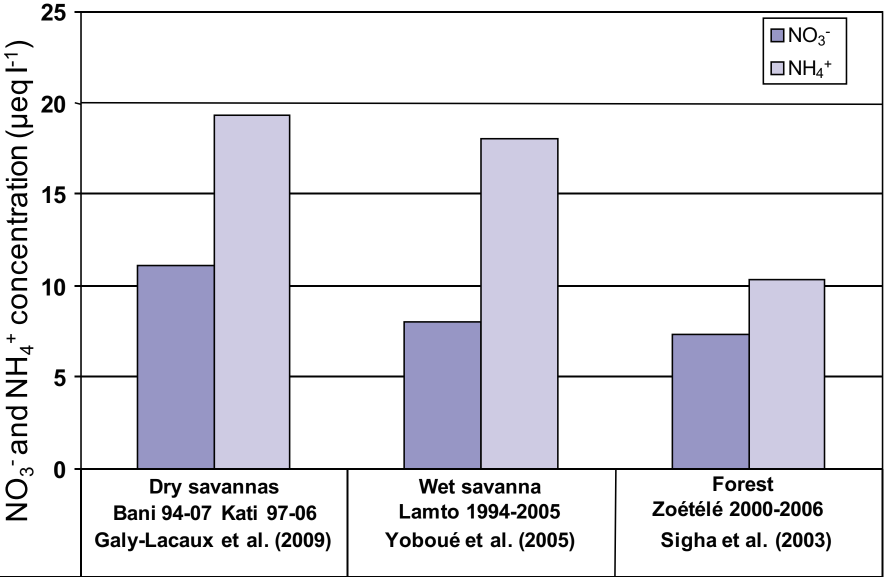
10.3.1 Wet Deposition

An automatic precipitation collector specially designed for the IDAF network has been installed in all stations. A local operator collects water from each rainfall event in a Greiner tube (50 ml). Preserving the rainwater samples from contamination is an important issue since microbial input could modify its chemical composition. Samples are refrigerated at 4°C and preserved with 15 mg of thymol biocide or stored in a deep freeze environment. Ion Analytical, and Ionic Chromatography procedures are given in Galy-Lacaux and Modi (1998).

The laboratory of Aerologie participate since 1996 to the international intercomparison program organized annually by WMO. According to prior results and through intercomparison tests organized by WMO, analytical precision is estimated to be 5% or better for all ions, within the uncertainties on all measured values presented here. Combining all the uncertainties of measurements and calculations, the uncertainty of the wet deposition fluxes is estimated to be about 10%.

To calculate wet N deposition in African dry savannas, we have compiled the annual volume weighed mean concentrations of nitrate and ammonium from the precipitation collected at 5 IDAF stations. The computation of nitrate and ammonium wet deposition has been done according to a mean annual rainfall for the studied period of each sites. The mean rainfall depth registered in Banizoumbou (Niger) and Katibougou (Mali) representative of dry savannas is 632 mm, in Lamto (Côte D'Ivoire) for wet savanna 1208 mm and in Zoétélé Cameroon for equatorial forests 1567 mm.

Figure 10.2 presents annual volume weighed mean concentrations of nitrate and ammonium for selected sites and integrated periods. Mean nitrate and ammonium concentrations in the dry savannas sites measured from 1994 to 2005 in Niger and from 1997 to 2006 in Mali are around 11 μeq L^{-1} of NO_3^- and 19 μeq L^{-1} of NH_4^+ (Galy-Lacaux et al. 2009). In the wet savanna, measurements performed from 1995 to 2002 give mean values of 8 μeq L^{-1} of NO_3^- and 18 μeq L^{-1} of NH_4^+ (Yoboué et al. 2005). In a forested ecosystem, Sigha-Nkamdjou et al. (2003) measured mean values of 7 μeq L^{-1} of NO_3^- and 10 μeq L^{-1} of NH_4^+ from 2000 to 2007. The chemical composition of rain shows a strong gradient of nitrate content. In the dry savannas, biogenic emissions of NO_x from soils have been identified as the major



	Dry savannas	Wet savanna	Forest
NO_3^-	11.1	8	7.3
NH_4^+	19.3	18	10.3

Fig. 10.2 Volume Weighed Mean (VWM) concentrations of nitrate and ammonium (µeq l^{-1})

contributor to the nitrate content of rain, while the high ammonium content is related to ammonia emission from animals (Serça et al. 1998; Galy and Modi 1998; Galy-Lacaux et al. 2009; Delon et al. 2010). Wet deposition of nitrate is estimated to be around 1 kg N-NO_3^- ha^{-1} year^{-1} and 1.7 kg N-NH_4^+ ha^{-1} year^{-1} in dry savannas, 1.4 kg N-NO_3^- ha^{-1} year^{-1} and 3 kg N-NH_4^+ ha^{-1} year^{-1} in wet savannas and 2 kg N-NO_3^- ha^{-1} year^{-1} and 3 kg N-NH_4^+ ha^{-1} year^{-1} in forests. The positive gradient of atmospheric nitrate and ammonium wet deposition fluxes is strongly dependent of the rainfall amounts gradient recorded along the studied ecosystems transect.

10.3.2 Dry Deposition

Considering the difficulties to measure directly dry deposition, the DEBITS program has adopted a strategy to infer indirect dry deposition measurements. Dry deposition is estimated on one hand from measurements of gaseous and particulate species based on continuous measurements of gaseous concentrations through passive gas sampling (NO_2, NH_3, HNO_3), and on bulk air sampling (ammonium and nitrate particulate content). On the other hand, realistic dry deposition velocity according to the site and the species needs to be calculated in order to estimate dry deposition fluxes.

Dry deposition of nitrogen from particles was calculated according to particulate ammonium (pNH_4^+) and nitrate (pNO_3^-) concentrations determined in the water soluble content of the aerosols. We calculated annual mean concentrations values for the period 1998–2000. In order to estimate nitrogenous dry deposition fluxes of particles, we used a dry deposition velocity value of 1–2 mm s^{-1} (Whelpdale et al. 1996). The calculation shows that total dry deposition of (pNH_4^+) and (pNO_3^-) are of the same order of magnitude for all types of ecosystems with relatively low values. As an example, mean particle concentrations have been measured in Banizoumbou and Katibougou, and are very low: $pNH_4^+ = 0.31 \pm 0.02$ ppb and $pNO_3^- = 0.16 \pm 0.03$ ppb in Banizoumbou, $pNH_4^+ = 0.17 \pm 0.06$ ppb and $pNO_3^- = 0.23 \pm 0.06$ ppb in Katibougou. The other ecosystems present comparable particulate nitrate and ammonium concentrations in aerosols. The comparison of these concentrations in aerosol with gaseous NH_3 concentrations in the two dry savannas sites (2.9–10.4 ppb in Banizoumbou, 1.8–6.9 ppb in Katibougou) leads to the conclusion that particulate deposition is negligible. The mean annual deposition fluxes ($pNH_4^+ + pNO_3^-$) in the semi-arid, wet savanna and forested ecosystems are around 0.3, 0.4 and 0.06 kg N ha^{-1} $year^{-1}$, respectively. One should note that particulate dry deposition of nitrogen is smaller by an order of magnitude than the wet deposition.

Gaseous dry deposition of nitrogen has been calculated as the sum of dry deposition fluxes of ammonia (NH_3), nitric acid (HNO_3) and nitrogen oxide (NO_2). Gaseous measurement (NH_3, HNO_3, NO_2) are monthly integrated samples using passive sampling techniques following the work of Ferm (1994). This technique has been tested in different tropical and subtropical region (Ferm and Rodhe 1997; Carmichael et al. 2003; Martins et al. 2007). Adon et al. (2010) presents ten year of gases monitoring on 7 IDAF sites. Mean annual concentrations from the whole database have been performed. Figure 10.3 presents the mean annual concentrations of NO_2, HNO_3 and NH_3 for the different IDAF sites measured over the period 1997–2007. Concentrations are ranged from 1 to 2 ppb for NO_2, from 0.2 to 0.5 ppb for HNO_3 and from 3.5 to 6 ppb for NH_3, respectively.

The major uncertainty in the estimation of trace gases dry deposition is due to the computation of the dry deposition velocity. Monthly dry deposition velocities have been calculated for 4 years (2002, 2003, 2004 and 2006) to follow the monthly seasonal cycle of measured gases (Delon et al. 2010). In the present work, we have calculated annual means of deposition velocities for NO_2, HNO_3 and NH_3 for each ecosystem type. Annual deposition velocities (2002–2006) range from 2 to 5 mm s^{-1} for NO_2, from 6 to 18 mm s^{-1} for HNO_3 and from 2 to 8 mm s^{-1} for NH_3. We estimate the total uncertainty applied to the dry N fluxes. The uncertainties are mainly linked to the concentration measurements and the estimation of the deposition velocities. For dry deposition of gases, the total rate of uncertainty applied for deposition fluxes is 70 % for NO_2, 31 % for NH_3 and 38 % for HNO_3.

NO_2 dry deposition fluxes presents a small variability according to the type of ecosystem, with fluxes varying from 0.5 kg N ha^{-1} $year^{-1}$ in the wet savanna, 0.82 kg N ha^{-1} $year^{-1}$ in the dry savanna, to 1 kg N ha^{-1} $year^{-1}$ in forested ecosystem.

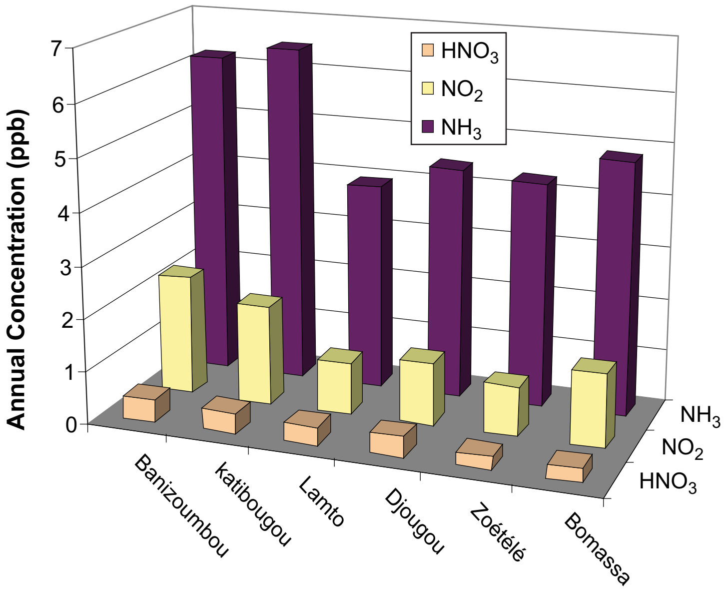


Fig. 10.3 Annual mean concentrations of nitric acid, ammonia and nitrogen dioxide over the period 1997–2007 in part per billion by volume (ppb). (Adon et al. 2010)

NH_3 dry deposition fluxes present higher values with 2 and 2.3 kg N ha^{-1} year^{-1} in dry savanna and wet savanna, respectively and 6 kg N ha^{-1} year^{-1} over the forest. Major sources of NH_3 include bacterial decomposition from urea in animal excreta and emissions by natural or fertilized soils (Schlesinger and Hartley 1992). In Africa, another significant source of ammonia is produced by savanna fires and domestic fuelwood burning (Delmas et al. 1995). Dry deposition fluxes of HNO_3 are very low compared with NO_2 and NH_3, with values ranged between 0.4 and 0.8 kg N ha^{-1} year^{-1} for all the ecosystems. This result is correlated to very low HNO_3 concentrations measured on all the stations.

10.4 Nitrogen Deposition Budget

Dry deposition fluxes, estimated for the three African ecosystems were combined with those associated with wet deposition to provide a first estimate in western-central Africa for the annual nitrogen atmospheric deposition. The total N deposition is estimated to be around 6 kg N ha^{-1} year^{-1}, 6.5 kg N ha^{-1} year^{-1} and 13 kg N ha^{-1} year^{-1} respectively over dry savanna, humid savanna and over the forest. These values should be taken with caution and we estimated the uncertainties on the budget to be around 30 %. If the estimations of wet deposition fluxes are known within a 10 % margin, dry deposition fluxes present larger uncertainties mainly due to dry deposition calculation. It is also important to note that our budget does not take into account all nitrogenous species, especially organic N species.

An important result highlighted by this budget is the importance of dry deposition processes in West Central Africa, especially for nitrogenous gaseous compounds. In dry savanna and forest, the relative contribution of dry deposition is about 60 %. In the wet savanna the contribution is around 50 %.

Acknowledgments This work is part of the IDAF (IGAC/DEBITS/AFRICA) project; and was funded by INSU/CNRS "Institut National des Sciences de l'Univers/Centre National de Recherche Scientifique" and the API "African Monsoon Multidisciplinary Analysis" (AMMA in 2005). The authors are grateful to all the field technicians at the African station and IRD (Institut de Recherche pour le Developpement) for logistical support.

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Chapter 11
Interannual Variability of the Atmospheric Nitrogen Budget in West African Dry Savannas

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Abstract Surface emission and deposition fluxes of reactive nitrogen compounds have been studied in three sites of West Africa during the year 2006, representative of dry savannas ecosystem, and part of the IDAF network: Agoufou (Mali, 15.3°N, 1.4°W), Banizoumbou (Niger, 13.3°N, 2.4°E) and Katibougou (Mali, 12.5°N, 7.3°W). Dry deposition fluxes are calculated from surface measurements of NO_2, HNO_3 and NH_3 concentrations (from passive samplers) and simulated deposition velocities, and wet deposition fluxes are calculated from NH_4^+ and NO_3^- concentration in samples of rain. Emission fluxes are evaluated including simulated NO biogenic emission from soils, emissions of NO_x and NH_3 from biomass burning and

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domestic fires, and volatilization of NH_3 from animal excreta. From these 3 sites, the average deposition flux, attributed to dry savanna ecosystems in Sahel, is 7.5 (±1.8) kg N ha^{-1} year^{-1}, and the average emission flux is from 8.5±3.8 kg N ha^{-1} year^{-1}. This budget is dominated by the NH_3 contribution (due to volatilization of animal excreta). Biogenic emissions from soils are the second most important contribution in emission fluxes. Total estimated deposition is 1.84±0.44 Tg N year^{-1} and the estimated emission is 2.0±0.9 Tg N year^{-1} for the Sahel region. Limited interannual variability (between 2002 and 2007) in precipitation is responsible for small variability in local emission sources and hence deposition fluxes.

Keywords Atmospheric nitrogen cycle • Biogenic emissions, • Deposition • Dry savanna • Sahel

11.1 Introduction

Nitrogen (N) is a key compound both as a nutrient for plants and animals and as an atmospheric pollutant. In the atmosphere, several N trace compounds are present, such as nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), nitrous oxide (N_2O) and ammonia (NH_3), as well as particulate and aqueous forms such as nitrate (NO_3^-) and ammonium (NH_4^+).

In semi-arid and arid regions, limited water resources have significant consequences on N cycling in the soil and the atmosphere. The seasonal rainfall distribution leads to an accumulation of N in soils during the dry season, and to large pulses of N emission at the beginning of the rainy season (Jaeglé et al. 2004). In this study, we focus on simulated biogenic soil emissions of nitrogen oxides (NO_x=NO+NO_2) calculated biomass burning and domestic fuel emissions of NO_x and NH_3, and calculated volatilization of NH_3 from animal manure, as well as dry and wet deposition of N compounds measured in three stations of the IDAF (IGAC/DEBITS/AFRICA) network.

The objective of this study is the calculation of the balance between N compounds emission and deposition, in order to quantify the atmospheric N budget in dry savannas. A focus is made in three study sites which are representative of rural semi-arid savannas: Banizoumbou (Niger, 13.33°N, 2.41°E), Katibougou (Mali, 12.5°N, 7.3°W) and Agoufou (Mali, 15.3°N, 1.5°W), firstly for the year 2006, and secondly from 2002 to 2007. The purpose of this last part of the study is to assess the impact of the interannual variability in precipitation on the interannual variability in emission and deposition of N compounds. Further details are reported by Delon et al. (2010).

11.2 Deposition

11.2.1 Dry Deposition

Gaseous measurements (NH_3, HNO_3, NO_2) are made by monthly, time-integrated passive sampling techniques, following the work of Ferm et al. (1994). The monthly estimated dry deposition flux is computed using the inferential method, which is defined as taking the product of the measured gas concentration in the air and the corresponding deposition velocity. The deposition velocities are estimated for each site and species, using the Soil Vegetation Atmosphere Transfer (SVAT) big-leaf model ISBA (Noilhan and Mahfouf 1996). The monthly means deposition velocities range from 1 to 3.3 mm/s for NO_2, from 3.4 to 6.1 mm/s for HNO_3 and from 1.1 to 3.9 mm/s for NH_3, the higher values found during the wet season. The inferential method is not the best one to evaluate NO_2 and NH_3 fluxes (compensation point concept and chemical reactions are not taken into account), but the lack of micrometeorological data in the Sahel prevents from parameterizing key parameters for these two processes.

Particulate N dry deposition (pNH_4^+ and pNO_3^-) is not taken into account in this budget, because the particle concentrations measured *in situ* are very low. The total uncertainty applied to the fluxes is linked to the concentration measurements, the deposition velocity, the missing covariance (plus a term of flux divergence for NO_2), and is 70 % for NO_2, 31 % for NH_3 and 38 % for HNO_3.

11.2.2 Wet Deposition

An automatic precipitation collector specially designed for the IDAF network has been installed at all stations. A local operator collects water from each rainfall event. To calculate wet N deposition, we have compiled the annual Volume Weighed Mean (VWM) concentrations of nitrate and ammonium from the precipitation collected at the 3 IDAF stations. In the Sahel region, the major source of precipitation nitrate content comes from natural NO_x emissions from soils. The highest values of ammonium compounds in precipitation registered have been attributed to strong sources of ammonia from domestic and pastoral animals during the wet season (Galy-Lacaux and Modi 1998). The concentration of dissolved organic nitrogen (DON) in rain is not measured within the IDAF network.

11.3 Emission

11.3.1 Biogenic Nitric Oxide Emissions from Soils

Biogenic emissions from soils are derived from an Artificial Neural Network (ANN) approach. The resulting algorithm provides on line biogenic NO emissions. It is fully coupled to the SVAT model ISBA. Nitric oxide emissions from soils in ISBA are obtained for the years 2002 to 2007 at a spatial resolution of 0.5° and a time resolution of 3 h. The meteorological forcing has been developed within ALMIP (Boone et al. 2009). The NO flux from soil is a non linear function of seven soil surface parameters: surface WFPS, surface and deep soil temperatures, pH, sand percentage, fertilization rate and wind speed (Delon et al. 2007). The fertilization rate provided to the model is based on the calculation of N released by

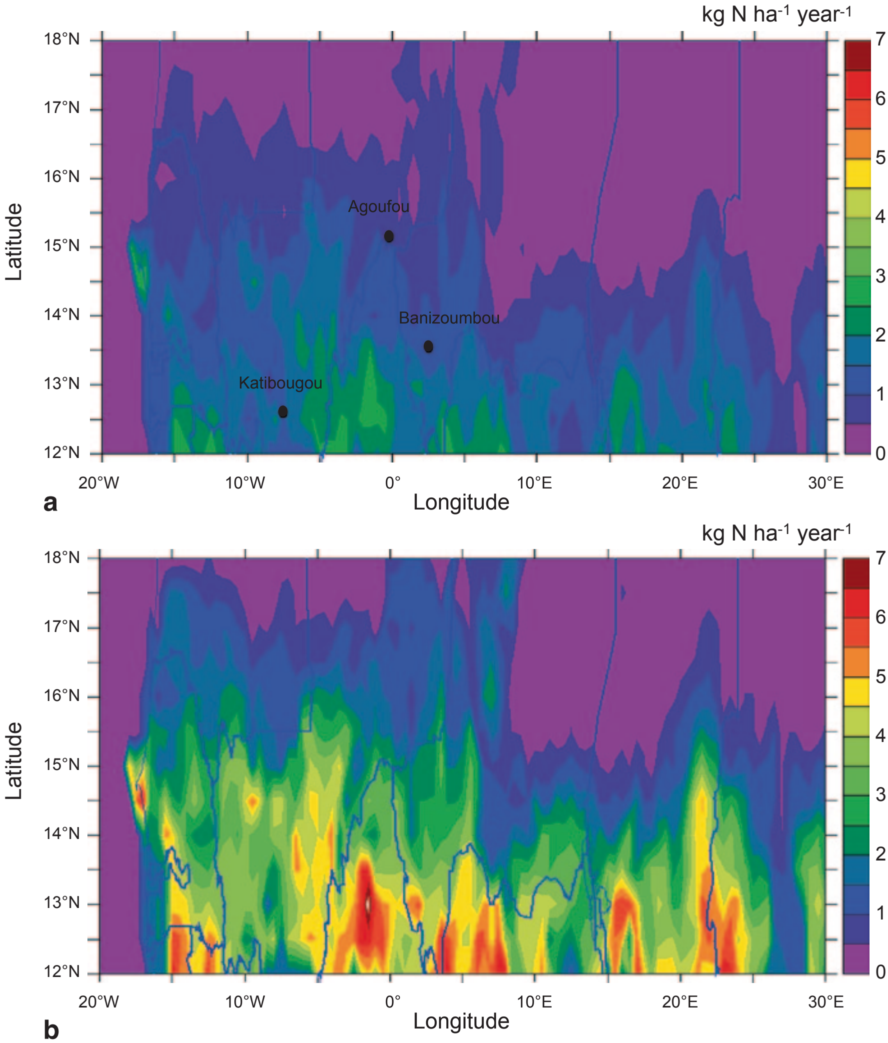


Fig. 11.1 Simulated biogenic NO flux from soils in kg N ha^{-1} year^{-1} in North West Africa (**a**) annual mean, (**b**) JJAS mean. Adapted from Delon et al. (2010) Atmos.Chem.Phys., 10, 2691–2708

organic fertilization (i.e., cattle dung), for each country. The N quantity released by livestock is calculated from Schlecht et al. (1998), in g N head^{-1} day^{-1}, for cows, sheep and goats. This estimate is multiplied by the number of animals per km^2 in each country. 30 % of this N input is used for the calculation of NH_3 volatilization, the rest is used as input for the calculation of NO biogenic emissions by the ANN algorithm in ISBA. Figure 11.1 shows the NO biogenic flux from soils in the simulation domain in terms of the annual mean in Fig. 11.1a and JJAS mean (June, July, August and September) in Fig. 11.1b.

11.3.2 Ammonia Emission by Volatilization.

In semi-arid regions like the Sahel, the NH_3 volatilization is favoured by high temperatures, low soil moisture and bare soil surfaces. As a consequence, a 30 % loss rate has been applied to the input of N by animal manure previously prescribed for the calculation of NO emissions. This leads to an N-NH_3 volatilization estimated around 7.2 ± 3.7 kg N ha^{-1} year^{-1} in Agoufou, 8.1 ± 4.2 kg N ha^{-1} year^{-1} in Banizoumbou, and 3.9 ± 2.2 kg N ha^{-1} year^{-1} in Katibougou.

11.3.3 Nitrogen Oxides and Ammonia from Biomass Burning

Global biomass burning inventories for gases and particles are on the Laboratoire d'Aérologie website (http://www.aero.obs-mip.fr:8001). These global inventories use the L3JRC burnt area product based on the SPOT-VGT vegetation satellite and Global Land Cover (GLC) vegetation map, together with data on biomass densities and burning efficiencies. The total uncertainty for both NH_3 and NO_x fluxes is 54 %.

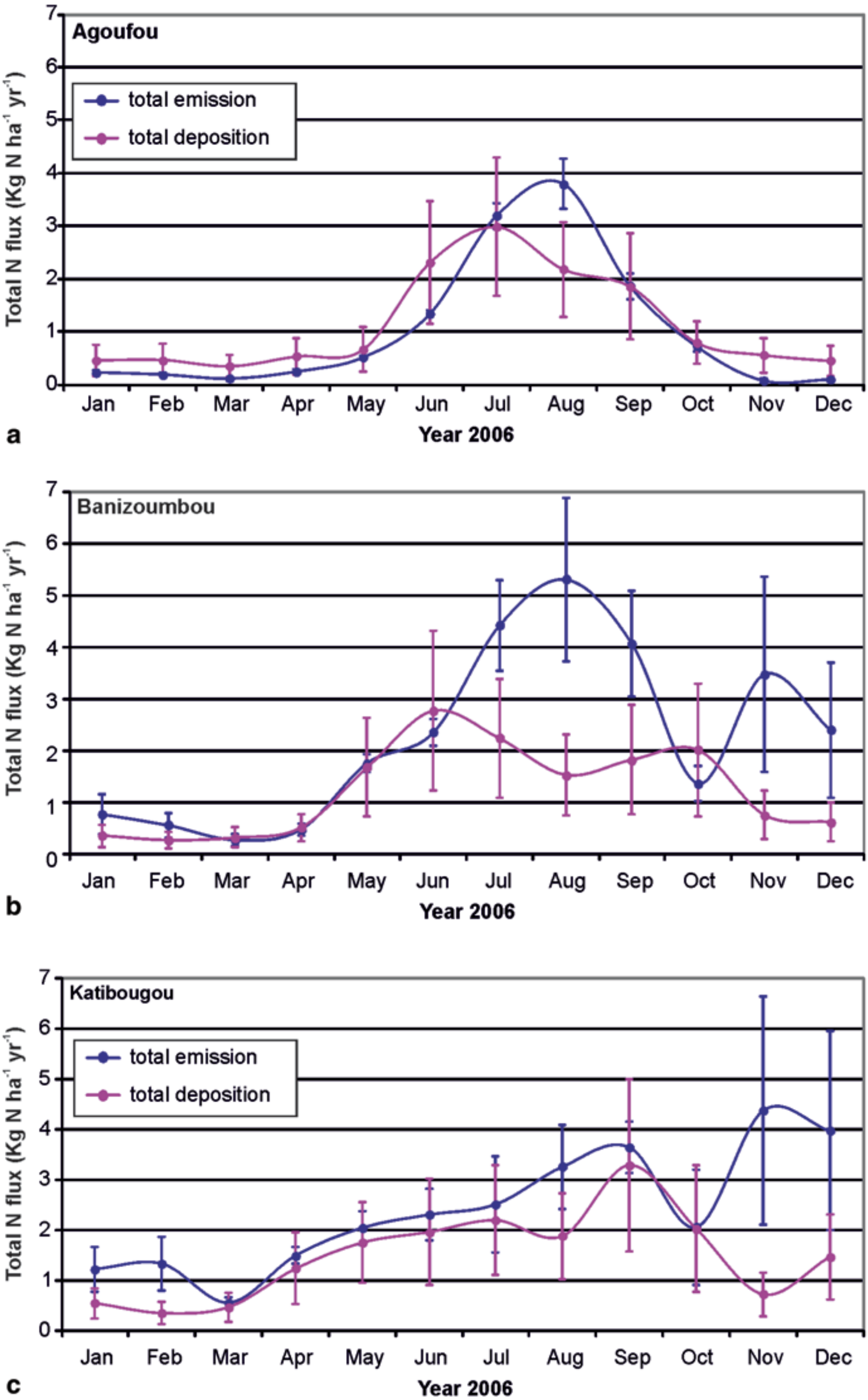
11.3.4 Nitrogen Oxides and Ammonia from Domestic Fires

Combustion of biofuel is mainly used for cooking in the Sahel. In the present study, NO_x and NH_3 emission from domestic fires uses the methodology from Junker and Liousse (2008), for the most recent existing year (2003). Annual emissions are calculated country by country, and gridded at 25×25 km resolution. The monthly input of nitrogen compounds is therefore constant all year long. Uncertainties are mainly linked to wood and charcoal consumption and emission factors. The total uncertainty applied to domestic fires is 60 % for both compounds.

11.4 Results and Discussion

11.4.1 Monthly Evolution of Oxidized Nitrogen Compounds in 2006

The emission of NO (both biogenic and anthropogenic) at the surface is the beginning of the formation of all other reactive oxidized nitrogen compounds in the atmosphere. As a consequence in this study, the total NO_x emission flux is defined as the sum of biogenic NO soil emission flux + biomass burning NO_x flux + domestic fire NO_x flux. It is compared to deposition flux of oxidized components, defined as the sum of estimated dry deposition of $NO_2 + HNO_3$ in the gas phase, $+ NO_3^-$ wet deposition flux. Figure 11.2 presents the monthly evolution of emission and deposition oxidized N fluxes in Agoufou, Banizoumbou and Katibougou. The first maximum during the wet season corresponds to biogenic emissions. Emission and deposition


Agoufou
total emission
total deposition
Total N flux (Kg N ha⁻¹ yr⁻¹)
0
1
2
3
4
5
6
7
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Year 2006
a
Banizoumbou
b
Katibougou
c

fluxes increase simultaneously, but the deposition maximum is early compared to the emissions. Two factors may explain this: the emission module emits longer than it should, and sometimes rain events do not compare well between measurements and model. A second emission maximum is observed in November in Banizoumbou and Katibougou, and corresponds to fire occurrence during the dry season, which implies an increase in NO_x emissions. A second maximum in deposition is observed in September in Katibougou, and in October in Banizoumbou, which is shifted in time compared with the emission maximum, and is less intense than the emission maximum. The shift could be due to an overestimate of fire emissions compared to local deposition measurements. The comparison of these fluxes in Fig. 11.2 at the monthly scale shows a good agreement between emission and deposition magnitude, while underscoring the difficulties of analysing the N budget in such remote areas where too few measurements are available.

11.4.2 Annual Budget of Oxidized and Reduced Nitrogen Compounds at Each Station, and Scaled up to the Regional Scale.

Figures. 11.3 and 11.4 show the total deposition and emission fluxes of oxidized and reduced N compounds at the annual scale for each station. Uncertainties are shown in parenthesis. These figures show that the (wet and dry) deposition and emission fluxes are dominated by the NH_3 contribution, with respectively 77 %, 68 % and 52 % at Agoufou, Banizoumbou and Katibougou stations for deposition flux, and respectively 84 %, 79 % and 63 % at Agoufou, Banizoumbou and Katibougou for the emission. The second most important emission flux is given by the biogenic NO from soils. From these three sites, the average deposition flux, attributed to dry savanna ecosystems in Sahel, is 7.5 (± 1.8) kg N ha^{-1} $year^{-1}$, and the average emission flux is from 8.5 ± 3.8 kg N ha^{-1} $year^{-1}$.

Common characteristics (same climate regime, same type of emission sources and amplitude, same type of vegetation and soil characteristics) deduced from these three stations, can be attributed to dry savanna ecosystems (representative of the main Sahelian ecosystem, according to White 1986) and may also be scaled up to the Sahelian region. A N annual budget for Sahelian ecosystems is therefore calculated. Figure 11.5 gives the mean repartition calculated for the Sahel concerning nitrogen compound emission and deposition fluxes. Total estimated deposition is 1.84 ± 0.44, (1.3 ± 0.2 Tg N $year^{-1}$ for reduced compounds, 0.5 ± 0.2 Tg N $year^{-1}$ for oxidized compounds). The estimated emission is 2.0 ± 0.9 Tg N $year^{-1}$ (1.5 ± 0.8 Tg N yr^{-1} for reduced compounds and 0.5 ± 0.1 for oxidized compounds), for the Sahel region. Our mean estimate of N compound emissions for the Sahel is around 2 % of the estimate of global $NH_3 + NO_x$ emissions, from only 0.48 % of the global surface area.

Fig. 11.2 Monthly evolution of fluxes and associated uncertainties: in purple, dry deposition of oxidized compounds, in blue, NO emission from soils and NO_x from biomass burning and domestic fires in kg N ha^{-1} $year^{-1}$ for IDAF dry savanna stations. Adapted from Delon et al. (2010) Atmos.Chem.Phys., 10, 2691–2708

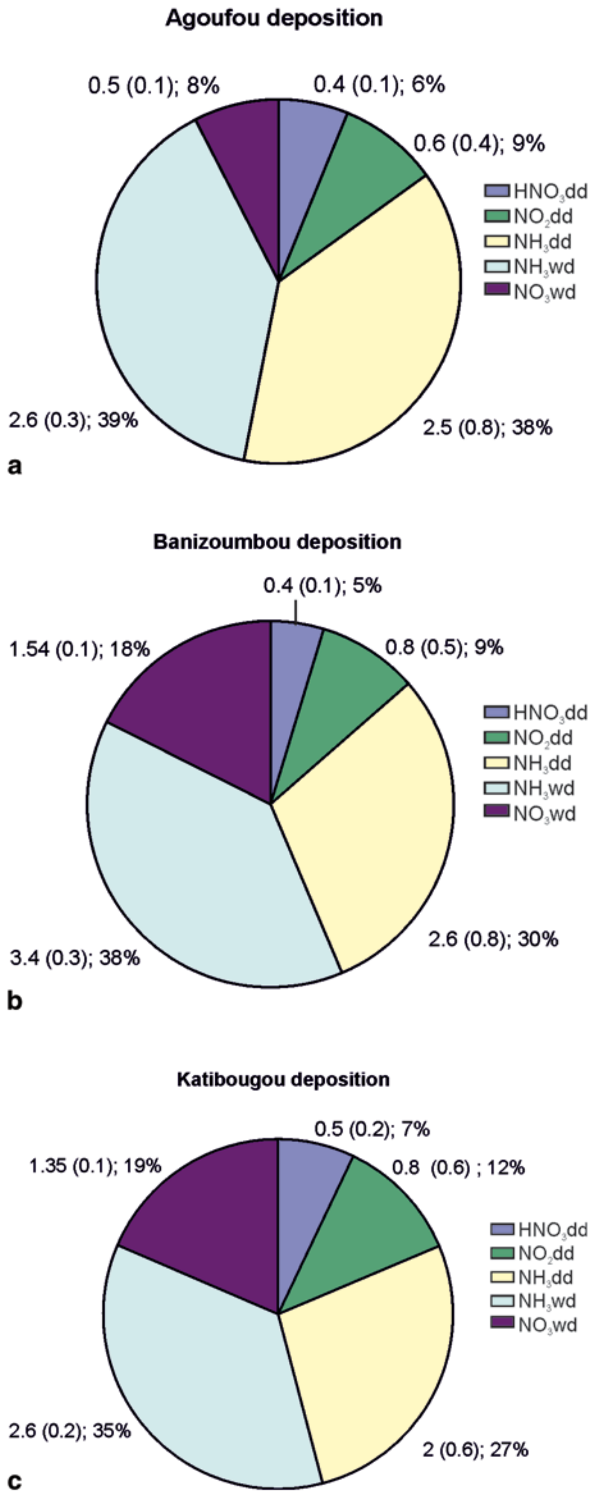


Fig. 11.3 Dry and wet deposition fluxes at Agoufou, Banizoumbou and Katibougou of oxidized and reduced nitrogen compounds. Annual means, given as absolute value (relative uncertainty); contribution in %. Adapted from Delon et al. (2010) Atmos.Chem.Phys., 10, 2691–2708

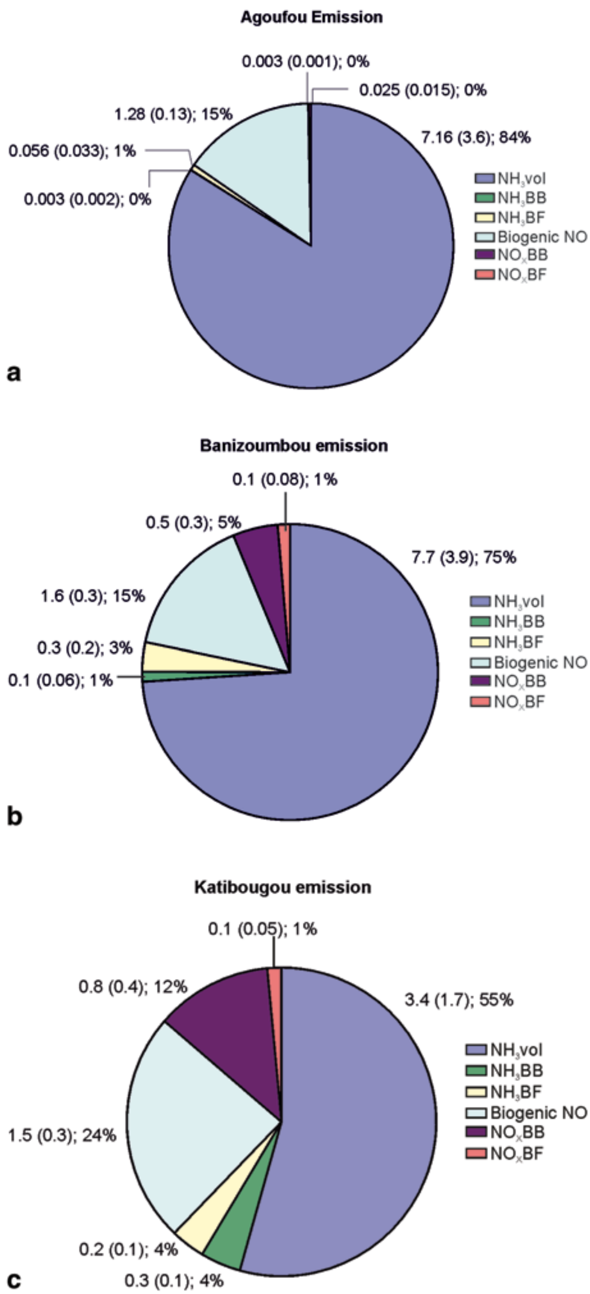


Fig. 11.4 Emission fluxes at Agoufou, Banizoumbou and Katibougou of oxidized and reduced nitrogen compounds. Annual means, given as absolute value (relative uncertainty); contribution in %. Adapted from Delon et al. (2010) Atmos.Chem.Phys., 10, 2691–2708

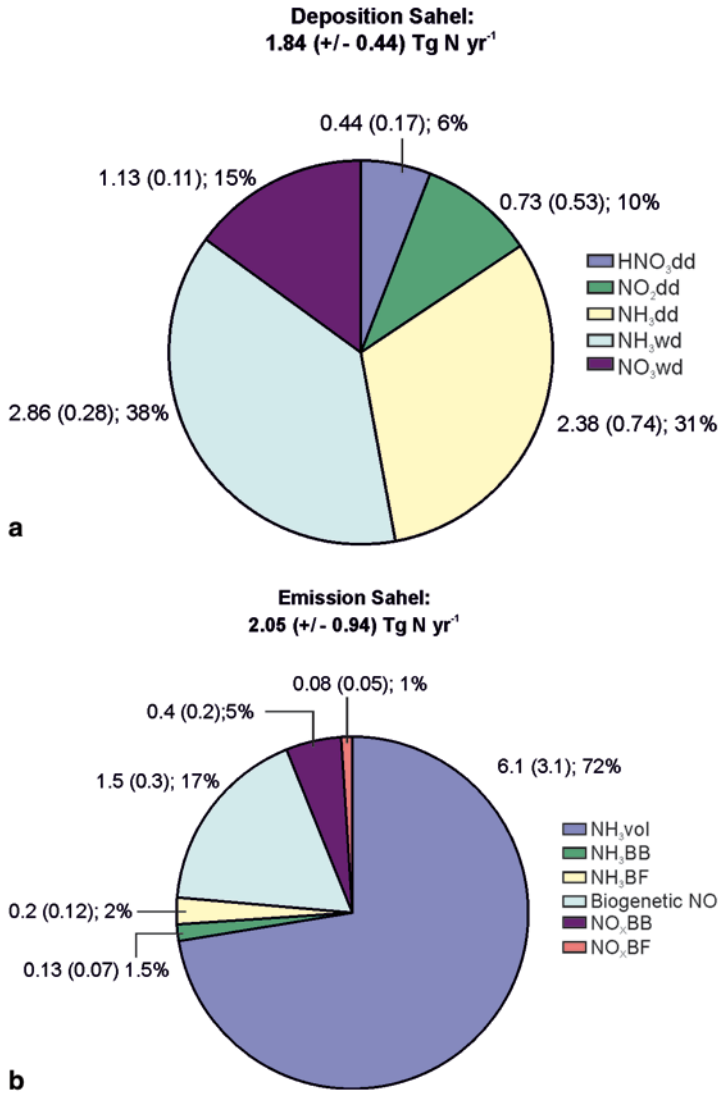


Fig. 11.5 Mean repartition of emission and deposition (oxidized and reduced) N fluxes, scaled up at the Sahelian region (2.4 million km^2). Given as absolute value (relative uncertainty); contribution in %. Adapted from Delon et al. (2010) Atmos.Chem.Phys., 10, 2691–2708

11.4.3 Interannual Variability 2002–2007

Figure 11.6 presents the biogenic NO emission from soils and the dry oxidized deposition fluxes with simulated and measured rain in dry savanna sites, from 2002 to 2007. As observed above for the year 2006, the deposition peak is earlier and less

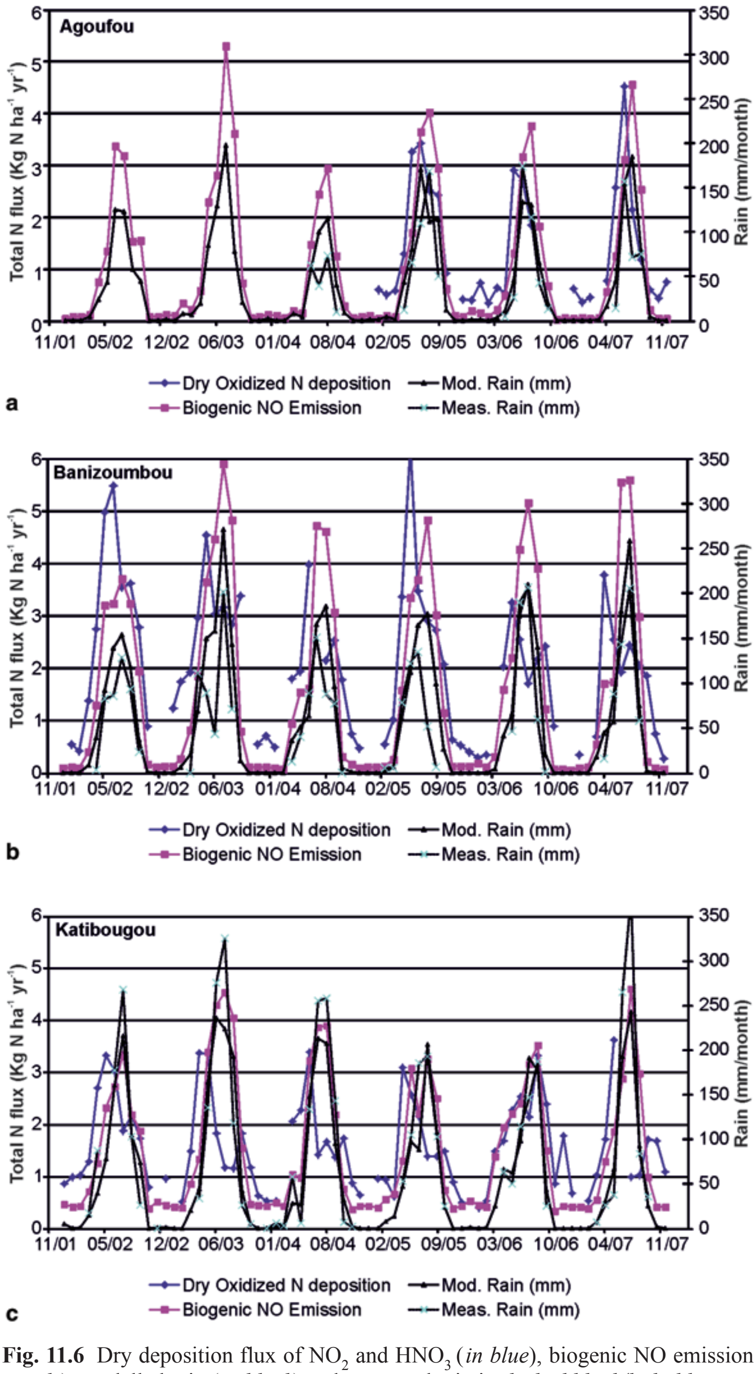


Fig. 11.6 Dry deposition flux of NO_2 and HNO_3 (*in blue*), biogenic NO emission from soils (*in purple*), modelled rain (*in black*) and measured rain in *dashed black/light blue crosses*

intense than the biogenic emission at the three stations for all years. Deposition and emission begin to increase with the first significant rain (above 10 mm). High correlation is found between rain and deposition (0.8, 0.6, 0.4 respectively for Agoufou, Banizoumbou and Katibougou).

Interannual variability in precipitation is responsible for variability in emission and deposition fluxes, due to changes in meteorological and physical parameters, like soil moisture and temperature (which changes will influence the soil biogenic emission, the occurrence of fires, the soil resistance and hence the deposition velocity of N species), turbulence (which variability will influence the aerodynamic resistance and the deposition velocity of species). Deposition depends also on occurrence of fires, particularly in Katibougou, but fire emission is not quantified here.

11.5 Conclusions

This study is a first and original attempt to estimate both deposition and emission fluxes of a set of N species in dry savanna ecosystems, using simulated and calculated inventories, and *in situ* measurements. In this study, we have first tried to reproduce the N oxidized compound emission and deposition evolution month by month at three different IDAF stations in dry savanna areas during 2006 at first, and from 2002 to 2007 at second. The magnitude of deposition and emission fluxes is similar, but the maximum emission is later and larger than the maximum deposition during the rainy season. An annual budget of reduced and oxidized N emission and deposition fluxes has been calculated. It gives a mean estimate of 7.5 (±1.8) kg N ha^{-1} $year^{-1}$ for total deposition, slightly dominated by wet deposition (53 % of the total), and 8.4 (±3.8) kg N ha^{-1} $year^{-1}$ for total emission during the year 2006, dominated by NH_3 volatilization (72 %) and biogenic emission from soils (17 %), whereas emissions from biomass burning and domestic fires accounts for 11 % only. The estimated emission in the Sahel is 2.0 (±0.9) Tg N $year^{-1}$, whereas estimated deposition is 1.8 (±0.4) Tg N $year^{-1}$. The uncertainties are numerous, but they are linked to necessary assumptions considering the small amount of data available in this region. The overall uncertainty in emission is 45 %, and 25 % in deposition. All this work is published in Delon et al. (2010).

The interannual variability of rains between 2002 and 2007 (13–17 % in simulated rain from 1 year to the other, 10–30 % in measured, rain depending on the site) is responsible for changes in fluxes, at a rate of 10–24 % for N oxidized compounds deposition, and 10–17 % for biogenic emission. Further work is necessary to quantify the reduced compounds contribution in deposition fluxes, as well as the NO_x and NH_3 emission from biomass burning and domestic fires.

This work does not claim to give an exhaustive budget of N, but wants to bring a supplementary knowledge for the unknown Sahel region. These values show that dry savanna ecosystems in the Sahel have to be taken into account for the N budget calculation. A lot of work remains to improve this budget however.

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Chapter 12
Assessment and Characterisation of the Organic Component of Atmospheric Nitrogen Deposition

Sarah E. Cornell

Abstract The organic component of atmospheric reactive nitrogen is known to be important for biogeochemical cycles, climate and ecosystems, but it is still not routinely assessed in atmospheric deposition studies, and most worldwide air quality monitoring networks disregard it. The available jigsaw puzzle pieces of knowledge from diverse sources can now give a richer picture of global patterns of organic nitrogen deposition. This effort at data synthesis highlights the need for more data, but also suggests where those data gathering efforts should be focused. The development of new analytical techniques allows long-standing conjectures about the nature and sources of the organic matter to be investigated, with tantalising indications of the complex interplay between natural and anthropogenic sources, and links between the nitrogen and carbon cycles. Atmospheric emission and deposition models are needed, along with new chemical process models, to let us explore questions about the role and dynamics of organic nitrogen.

Keywords Anthropogenic global change • Atmospheric deposition • Biogeochemical cycles • Organic nitrogen • Pollution monitoring

12.1 Introduction

Organic nitrogen is something of a castaway in global biogeochemistry research. The global monitoring networks, model developments, and environmental policies created in response to the serious nitrogen (N) linked issues of acid rain, eutrophication and urban pollution in recent decades have focused on emissions and deposition of inorganic reactive N species and rather ignored the organic N component. Organic N has long been known to be a quantitatively significant component of atmospheric N deposition (reviewed in Neff et al. 2002; Cornell et al. 2003). Organic N is known to play a role in atmospheric particle formation, affecting atmospheric visibility, light-scattering, and climate. It is a component of polluted fogs and smogs,

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forms of atmospheric aerosol that are of environmental and public health concern. It is known to be bioavailable, a nutrient source to marine/aquatic and terrestrial environments, and to be important in the long-range transport of N. Given this knowledge of its implications for biogeochemistry and ecosystem and human health, the fact that organic N is still not routinely measured—or even roughly factored-in to quantitative evaluations of N fluxes—is something of an awkward anomaly. When it does get mentioned, it is with the caveat that it is "still poorly understood".

Here, I trace the recent history of organic N research, trying to highlight the new research directions that offer promising ways to fill in the gaps in our nitrogen budgets and understanding of organic N behaviour.

12.2 Is Organic Nitrogen Really Important?

Neff et al. (2002) and Cornell et al. (2003) published reviews addressing the chemistry, deposition and analytical methods for determining atmospheric organic N, using essentially the same data drawn from nearly a century of literature. For the analysis presented here, that original database has been updated with reports published over the last decade of studies of organic N in rainwater.

The quantitative significance of the organic component of atmospheric N deposition has been recognised for a long time. The earliest reports relate to the Rothamsted Experimental Station's long time-series of rainwater composition (Miller 1905; Russell and Richards 1919), where organic N (methods not described) ranged from 2 to 50 μmol N l^{-1}, averaging 14 μmol l^{-1} and contributed about a quarter of the total N deposited. This seems a substantial proportion of N deposition to disregard, but for several decades, organic N was only sporadically measured (e.g., Eriksson 1952; Brezonik et al. 1969). Growing concerns about air quality led to some renewed interest. Figure 12.1 shows that published studies of organic N in rainwater became more frequent and geographically widespread around the time of the 1977 Clean Air Act Amendment in the USA and the 1979 International Convention on Long-Range Transboundary Pollution.

Figure 12.1 also shows that organic N is consistently a significant component of total dissolved N in rain samples collected in all types of location—continental (shown in the graph as open diamond symbols), remote marine (filled triangles) and coastal or island (squares)—over the last 50 years. Miller's first assessment in 1905 that "about a quarter" of total N deposited is organic still seems to hold true. However, the proportion that is organic is highly variable, ranging from mere traces up to nearly all of the N in rainwater. The kind of sampling location (continental, remote marine and mixed-influence) is not itself a determinant of the quantitative importance of organic N. This apparently random pattern may be part of the reason that organic N has not been systematically analysed and monitored.

However, the global data set is growing steadily. At the last count, there were 161 separate studies reporting organic N in wet deposition (including snow and bulk deposition, which include some dry deposition component). Data are now available

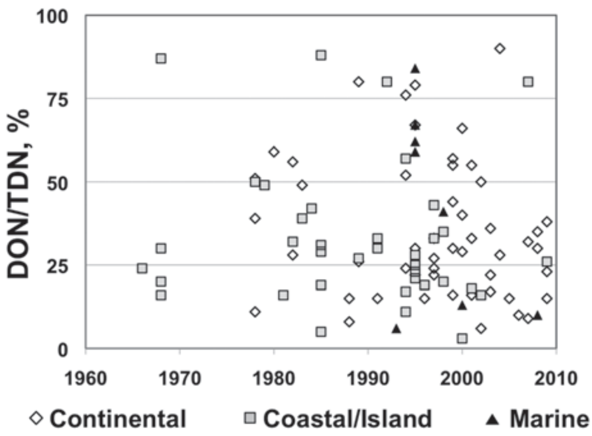

Fig. 12.1 Reported organic nitrogen in rainwater and bulk deposition, as a proportion of total dissolved nitrogen (TDN), from studies in different types of location over the last 50 years. Reproduced with permission from Cornell (2011) Environmental Pollution 159, 2214–2222.

Table 12.1 Numbers of published studies of atmospheric organic nitrogen deposition, by geographical location

Atlantic Ocean	7	Antarctica	1
Caribbean/Central America	9	Australia/New Zealand	8
Mediterranean Sea	1	China	2
North Sea	6	Europe	33
Baltic Sea	1	Japan	3
Pacific Ocean	1	N America	82
		S America	7

for most continents and marine environments (Table 12.1). Admittedly these data sets are mostly very short term, typically reporting on rain events collected over a period of days to weeks (indeed some studies report data based on just a couple of samples); the sampling locations are very sparsely distributed; and information about sampling and analysis protocols is still woefully limited.

Figures 12.2 and 12.3 summarise the information from these studies. Organic N is globally ubiquitous. Average concentrations of rainwater organic N in marine locations are typically around 5 µmol l^{-1}. Australasia and Antarctica samples are slightly higher. Northern hemisphere continental/land-influenced samples are generally about 10 µmol l^{-1}, except for North America—the most studied region—where concentrations average about 25 µmol l^{-1}. In Europe and Asia, up to a quarter of total N is organic. Across the Americas, the proportions seem systematically different: more like a third of total N is organic. A speculative hypothesis is that the Americas combine high biogenic gas emissions from the large forested areas (e.g., Wiedinmyer et al. 2006) with high levels of anthropogenic NO_x from car use and industry e.g., Benkovitz et al. 1996), providing precursors for the formation the organic N. In open ocean regions, organic N contributes a greater proportion of total N.

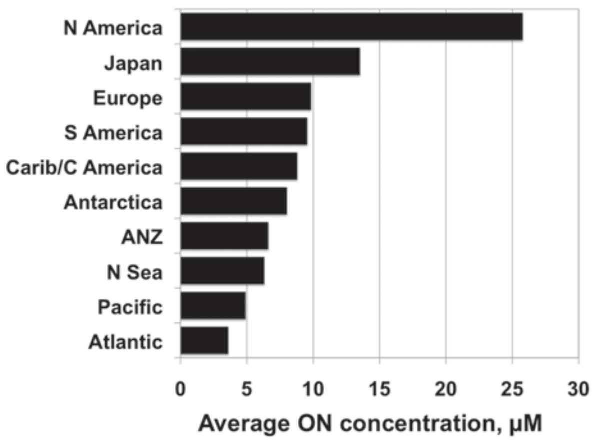

Fig. 12.2 Organic nitrogen (ON) concentration in rainwater from different geographical regions (arithmetic averages of data from multiple studies). *ANZ* Australia and New Zealand

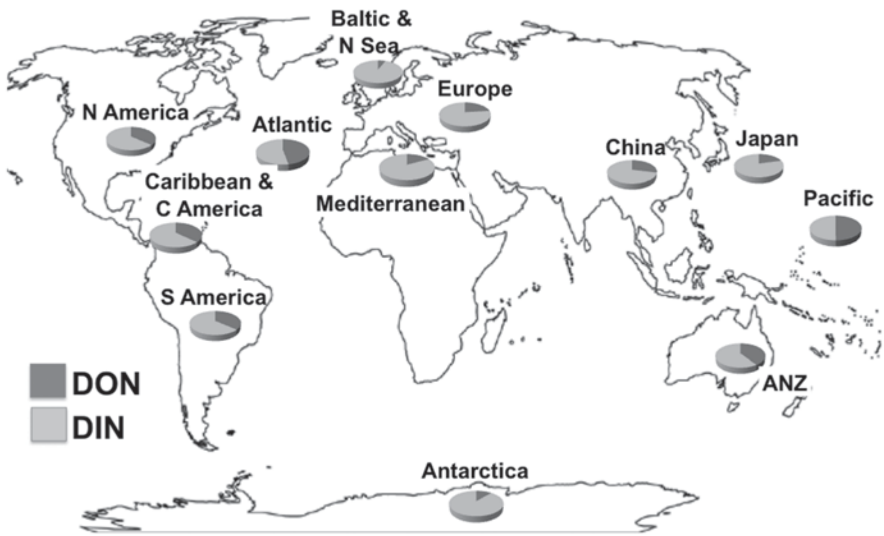

Fig. 12.3 Proportions of dissolved organic (DON) and inorganic nitrogen (DIN) in rainwater or bulk deposition, by region. *ANZ* Australia and New Zealand

12.3 What is Organic Nitrogen?

Another reason organic N is left out of many assessments of impacts of biogeochemical perturbations is because it is so poorly characterised. Despite valiant efforts in various research groups worldwide, the overall picture of the composition of rain and aerosol organic N in is still sketchy. It is evidently a "soup":

- "mainly aliphatic oxygenated compounds, a small amount of aromatics" (Reyes-Rodriguez et al. 2009)
- peptides and dissolved free amino acids could be 20–50 % of dissolved organic N (Kieber et al. 2005; Matsumoto and Uematsu 2005; Mace et al. 2003a, b; Spitzy 1990)
- amines—but these probably contribute much less than 10 % (Calderon et al. 2007; Gibb et al. 1999; Gorzelska et al. 1992; Mopper and Zika 1987)
- urea could account for anything from < 10 % to nearly all the organic N (Timperley et al. 1985; Cornell et al. 1998, 2001; Seitzinger and Sanders 1999; Mace et al. 2003a, b, c), and at present, rain and aerosol data appear to show different patterns.

Perhaps as a result, there has been comparatively little consensus on *how* to measure it or what fractions or modes should be measured. Organic N techniques developed for river and seawater are used for rain and aqueous aerosol extracts, although matrix and concentration differences affect the efficiency and precision of the analysis. Organic N is still normally defined as the difference in total measurable N before and after some organic-destroying treatment; the differences in treatments—UV, chemical oxidation, and so on—are themselves "still poorly understood". There is no simple, specific, field-deployable method for organic N (perhaps the third reason it is not included in deposition studies). Nevertheless enough meticulous investigation is emerging to inform a consensus on sampling and analysis protocols (e.g., Keene et al. 2002; Scudlark et al. 1998; Cape et al. 2001).

Observation networks for other atmospheric species have expanded steadily over the past 30 years. As part of the Global Atmosphere Watch programme, there is now good continental-scale coverage of North America and Europe (e.g., the US National Atmospheric Deposition Program and National Trends Network, http://nadp.sws.uiuc.edu; and the European Monitoring and Evaluation Programme http://www.nilu.no/projects/ccc). Other GAW partners extend the worldwide sampling, analysis and data management infrastructure:

- Deposition of Biogeochemically Important Trace Species (DEBITS)
- US Global Precipitation Chemistry Program (GPCP)
- Canadian Air and Precipitation Monitoring Network (CAPMoN)
- Acid Deposition Monitoring Network in East Asia (EANET)

None of these address organic N deposition routinely. An exception to this general pattern is Fluxnet Canada, part of a worldwide programme to assess biosphere-atmosphere carbon fluxes. Its 2003 protocols (Fluxnet Canada 2003) propose analysing for dissolved organic and inorganic N in ~10 % of the samples collected for dissolved organic carbon (C). Fluxnet links more than 10 national and regional networks, with over 540 sites, giving a fair global coverage (http://en.wikipedia.org/wiki/File:Fluxnet_Map.jpg). If all these partners followed Fluxnet Canada's example, using agreed protocols defined with the input of the organic N research community, the resulting organic N data would allow for clearer patterns to be established and more detailed characterisations to be made.

12.4 What Can We Say About Its Role?

In developing global N budgets and process understanding, we are often really only considering three-quarters of the real picture. As a result of data sparseness and poor characterisation, the role of organic N in ecosystems and Earth system processes remains much less clear than for other species. With the exception of the gas-phase organic nitrates, important in secondary organic aerosol formation processes, deposition and atmospheric chemistry models have only cursory representations of organic N and its multiphase behaviour. We have limited options for testing hypotheses about its sources, behaviour and consequences.

Understanding this invisible quarter of deposited N would help in understanding nutrient enrichment, especially for coastal zones and forest and bog ecosystems where concerns about exceedance of critical loads of atmospheric pollution are serious. It is implicated in "renoxification" processes, where reservoir species such as peroxyacytyl nitrate (PAN) transport NO_x-derived anthropogenic N over long distances, extending the range of adverse impacts of pollution. Much more needs to be known about its behaviour in association with particulate matter, perhaps playing an important role in aerosol and cloud formation (e.g. Zhang and Anastasio 2001). Russell et al. (2003) and Sandroni et al. (2007) report significant deposition of "insoluble N" in atmospheric aerosol, strongly associated with anthropogenic emissions, raising new questions about bioavailability.

The question of the balance of anthropogenic and natural sources for organic N is still wide open. Part of the reasoning in the original Rothamsted studies for disregarding organic N was their assessment that it was likely to be from locally recycled natural material, and they were focusing on known anthropogenic additions. The pattern that is emerging in the literature now is that organic N (as seen in rain and aerosol) is a nexus of biogenic and anthropogenic emissions. Contributory processes are the reactions of biogenic C compounds with NO_x (most recently, Goldstein et al. 2009); reactions of soot with NO_x and ammonia (Chang and Novakov 1975); and even the action of methane oxidiser bacteria on fossil fuel leaks (Davis et al. 1964). Isotopic studies so far (Cornell et al. 1995; Russell et al. 1998; Kelly et al. 2005; Chen 2008) have not untangled the pattern of sources; if anything, new results are adding to the perplexity. Huygens et al. (2005) describe method improvements for ^{15}N analysis in total dissolved N in aquatic samples, using pre-combustion and an elemental analyser for sample introduction, but overall, robust separation methods for organic ^{15}N analysis remain a challenge.

New analytical techniques are being applied to aerosol and rain analysis that will enrich this picture. Methods include Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry (Altieri et al. 2009; Koch and Dittmar 2006), giving elemental compositions of N-containing compounds with positive and negative ion detection. These studies confirm that much of what we see as organic-N are actually not N-rich compounds, and indicate that reduced N species, rather than oxidised forms, are important contributors. They offer scope for improved fingerprinting, say for thermogenic compounds. Time-of-Flight mass spectrometry (Bruns et al.

2010) enables steadily improved identification of multifunctional compounds, and single-particle methods (e.g., laser ablation) give information on composition and formation (e.g., internally or externally mixed systems). Developments in nuclear magnetic resonance mean that bulk matter can be better characterised into known biogenic and anthropogenic compounds. For example, Herckes et al. (2007) show that in fog, biogenic organic C is important, while the organic N includes amines, nitrate esters, peptides and nitroso compounds—direct evidence of a complex, polydisperse "soup".

12.5 Next Steps

The indications in recent research that organic N is the product of mixed anthropogenic and biogenic sources may not be surprising from a chemical point of view, but it presents new challenges for global-scale assessment and any model-based projections. The impetus in modelling for improved understanding of the climate system is focusing attention on multi-phase atmospheric processes (particularly secondary aerosol formation) and representations of the dynamic coupling of nitrogen and other key elements with the C cycle. A key challenge is the attribution of climatic changes, natural system variability and anthropogenic perturbation to the patterns and trends being observed. What we already know about organic N brings a different perspective to processes such as biomass burning, deforestation or afforestation, and changing energy sources, which are seen as carbon issues. We need tools that will enable us to explore climate and biogeochemical feedbacks, which in turn requires a rethink of research method design. Organic N is one instance where model development and process understanding is still constrained by a shortage of data and an unmet need for an overarching synthesis.

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Chapter 13
Wet Deposition of Nitrogen at Different Locations in India

P. S. P. Rao, P. D. Safai, Krishnakant Budhavant and V.K. Soni

Abstract The wet deposition data for Pune (2000–2007), for the other locations representing different environments (i.e., urban, rural, industrial, high altitude, marine, traffic etc.) for different time periods during 2001–2007, and for ten Global Atmospheric Watch (GAW) locations in India for a period of 8 years (2000–2007) are considered in this chapter. All the rain water samples were analyzed for pH, conductivity, anions (Cl, SO_4 and NO_3) and cations (NH_4, Na, K, Ca and Mg). In general, in India the rain water was found to be in the alkaline range. Out of ten GAW stations, the 8 years average pH was slightly acidic (pH 5.15–5.36) at only three locations. At the remaining seven locations the pH was alkaline (pH > 5.65). This alkaline nature is due to high dust levels. Neutralization factors indicated that calcium (Ca) is the major neutralizing cation in wet deposition. Calcium concentrations were higher in north and northwestern regions and lower in southern and northeastern regions. Non-sea salt component and back trajectory analyses showed that Ca and SO_4 aerosols were transported to the Indian sub-continent from North African and Gulf countries. The wet deposition fluxes were estimated for all the ionic components including nitrogen (N). The 8 year average annual wet deposition of N for ten locations varied between 4.7 and 34.3 kg N ha^{-1} $year^{-1}$ and yearly depositions varied between 1.8 and 57 kg N ha^{-1} $year^{-1}$. At all the locations, the

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NO_3-N depositions were higher compared to NH_4-N. At some of the locations, even though the concentrations are low, the depositions were higher due to the high rainfall amounts. In regional perspective, the excess SO_4-S deposition was higher at an industrial location and the N deposition was higher at a traffic junction in Pune region. At a high altitude rural location (Sinhagad) nearby Pune, the concentrations of excess SO_4, NO_3 and NH_4 were lower but their depositions were higher due to higher rainfall amounts. The total N deposition at four different locations in Pune region varied from 10.4 to 13.2 kg N ha^{-1} $year^{-1}$.

Keywords GAW locations • Long range transport • Oxidized/reduced nitrogen • Spatial variation • Wet deposition

13.1 Introduction

Nitrogen (N) is a major nutrient in terrestrial ecosystem and an important catalyst in tropospheric photochemistry. Atmospheric N compounds affect the Earth's radiation budget, acidify ecosystems, and cause degradation and eutrophication of lakes, estuaries and coastal oceanic regions (Galloway et al. 2004). Among inorganic N species, NH_4, NO_3 and their precursors are the most dominant species present in the atmosphere. In the present-day scenario, the major sources of atmospheric NH_4, NO_3 and their precursors (NH_3 and NO_x) are attributed to vehicular emissions, biomass and fossil-fuel burning, human and animal excreta, microbial decomposition of biomass etc. During their long-range transport, these species undergo a variety of physicochemical transformation processes and are ultimately removed from the atmosphere via dry and wet deposition. The wet deposition is considered to be the major removal pathway of N-species, accounting for > 80 % in many regions.

Deposition of air pollutants especially sulphur (S) and N affect the various ecosystems like forest, soil, and lakes. The studies related to them are essential to understand the acid rain phenomenon, air quality, removal processes and major biogeochemical cycles. There is ample evidence that increasing human activities seriously disturb the natural N cycle. Reactive nitrogen N_r (NO_y and NH_x) enters the environment through a number of processes related to fertilization, waste discharge and atmospheric emissions, transport and deposition.

Excess atmospheric deposition of N_r compounds can cause adverse effects on biological diversity and thereby affect ecosystem structure and functions. These impacts are triggered by both acidification and eutrophication. However, acidification is not only caused by N deposition, but also by S deposition, contributing significantly to the acidification risk for ecosystem health in many regions of the world.

In India many studies are available on precipitation chemistry (Rao et al. 1995, 2002; Khemani et al. 1989; Ali et al. 2004; Safai et al. 2004; Momin et al. 2005; Rastogi and Sarin 2005; Praveen et al. 2007), but studies relating to both concentrations and deposition fluxes are scanty (Rao et al. 1992; Kulshreshta et al. 2005; Rastogi and Sarin 2006). Therefore the wet depositions of major ionic components including N at different locations in India have been reported in this chapter to understand their spatial variation.

13.2 Sampling and Analysis

Daily wet deposition samples are being collected at Pune and at other locations (for limited period) representing different environments (i.e., urban, rural, industrial, high altitude, marine, traffic etc.) in India by using standard rain collectors. All the rain water samples were analyzed for pH, anions (Cl, SO_4 and NO_3) and cations (NH_4, Na, K, Ca and Mg). The anions were analyzed by using Ion Chromatograph (Dionex). The cations Na, K, Ca and Mg were analyzed by Atomic Absorption Spectrophotometer (Perkin Elmer). The NH_4 is analyzed by the colorimetric method. The wet deposition data for Pune for the period 2000–2007 and for the other locations for the different time periods during 2001–2007 were considered in this study. Also, the wet deposition data for the ten Global Atmospheric Watch (GAW) locations in India for a period of 8 years during 2000–2007 were studied. The wet deposition fluxes of N along with the other major ionic components were estimated. WMO criteria have been followed for QC/QA checks and the laboratory participated in the WMO's and EANET's laboratory intercomparison studies.

13.3 Results and Discussion

The details of the ten GAW sampling locations used in this study are given in Table 13.1. The wet deposition fluxes were estimated for all the ionic components including N. The spatial variation of deposition and concentrations for total N, NH_4-N, NO_3-N, excess SO_4-S, Ca and pH are shown in Fig. 13.1.

In general, the rain water was found to be in alkaline range in India. Out of ten GAW stations, the 8 years average pH was slightly acidic (pH 5.15–5.36) at only three locations. At the remaining seven locations the pH was alkaline (pH > 5.65). This alkaline nature is due to high dust levels. Neutralization factors indicated that calcium (Ca) is the major neutralizing cation in wet deposition. Calcium concentrations were higher in north and northwestern regions and lower in southern and northeastern regions.

13.3.1 Spatial Variation of NO_3-N, NH_4-N Concentrations and Total Nitrogen Wet Deposition

The average wet deposition of NO_3-N ($N_{oxidized}$) for a period of 8 years (2000–2007) varied between 2.7 and 24.3 kg N ha^{-1} $year^{-1}$. The northeastern region and eastern region of India showed very high $N_{oxidized}$ deposition. The higher deposition at the northeastern location is to a large extent due to the high amount of rainfall. But the maximum deposition at an eastern location, Visakhapatnam, is due to high concentration

Table 13.1 Details of ten Global Atmospheric Watch (GAW) sampling locations reported in this study

GAW Stations	Altitude (metres)	Type of environment
Srinagar	1587	Urban, high altitude
Allahabad	98	Urban
Jodhpur	217	Urban
Mohanbari	111	Rural
Nagpur	310	Urban
Pune	559	Urban
Visakhapatnam	60	Urban, coastal
Minicoy	2	Rural, island
Portblair	79	Rural, island
Kodaikanal	2343	Rural, high altitude

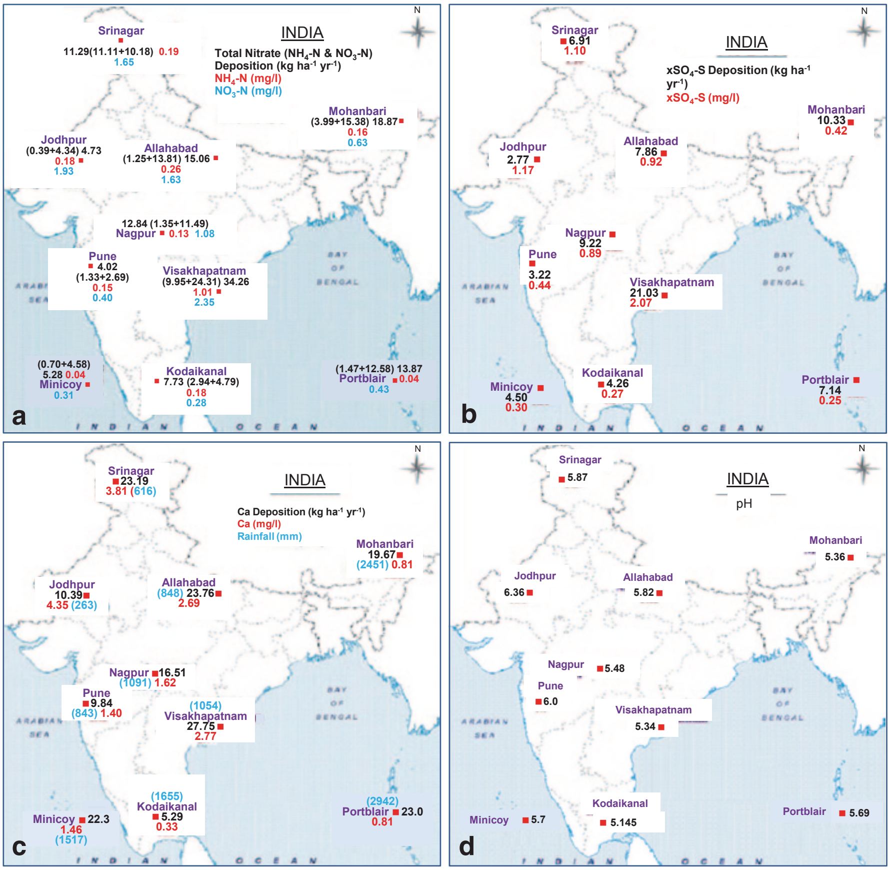

Fig. 13.1 Spatial variation of pH, total N, NH_4-N, NO_3-N, xSO_4-S, Ca and pH in India

of N due to more growth in urbanization and industrialization. The low deposition values in the west of India may be due to the small amount of rainfall. In general, at all the locations the $N_{oxidized}$ depositions were higher than the S depositions. This indicates the dominance of vehicular pollution on wet deposition chemistry.

The spatial distribution of $N_{oxidized}$ concentration in precipitation is entirely different than that of the wet deposition because precipitation amounts influence the total amount of deposition. The concentrations are very low in the south, at island locations, and in the west. They are high in east, north, north-west, central and north-east locations of India.

The average NH_4-N ($N_{reduced}$) depositions for a period of 8 years (2000–2007) varied between 0.4 and 11.4 kg N ha^{-1} $year^{-1}$. At all the locations, the values of $N_{reduced}$ wet deposition are much less than the $N_{oxidized}$ wet deposition. This further suggests the dominance of combustion-based anthropogenic sources for total N wet deposition. The highest deposition of $N_{reduced}$ is at Visakhapatnam in the east, as in the case of oxidized N deposition. Higher precipitation amounts were responsible for higher $N_{reduced}$ deposition at a northeastern location, island locations in the Arabian Sea and the Bay of Bengal and a high altitude location in the south.

The average Total N deposition for a period of 8 years (2000–2007) varied between 4 and 34.3 kg N ha^{-1} $year^{-1}$. Similar variations were observed for Total N wet deposition as for $N_{oxidized}$ deposition.

13.3.2 Spatial Variation of Wet Deposition in Pune Region

To study the spatial variation in Pune region, the rain water samples were collected at locations with different environments i.e., urban (Pashan), industrial (Bhosari), traffic junction (Swargate) and high altitude rural (Sinhagad) during 2006–2007. In this regional perspective, the excess SO_4-S deposition was higher at the industrial location and the N deposition was higher at the traffic junction in Pune region. The spatial variation of pH and wet deposition of NH_4-N, NO_3-N and Ca is shown in Fig. 13.2. The average pH at these four locations varied between 5.8 and 6.7 indicating alkaline rain. At the high altitude rural location (Sinhagad) nearby Pune, the concentrations of excess SO_4, NO_3 and NH_4 were lower, but the amounts of deposition were higher due to higher rainfall amounts. The total N wet deposition at four different locations in Pune region varied from 10.4 to 13.2 kg N ha^{-1} $year^{-1}$.

13.3.3 Marine Precipitation Chemistry

The average pH and chemical composition of rain water collected on board the ship 'Sagar Kanya' over the Arabian Sea during 21st June—16th August 2002 (summer monsoon) and during 14th March—9th April 2003 (winter monsoon or pre-monsoon) under the Arabian Monsoon Experiment (ARMEX) is given in Table 13.2. It is observed that the pH is alkaline (pH 6.4) in the monsoon season and slightly acidic

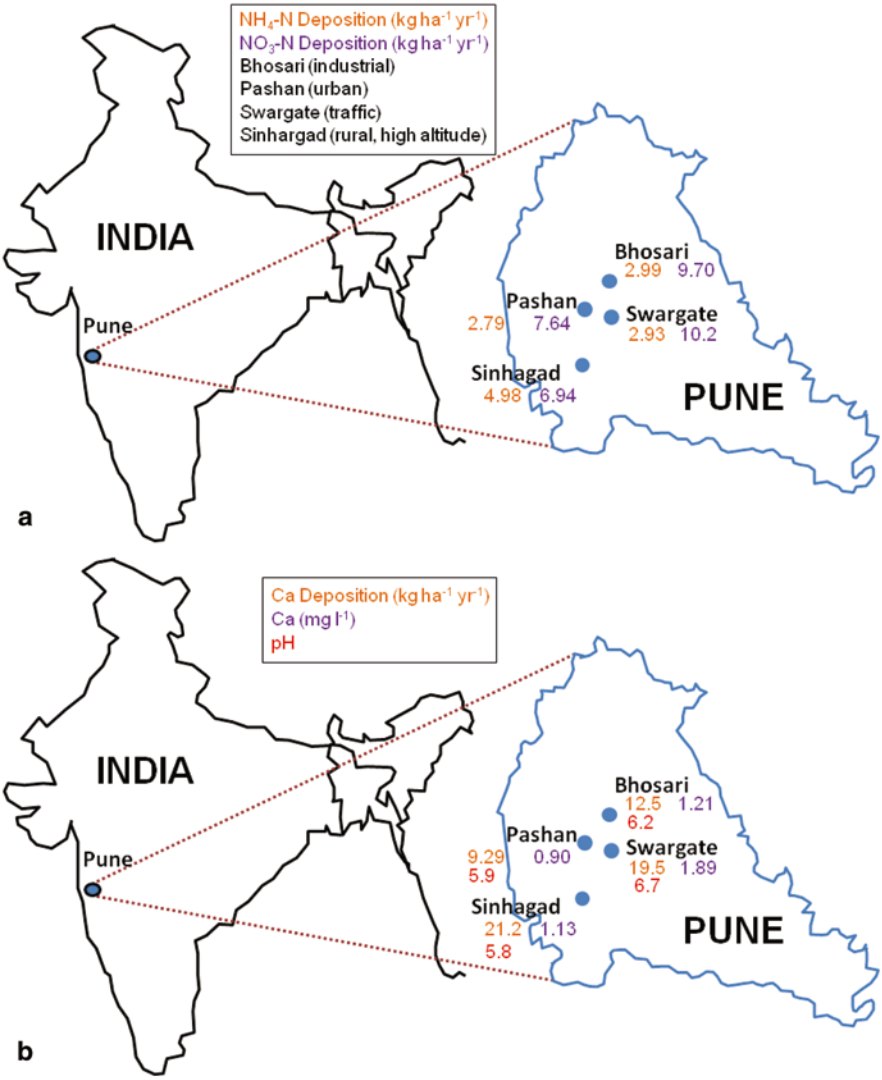

Fig. 13.2 Spatial variation of pH and wet depositions of NH_4-N, NO_3-N and Ca in Pune region (2006–2007)

(pH 5.4) in the winter monsoon. Sea salt concentrations are very much higher in the summer monsoon compared to the winter monsoon. This is due to higher bubble bursting activity in the summer monsoon due to high wind speeds. Both the oxidized and N_r concentrations were higher in the winter monsoon season than in the summer monsoon season. The non-sea salt component and back trajectory analyses indicated the long-range transport of Ca and SO_4 aerosols over the Arabian Sea from North African and Gulf countries during the summer monsoon. More details of this study can be seen in Praveen et al. (2007).

Table 13.2 Average pH and concentration of major ionic components (mg/l) in rain water over the Arabian Sea (2002–2003) during ARMEX (Arabian Monsoon Experiment)

Collector	Cl	SO_4	SO_4-S	NO_3-N	NH_4-N	Na	K	Ca	Mg	pH
Wet-Only (SM)	11.9	0.66	0.22	0.02	0.008	6.67	0.26	1.42	0.54	6.43
Bulk (SM)	16.3	1.45	0.48	0.03	0.008	9.15	0.39	2.16	0.81	6.48
Bulk (WM)	3.34	1.16	0.39	0.25	0.055	1.62	0.11	0.98	0.21	5.36

(*SM*)—Summer Monsoon, (*WM*)—Winter Monsoon

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Part II
Nitrogen Impacts on Terrestrial and Aquatic Ecosystems

Chapter 14
Factors Affecting Nitrogen Deposition Impacts on Biodiversity: An Overview

Roland Bobbink and W. Kevin Hicks

Abstract The main mechanisms of nitrogen (N) deposition impacts on terrestrial biodiversity, mainly from studies in Europe, are identified as: direct foliar impacts; eutrophication; acidification; negative effects of reduced N; and increased susceptibility to secondary stress and disturbance factors such as drought, frost, pathogens or herbivores. The relation of several of these mechanisms to aquatic ecosystems is also described, as is the relative lack of N impact studies on faunal species/communities compared to floral ones. The factors that moderate N impacts on ecosystems are also considered and are categorized as: (1) the duration and total amount of the N inputs; (2) the chemical and physical form of the airborne N input; (3) the intrinsic sensitivity to the changes in N availability of the plant and animal species present; (4) the abiotic conditions (such as the ability of soils and waters to neutralize acidification effects); and (5) the past and present land use or management. The increased susceptibility of plants (or animal) species to stresses and disturbances, induced by enhanced atmospheric N loads, is highly dependent of the large differences in the physiological functioning of individual species. Therefore, the generalization of the effects of N deposition over a range of ecosystems is hardly, if at all, possible, although these impacts have been demonstrated to be of major importance in some ecosystems.

Keywords Acidification • Biodiversity • Eutrophication • Impact mechanisms • Nitrogen deposition

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14.1 Introduction

The emissions of ammonia (NH_3) and nitrogen oxides (NO_x) strongly increased in the second half of the twentieth century (e.g., Sutton et al. 2008). Ammonia is volatilized from agricultural systems, such as dairy farming and intensive animal husbandry, whereas NO_x originates mainly from burning of fossil fuel by traffic, the power generation sector and industry. Because of short- and long-range transport of these nitrogenous compounds, atmospheric nitrogen (N) deposition has clearly increased in many natural and semi-natural ecosystems across the world. Areas with high atmospheric N deposition are nowadays found in central and western Europe, eastern USA and, since the 1990s, Eastern Asia (e.g. Dentener et al. 2006). For more details on N deposition see Chap. 2 (Dentener et al. 2014; this volume). In this background paper we firstly give a short overview of the "mechanisms" which lead to change in species performance, composition and diversity after N enrichment. Secondly, factors that affect the extent or severity of the N deposition impacts on biodiversity are identified. Sensitivities of different major ecosystems with respect to biodiversity effects and their effect thresholds, will not treated in this paper, but for details on this topic, see Bobbink et al. (2010). Finally, we present a list of major questions, which have to be solved in the future.

14.2 Impacts on Plant Biodiversity

The series of events which occurs when N inputs increase in a region with originally low background N deposition rates is highly complex. Many ecological processes interact and operate at different temporal and spatial scales. Despite this highly diverse sequence of events, the following main impact "categories" can be recognised. A schematic overview of the possible sequence of events is given in Fig. 14.1.

14.2.1 Direct Foliar Impacts

An important effect of N gasses, aerosols and dissolved compounds can be direct toxicity to the above-ground parts of individual plants. Nitrogen dioxide (NO_2), NH_3 and ammonium (NH_4) in particular are phytotoxic. The impacts have been mostly studied for crops, and young trees (saplings), but studies with native herbaceous or dwarf-shrub species in open top chambers (OTCs) have also demonstrated leaf injury, changes in physiology and reductions in growth at (very) high air concentrations of airborne N pollutants (e.g. Pearson and Stewart 1993; Krupa 2003). These impacts were observed in parts of Europe and Northern America in 1980s but are nowadays very rare in these regions because of pollutant control measures. However, increasing air N pollutant concentrations are now found in Asia (China and India), potentially causing direct foliar impacts. In addition,

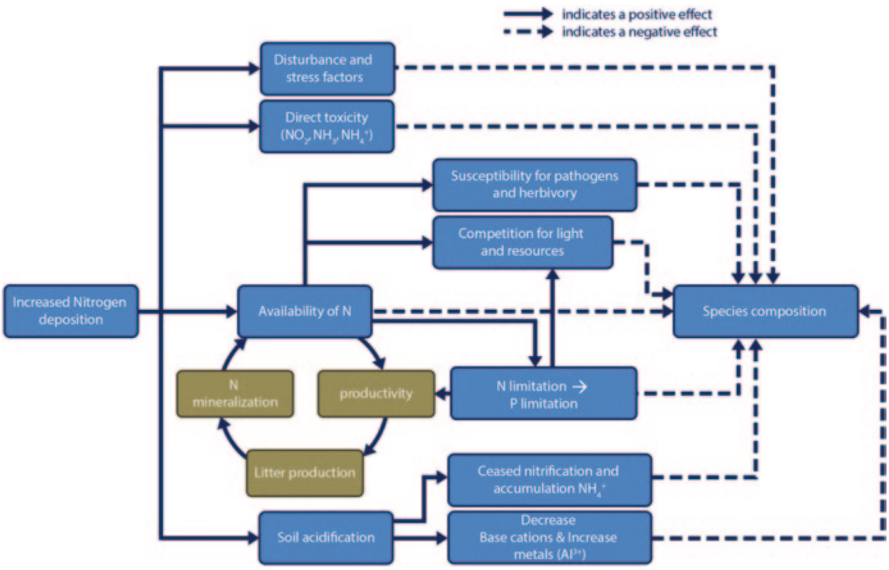

Fig. 14.1 Schematic of the main impacts of enhanced N deposition on ecosystems as demonstrated by studies on temperate ecosystems in Europe and North America. Stress is considered to occur when external constraints limit the rate of dry matter production of the vegetation, whereas disturbance consists of mechanisms which affect plant biomass by causing its partial or total destruction

lichens are clearly the most sensitive organisms with respect to direct toxicity of dry deposited NH_3 (Van Herk et al. 2003) whereas direct toxic effects of wet deposited N have been reported for bryophytes and lichens at rather low deposition rates (Bates 2002).

14.2.2 Eutrophication

Nitrogen is the limiting nutrient for plant growth in many natural and semi-natural terrestrial ecosystems, especially of oligotrophic and mesotrophic conditions. Research in the temperate ecosystems of Europe and North America has shown that enhanced N deposition results in an increase in the availability of inorganic N in the topsoil in the short-term. This gradually leads to an increase in plant productivity in N-limited vegetation and thus to higher annual litter production. Because of this, N mineralisation will gradually increase, which may cause an extra increase in plant productivity. This is a positive feedback, because higher N mineralisation gives higher N uptake, etc. Above a certain level of primary productivity, local species diversity declines as production increases. Observational studies across N deposition gradients and many N-addition experiments demonstrated this effect in the longer-term. Competitive exclusion (“overshading”) of characteristic species of oligotrophic or mesotrophic habitats by relatively fast-growing nitrophilic species is to be expected and especially rare species with low abundances or a low stature are at risk (e.g. Bobbink et al. 1998, 2003; Suding et al. 2005). The rate of N cycling in the ecosystem is clearly enhanced in this situation, although the response time to enhanced N inputs can be long in this respect in highly organic soils with a high C:N ratio, or, perhaps in any soil with large potential N sinks. When the N deficiencies in the ecosystem are no longer limiting, plant growth becomes restricted by other resources, such as phosphorus (P) or water. In this situation, the productivity of the vegetation will not increase further. Nitrogen concentrations in the plants will, however, tend to increase because N availability still increases, which may affect the palatability of the vegetation for herbivores or the sensitivity to pathogens (see later). In addition, it is to be expected that the shift from N to P limitation and the abnormal ratio between them, high N and low P, will gradually lead to changes in plant species composition.

Productivity of aquatic ecosystems is generally considered to be limited by phosphorus. However, there is clear evidence that N is also a very important limiting factor in (sub)alpine lakes, high-latitude lakes, (shallow) soft water bodies and shallow coastal seas. In these situations, N enrichment in originally pristine areas can lead to significant changes in algal communities, or even algal blooms. This may also lead to related foodweb-based shifts in these aquatic systems. In shallow N-limited lakes, macrophyte composition can also be highly affected by eutrophication via N inputs (e.g. Roelofs 1983).

14.2.3 Acidification

Soil or water acidification is characterized by a wide variety of long-term effects. It is defined as the loss of buffering capacity (Acid Neutralizing Capacity (ANC) or alkalinity in water) and may lead to a decrease in pH. Decreases in pH are dependent on the buffering capacity of the soil or water layer (e.g. Ulrich 1983, 1991).

Acidifying inputs (as N and sulphur (S)), deposited on calcareous soils, will at first not give a change in acidity. In these soils HCO_3^- and Ca^{2+} ions leach from the system, but the pH remains the same until almost all calcium carbonate has been depleted. In soils dominated by silicate minerals (pH 6.5–4.5) buffering is carried out by cation exchange processes of the soil adsorption complexes. In this situation, protons are exchanged with Ca^{2+} and Mg^{2+}, and these cations are leached from the soil together with anions (mostly nitrate or sulphate). Because of the restricted capacity of this buffering system, soil pH will soon start to decrease. In mineral soils with a large cation exchange capacity and high base saturation, this buffering may, however, hold for several decades, even at relatively high acidic inputs. At low pH (<5.0), clay minerals are broken down and hydrous oxides of several metals are dissolved. This causes a strong increase of the concentration of toxic Al^{3+} and other metals in the soil solution. As a consequence of the decrease in pH, nitrification is strongly hampered or even completely absent in most soils. This may lead to accumulation of ammonium, whereas nitrate decreases to almost zero at these low pH values (e.g. Roelofs et al. 1985). In addition, the decomposition rate of organic material in the soil is lower in these acidified soils, which leads to increased accumulation of litter (e.g. Van Breemen et al. 1982; Ulrich 1983, 1991). As a result of this complex of changes, growth of plant species and the species composition of the vegetation can be seriously affected; acid-resistant plant species will gradually become dominant, and several species typical of intermediate and higher pHs disappear.

The buffering of the water layer in aquatic systems is highly dependent on the bicarbonate concentrations in the water. Input of acidity (protons) will change the carbon dioxide-bicarbonate equilibrium, finally resulting in lowering of the alkalinity and the pH in the water layer. Aquatic systems with low bicarbonate concentrations or low inputs of bicarbonate from the catchment, as in many softwater lakes, are among the most sensitive with respect to acidification of all ecosystems across the globe.

14.2.4 Negative Effect of Reduced Nitrogen

In many regions with a relatively high rate of N deposition, a (very) high proportion of the deposited N originates from ammonia and ammonium (e.g. Asman et al. 1998; Fowler 2002). This may cause a change in the dominant N form in the soil from nitrate to ammonium, especially in habitats with low nitrification rates ($pH < 4.5$). The response of sensitive plant species can be significantly affected by this change. Species of calcareous or somewhat acidic soils are able to use nitrate, or a combination of nitrate and ammonium, as the N source, whereas early studies showed that species of acidic habitats generally use ammonium (e.g. Gigon and Rorison 1972; Kinzel 1982), because at least some of these plants do not have the nitrate reductase enzyme (Ellenberg 1996). Laboratory and field studies demonstrated that most forest understory species are favoured when both ammonium and nitrate can be taken up (Falkengren-Grerup 1998; Olsson and Falkengren-Grerup 2000). One of the impacts of increased ammonium uptake is the reduced uptake of base cations and exchange of these cations (K^+, Ca^{2+} and Mg^{2+}) to the rhizospere. Ultimately this can lead to severe nutritional imbalances, which are considered to be important in the decline in tree growth in areas with high ammonia/ammonium deposition (Nihlgård 1985; Van Dijk et al. 1990). High ammonium concentrations in the soil or water layer are also toxic to many sensitive plant species, causing disturbed cell physiology, cell acidification, accumulation of N-rich amino acids, very poor root development, and finally, inhibition of shoot growth. Strong evidence exists that several endangered vascular plants of grasslands and heathlands, and fen bryophytes are (very) intolerant to increased concentrations and high NH_4^+/NO_3^- ratios (De Graaf et al. 1998; Paulissen et al. 2004; Kleijn et al. 2008; Van den Berg et al. 2008). This phenomenon is also clearly demonstrated for macrophyte communities of soft-water lakes: increased high NH_4^+/NO_3^- ratios clearly inhibited the growth of the typical macrophytes of this system, but stimulated the growth of some resistant species, leading to strong monocultures of species.

14.2.5 Increased Susceptibility to Secondary Stress and Disturbance Factors such as Drought, Frost, Pathogens or Herbivores

The sensitivity of plants to stress, i.e. external constraints that limit dry matter production rate, or disturbance factors, i.e. mechanisms which affect plant biomass by causing its partial or complete destruction, may be significantly affected by N deposition. With increasing N deposition, the susceptibility to fungal pathogens and attacks by insects can be enhanced (e.g. Flückiger et al. 2002). This is probably due to altered concentrations of phenolic compounds (lower resistance) and soluble N compounds such as free amino acids, together with the lower vitality of individual plants as a consequence of air pollution. Negative impacts of pathogenic fungi have been found in N-addition studies and correlative field studies for several tree species, but for most ecosystems data are lacking and the influence on diversity is still unclear.

In general, herbivory is affected by the palatability of the plant material, which is strongly determined by the N content (Throop 2004). Increased organic N contents of plants, caused by N deposition, can thus result in increased (insect) herbivory. Data on this process are scarce, but it has been demonstrated for attacks by heather beetle in *Calluna* heathlands in the Netherlands (Brunsting and Heil 1985; Berdowski 1993). Outbreaks of heather beetle (*Lochmaea suturalis*), a chrysomelid beetle, can occur in dry lowland heaths. It forages exclusively on the green parts of *C. vulgaris*. Outbreaks of the beetle lead to the opening of closed *C. vulgaris* canopy, greatly reducing light interception and leading to enhanced growth of understorey grasses, such as *Deschampsia flexuosa* or *Molinia caerulea*. The frequency and intensity of these outbreaks were clearly related with N inputs and N concentrations in the heather, although the exact controlling processes need further quantification.

Furthermore, N-related changes in plant physiology, biomass allocation (root/shoot ratios) and mycorrhizal infection can also differentially influence the sensitivity of plant species to drought or frost stress, leading to reduced growth of some species and possible changes in plant interactions (e.g. Pearson and Stewart 1993; Bobbink et al. 2003).

14.3 Impacts of Nitrogen Deposition on Fauna

Until recently, research on the impacts of N deposition has mainly focused on plants/vegetation and abiotic processes. Experimental research on fauna is complicated, as different species use the landscape at different spatial scales and animal species richness is much higher than that of plants. Consequently, research on the effects of increased N inputs on faunal diversity in semi-natural and natural ecosystems is largely lacking. There is however a clear impact as N impacts can affect food and environmental conditions, including micro-climate, but also the vegetation structure and heterogeneity of the landscape, needed by animal species to complete their life-cycles.

Elevated N deposition causes changes in nutrient content of plant organic matter and plant species composition and thereby alters the micro-climate (temperature and moisture regimes) experienced by animals. As an example, increased N deposition has consequences for herbivorous animals like caterpillars, as their host plants may decrease or increase in abundance, or because of changes in food quality. It is likely that for caterpillars the species density declines in N-affected and less diverse vegetation, although direct experimental evidence is scarce (Weiss 1999; Ockinger et al. 2006). However, some caterpillar species may indirectly profit from N deposition if their preferred plant species becomes the dominant species as a consequence of the N inputs. Changes in the nutrient content of dead organic matter also has consequences for detritivores, as shown for aquatic invertebrates (e.g. Smith and Schindler 2009) and micro/mesofauna in forest soils (e.g. Bobbink et al. 2003).

Because of elevated N deposition, vegetation and landscape heterogeneity has also often declined due to e.g. extensive grass encroachment or the development of vegetation with low diversity (see Sect. 14.2, this chapter). The occurrence of animal species is related to landscape heterogeneity by at least three mechanisms. First, species may depend on specific conditions, which are only present in transitions between different biotopes. Second, many animal species require different parts (biotopes) of the landscape for reproduction, resting, foraging, etc. Third, heterogeneity creates the possibility of risk spreading, leading to a higher persistence of species. Thus, N deposition affects faunal diversity not only directly (e.g., changes in food quality and micro-climate), but also indirectly through changes in vegetation and landscape configuration and heterogeneity. To illustrate this, two examples are given of the impacts of N deposition on faunal diversity.

Ground beetle (Carabidae) assemblages on dry open coastal dune grasslands are characterised by species preferring drought and higher temperatures. N deposition, however, results in grass encroachment (e.g. Bobbink et al. 2003). Consequently, the characteristic micro-climate of coastal dune grasslands (very warm during day time, but fairly cold at night and continuously dry) changes to a buffered micro-climate (continuously cool and moist). Comparison of the ground beetle assemblage between 15 coastal dune grasslands on the Waddensea Isles Ameland and Terschelling showed that encroachment with the grasses *Calamagrostis epigejos* and, to a lesser extent, *Ammophila arenaria* results in a change in the relative numbers of drought vs. moisture preferring species. Thus, it is likely that because of N inputs the beetle assemblage is dominated by moisture preferring species, instead of the warmth and drought preferring species dominating in intact dune grasslands in low N-input regions (Nijssen et al. 2001).

The decline of the red-backed shrike (*Lanius collurio*) illustrates how the effects of elevated N deposition can have repercussions across an entire food web (Beusink et al. 2003). This bird species strongly declined from 1950 onwards throughout Western Europe. It has currently disappeared from the coastal dunes of the Netherlands and it is disappearing from the coastal dunes of northern Germany and southern Denmark. Only in the coastal dunes of northern Denmark is the population of red-backed shrikes still stable. This pattern in population trends is clearly correlated to atmospheric N deposition levels, although the occurrence of this bird species can of course not directly be related to higher N availability. Red-backed shrikes feed on large insects and small vertebrates (e.g. lizards) and carry only a single prey item to the nest at a time. Prey demands of the nestlings have to be met during the day under different weather conditions and also during the whole breeding period. To ensure a constant and sufficient energy supply, the red-backed shrikes require a high diversity of large prey species which in turn depends on landscape heterogeneity. In Dutch coastal dunes, increased N deposition led to the encroachment by tall grasses and bushes, a decrease of open sandy areas and a loss of succession stages rich in species. The decline in landscape heterogeneity seriously affected the prey availability for red-backed shrikes. In particular, the lack of sufficient large prey species because of grass encroachment in the areas with high N deposition (Netherlands) has been shown to be the main factor in the decline of the population of this bird species (Esselink et al. 2007).

14.4 Factors Affecting the Severity of Nitrogen Deposition Impacts

The severity of the different impacts of atmospheric N deposition (see Sect. 14.2, this chapter) depends on a complex number of factors, of which the most important are: (1) the duration and total amount of the N inputs; (2) the chemical and physical form of the airborne N input; (3) the intrinsic sensitivity to the changes of the plant and animal species present; (4) the abiotic conditions; and (5) the past and present land use or management. Buffer capacity (ANC; alkalinity), original soil nutrient availability (N, P), and soil factors which influence decomposition, nitrification, N immobilisation and denitrification rates, are especially important. As a consequence, high variations in sensitivity to atmospheric N deposition have been observed between different ecosystems across the globe (e.g. Bobbink et al. 1998, 2010).

Direct foliar effects by N pollutants are most strongly influenced by the intrinsic sensitivity of the physiology of the different species (groups) to this stress type. Eutrophication effects of atmospheric N enrichment are strongly related to several processes in the N cycling in ecosystems, such as mineralisation, nitrification, N immobilisation and denitrification rates. These processes can affect the rate of removal from the ecosystem (e.g. leaching of nitrate; N_2 or N_2O output via denitrification), the form of N (nitrification), but also the availability of N compounds. The original nutrient status of the system is also very important in this respect, whereas other limiting factors, such as P, K or water can highly influence the outcome of all the processes.

The amount of buffering capacity and the buffering rate in terrestrial or aquatic ecosystems are particularly related with their sensitivity to the acidifying consequences of atmospheric N deposition. Nitrification of deposited ammonium can be an important part in this process, because two protons are produced per N molecule in this process. Acidification can also reduce nitrification rates in soils or waters, leading to dominance of reduced N in regions with high reduced N loads and to increased risks of long-term negative effects of this N form. In addition, the effects of reduced N are observed particularly in formerly weakly buffered ecosystems (pH between 4.5 and 6.5), because many characteristic plants (and animals?) are adapted to nitrate as the dominant N form, and high ammonium availability leads to severe toxicity effects.

The increased susceptibility of plants (or animal) species to stresses and disturbances, induced by enhanced atmospheric N loads, is highly dependent on the large differences in the physiological functioning of individual species. Therefore, the generalization of the effects of N deposition over a range of ecosystems is hardly, if at all, possible, although these impacts have been demonstrated to be of major importance in some ecosystems. Further information on the sensitivity of European ecosystems to N deposition can be found in Nordin et al. (2011) and Bobbink and Hettelingh (2011).

14.5 Questions for Discussion

a. Which factors about N deposition actually affect the biodiversity?
   - is it soil chemistry?
   - is it a competitive response?
   - is it a combination of factors, such as climate change AND N deposition, sulphuric acid AND N deposition?
b. How confident are you in your results? How confident are you in extrapolating your results?
c. What are the major unknowns yet related to your area of speciality? How can they be addressed?

These questions and others were considered by the working group on effects of N deposition (see Baron et al. 2014; Chap. 49, this volume).

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Chapter 15
What Happens to Ammonia on Leaf Surfaces?

J. Neil Cape

Abstract The exchange of ammonia between leaf surfaces and the atmosphere is bi-directional, and depends on the relative solution concentrations in or on the leaf, and concentrations in the atmosphere. The amount of ammonia (as ammonium ions) present at equilibrium in solution on leaf surfaces depends on temperature, and on the presence of other gases such as carbon dioxide and sulphur dioxide, which act as acids to neutralise the hydroxide ions formed when ammonia dissolves. Under ambient conditions, with low concentrations of ammonia and sulphur dioxide, equilibrium may not be achieved even over many hours, because of aerodynamic limitations in the transfer between the air and the surface. Unless chemical reactions occur to 'fix' ammonium on the surface, for example as involatile ammonium sulphate or organic nitrogen, any deposited ammonia will be returned to the atmosphere as surface water evaporates. Results from a simple model are presented to show the effects of different atmospheric components and temperature, and also of the rate of oxidation of dissolved sulphur dioxide, on the retention of ammonium on leaf surfaces.

Keywords Co-deposition • Dry deposition • Oxidation rate • Sulphur dioxide • Surface reactions

15.1 Background

Micrometeorological measurements of ammonia fluxes show that the process is bi-directional, i.e. ammonia can be emitted from the surface, or can be deposited to the surface (Sutton et al. 1998). Emission occurs when there is a source of ammonia, either from decaying plant material, or if the equilibrium between ammonium ions in the leaf apoplast and ammonia gas in the surrounding air exceeds the air concentration. Deposition occurs when surface concentrations are less than those in the surrounding air. The process is dynamic—i.e. it changes with time, on time-scales

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of minutes, and for a given surface, fluxes may change direction as air concentrations and surface conditions vary. Wet surfaces provide additional complications, because ammonia will dissolve in any liquid (from rain or dew) on leaves or other surfaces. Although this dissolved ammonia will not usually enter stomata directly (but see Burkhardt and Eiden 1994; Burkhardt et al. 1999), it provides a potential source of ammonia gas for direct uptake by stomata if internal leaf ammonia concentrations are low enough.

Although such dissolution into surface water may be a measured sink for a deposition flux, what happens when surface water evaporates, for example after rain, or as dew evaporates in the morning? There is plenty of evidence that much of the dissolved ammonia is returned to the gas-phase as the water evaporates, in response to changing equilibrium concentrations in the surface solution (Flechard and Fowler 1998; Flechard et al. 1999). Similar behaviour has also been observed for sulphur dioxide. This chapter presents some model results to address the following questions:

- Is dissolved ammonia always returned to the gas-phase as surface water evaporates?
- Are there processes operating that would retain deposited ammonia, leading to a net deposition flux?
- If the source of the dissolved ammonia is from inside the leaf, do these processes lead to net retention of nitrogen (N) within the plant-soil system rather than loss to the atmosphere?

15.2 Simple Ammonia Chemistry

The ammonia molecule (NH_3) is highly soluble in water, and solubility increases as temperature decreases, with a 3-fold increase from 25 to 0 °C (Sutton et al. 1993). Ammonia reacts with water to give the ammonium (NH_4^+) ion and hydroxide (OH^-) ion, so that solutions of ammonia in pure water are slightly alkaline. For example, 1 ppb NH_3in equilibrium with pure water would generate a solution concentration of 1.2 µM NH_4^+ and a pH of 8.2 at 20 °C (Fig. 15.1). Because the dissociation equilibrium is also temperature-dependent, the overall solubility of NH_3 (unreacted and reacted) is less dependent on temperature, with only a 60 % increase from 25 to 0 °C. But in the atmosphere, and on a leaf surface, other components are present. Carbon dioxide (CO_2) is an acidic gas, and dissolves in water to neutralise the alkaline solution from the dissolved ammonia. At an air concentration of CO_2 of 360 ppm, 1 ppb NH_3 in equilibrium at 20 °C would generate a solution concentration of 37 µM NH_4^+ and a pH of 6.8 (Fig. 15.2). All of the dissolved NH_3 would disappear back to the gas phase when the water evaporated, unless other chemical reactions occurred on the leaf surface.

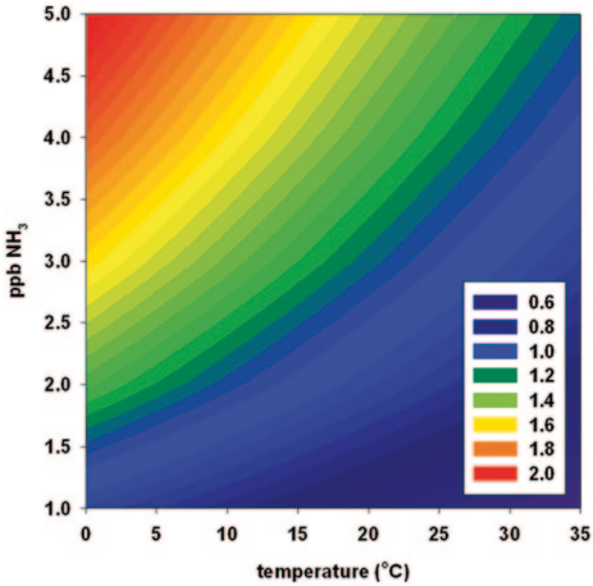

Fig. 15.1 Concentration (μM) of NH_4^+ in pure water as a function of NH_3 concentration and temperature

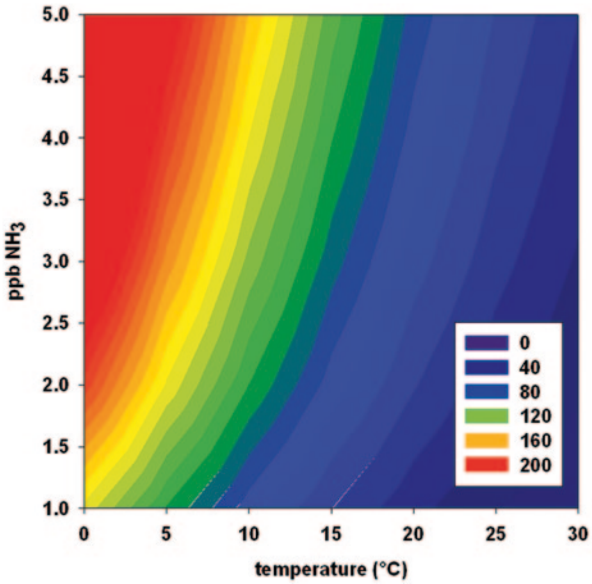

Fig. 15.2 Same as Fig. 15.1 but with CO_2 concentration of 360 ppm. Note 100-fold increase in NH_4^+

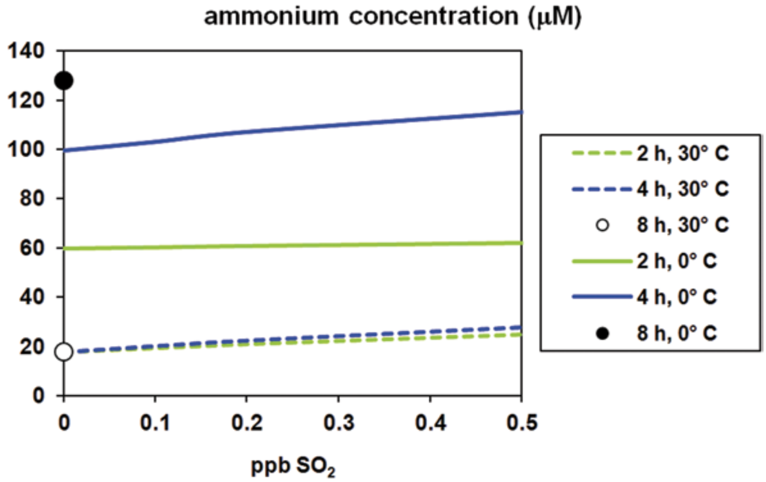

Fig. 15.3 Concentrations of NH_4^+ (μM) in solution for various times up to 8 h, for a water film 0.1 mm deep, and with a deposition velocity of 2 cm s^{-1}, for 1 ppb NH_3 and varying concentrations of SO_2 (x-axis) in equilibrium with 360 ppm CO_2 at 0 °C (*solid lines*) and 30 °C (*dashed lines*). Equilibrium is reached in less than 2 h at 30 °C but takes longer at 0 °C, where the final concentration is much larger

15.3 Other Acidic Gases

Just as CO_2 neutralises the alkaline solution, so do other acidic gases such as sulphur dioxide (SO_2). Air concentrations of SO_2 in the UK are now (2010) generally below 1 ppb (www.airquality.co.uk). How important is its role in affecting the solubility of ammonia?

A dynamic model (FACSIMILE for Windows 4) of gas transfer to a layer of water 0.1 mm deep, constrained by a gas-phase transfer rate equivalent to a deposition velocity of 2 cm s^{-1}, has been used to investigate the importance of SO_2 for NH_3 uptake. SO_2 solution equilibria were taken from Maahs (1982). As expected, the uptake of ammonia at 1 ppb, shown by the NH_4^+ concentration in solution, is much greater at 0 °C than at 30 °C (solid lines in Fig. 15.3), and equilibrium is reached much more quickly at higher temperatures because of the lower solubility. The uptake rate is dictated both by the air concentration of NH_3 and the rate of transfer from the atmosphere to the surface, expressed as the deposition velocity. In this example, with 1 ppb NH_3 and a maximum deposition velocity of 2 cm s^{-1} to a water layer 0.1 mm thick, the maximum flux to the surface would be around 14 ng NH_3 m^{-2} s^{-1} and so could only generate a solution concentration at a rate of 0.01 μM s^{-1}. The presence of small concentrations of SO_2 makes little difference to the ammonium concentration in solution after 2 h, 4 h or 8 h (Fig. 15.3). As with the case of carbon dioxide, when the solution evaporates, all the solutes would return to the gas phase as NH_3 and SO_2 unless other chemical reactions occurred while in solution.

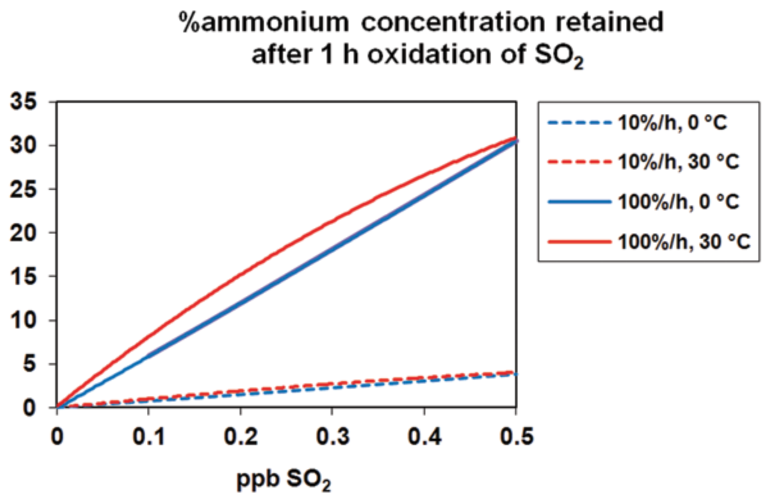

Fig. 15.4 Percentage of dissolved NH_3 retained as involatile $(NH_4)_2SO_4$in solution in the presence of SO_2 (x-axis) as a function of temperature and SO_2 oxidation rate, after 1 h oxidation at 10% h^{-1} or 100% h^{-1}

15.4 The Role of Oxidation Reactions

Oxidation of dissolved SO_2 in surface water films can in principle occur through reaction with ozone (which is not particularly water soluble), hydrogen peroxide (which is highly soluble, but present at low concentrations), by free radicals (e.g. hydroxyl) formed by light-driven or metal-catalysed reactions, or by molecular oxygen (particularly in the presence of metal catalysts). Overall reaction rates on leaf surfaces have not been measured experimentally, but observed oxidation rates in cloud droplets are very variable, and can be as high as 100% h^{-1} (Husain et al. 2000). As sulphate is produced in solution, acidity also forms, further neutralising the alkali formed as ammonia dissolves. When the water film evaporates, the sulphate salt (in this case ammonium sulphate) is involatile, and remains on the surface, thereby leading to net deposition and retention of the deposited NH_3 and SO_2.

The model can be used to calculate the fraction of the ammonium in solution that is retained through sulphate formation. Figure 15.4 shows the % retention for deposition of 1 ppb NH_3 to a 0.1 mm thick water layer, as a function of the SO_2 concentration, temperature and oxidation rate. The fraction increases with oxidation rate, and with SO_2 concentration, but is not very dependent on temperature for these model conditions. However, the absolute amount of NH_4^+ ions retained does depend on temperature, with the lower temperatures leading to higher absolute retention because of the higher solubility of SO_2 at lower temperatures (Fig. 15.5).

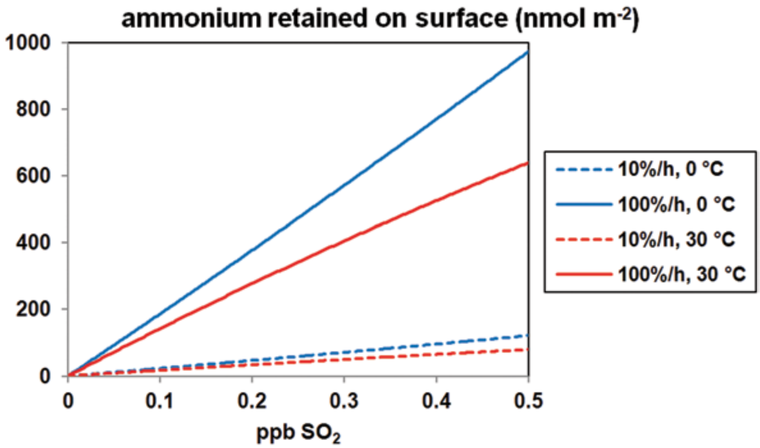

Fig. 15.5 Absolute amount of ammonium ion retained on surface as ammonium sulphate, following evaporation of 0.1 mm water film after exposure to 1 ppb NH_3 and varying SO_2 concentrations (x-axis) for 1 h, with oxidation rates of 10 % h^{-1} or 100 % h^{-1}

15.5 Discussion and Conclusions

Other chemical processes may act to retain ammonium ions on leaf surfaces. For example, the ammonium ions may exchange with other ions held on cation exchange sites at the surface, releasing metal ions such as potassium into solution. Whether the ammonium ions held on exchange sites are released back into solution, and thence to the atmosphere, as surface water evaporates would depend on the relative rates of ion exchange equilibration processes compared with the rate of change of solute concentrations as a water layer evaporated.

Biological processes may also act to retain deposited ammonia—there is evidence from several studies that organic N compounds are formed on leaf surfaces from deposited ammonia gas (Cape et al. 2010). Ammonium ions may also be metabolised by leaves on time-scales similar to those involved in wetting/drying cycles (Gaige et al. 2007).

However, the key process likely to operate even at the low levels of SO_2 observed in today's atmosphere, is the retention of ammonium ions with sulphate produced from the oxidation of SO_2. The model results in Fig. 15.4 possibly underestimate the actual oxidation rates on leaf surfaces, where there may be catalysts (especially metal ions like Fe and Mn) present for the oxidation process derived from the leaf surface itself (Burkhardt and Drechsel 1997).

The very large decrease in SO_2 concentrations over the past 20 years in the U.K. means that a smaller proportion of the dry deposited ammonia gas is now retained on vegetation surfaces than would have been the case previously. One of the effects of the reduction in SO_2 concentrations has therefore been an effective decrease in the long-term dry deposition rate of ammonia from the atmosphere. This process can be included in deposition/transport models by including a dependence of the deposition velocity for ammonia on the sulphur dioxide concentration (Smith et al. 2000).

In terms of the original questions:

- Is dissolved ammonia always returned to the gas-phase as surface water evaporates?
- Are there processes operating that would retain deposited ammonia, leading to a net deposition flux?

The answer must be 'no' to the first question, if there are chemical or biological processes operating which would lead to retention on the surface as water evaporates. In particular, this modelling study has indicated that the answer to the second question is 'yes', because even small concentrations of SO_2 can provide a means of retaining ammonium as the involatile ammonium sulphate, provided that oxidation of SO_2 to sulphate is sufficiently rapid.

- If the source of the dissolved ammonia is from inside the leaf, do these processes lead to net retention of N within the plant-soil system?

In principle, the retention of NH_3 as ammonium sulphate on the leaf surface does not depend on the source of the NH_3, so if air concentrations of NH_3 are low, leading to loss of the gas from leaves (for example, from fertilized crops with high apoplastic ammonium concentrations), then the presence of SO_2 in the atmosphere would act to retain the emitted N and prevent its further volatilisation and loss. Conversely, the very large reduction in SO_2 concentration in the U.K. over the past 20 years has probably led to a reduced capacity to retain NH_3, and consequently, increased loss from agricultural areas of the emitted NH_3, and a wider spatial impact of NH_3 emissions.

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Chapter 16
Effects of Nutrient Additions on the Diversity of the Herbaceous-Subshrub Layer of a Brazilian Savanna (Cerrado)

Thiago R. B. de Mello, Cássia B. R. Munhoz and Mercedes M. C. Bustamante

Abstract The anthropogenic increase of nutrient availability in natural ecosystems is related to different impacts as soil acidification and loss of biodiversity. The present work investigated the effects of nutrient additions on the diversity of the herbaceous-subshrub layer of a Brazilian savanna. The experimental design consisted of an unfertilized control and four fertilization treatments as follows: +N (100 kg N ha^{-1} $year^{-1}$ as $(NH_4)_2SO_4$), +P (100 kg of P ha^{-1} $year^{-1}$ as $Ca(H_2PO_4)_2 + CaSO_4.2H_2O$), +NP (100 kg of N + 100 kg of P ha^{-1} $year^{-1}$ as $(NH_4)_2SO_4$ plus $Ca(H_2PO_4)_2 + CaSO_4.2H_2O$) and +Ca (4,000 kg of dolomitic limestone and $CaSO_4.2H_2O$). Nutrient treatments were applied twice yearly between 1998 and 2006. Soil physic-chemical analyses were performed and related to the results of vegetation surveys performed in April 2009. Calcium (Ca) addition increased the soil pH in all Ca fertilized plots, while the additions of nitrogen (N), nitrogen and phosphorus (NP) and phosphorus (P) decreased soil pH. The floristic diversity was high in all treatments but differed significantly between them ($p < 0.01$). NP plots presented the lowest richness and the control plots showed the highest richness. Species cover and environmental variables were correlated to axes 1 and 2 in the Canonical Correspondence Analysis ($F = 1.14$; $p = 0.035$). In our study the invasive grass *Melinis minutiflora* (African C4 grass) responded to P and N + P treatments but was absent in the N plots, probably due to P limitation. The low cover of *M. minutiflora* in control and in Ca plots may be due to competition with native species, since these plots had a high H' index for the herbaceous-subshrub layer and were probably also P limited. The combination of N + P was especially detrimental to diversity, inducing the invasion by *M. minutiflora*. The invasion seems to be strongly limited by P and interespecific competition with native species.

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Keywords Interspecific competition • Invasive grass • Nutrient limitation • *Melinis minutiflora*

16.1 Introduction

The intensive use of fertilizers is one of the most striking practices among management systems used in agriculture in recent decades (Vitousek et al. 1997). Nitrogen (N) and phosphorus (P) are often limiting factors for plant growth in natural environments (Elser et al. 2007), so the local flora in general is adapted to a low availability of these nutrients. Among the effects caused by the increase in available N, are soil acidification (Fynn and O'Connor 2005) and loss of biodiversity (Willems et al. 1993). Phosphorus is a limiting element in older soils (Elser et al. 2007) and its addition can be toxic to native plants adapted to a low availability of this element (Lambers et al. 2008).

The Cerrado is a tropical savanna (Sarmiento 1983) that includes a vegetation complex presenting a wide range of physiognomies from grassland to tall woodlands (Eiten 1972), where deforestation occurs at a fast rate, in spite of the high biodiversity and the world's recognition of the region as one of the hotspots for biodiversity conservation (Myers et al. 2000). A large part of the flora comprises non-arboreal species, in a 5.6:1 proportion to trees (Mendonça et al. 2008) underlining the importance of the grassy layer for the region's biodiversity (Munhoz and Felfili 2006).

The present work investigated the effects of nutrient additions on the diversity of the herbaceous-subshrub layer of a cerrado *sensu stricto*.

16.2 Materials and Methods

16.2.1 Study Area

The study was carried out in the Ecological Reserve of the Brazilian Institute for Geography and Statistics (15° 56′ S, 47° 53′ W), at an altitude of 1,100 m. The study area is classified as cerrado *sensu stricto*, a woodland savanna type characterized by a continuous grass layer and a woody layer of trees and shrubs varying in cover from 10 to 60 %.

The soil is characterized as a Latossolo Vermelho (Brazilian Soil Taxonomy). It is acidic, with high Al levels, low cation exchange capacity and 0.6–2.4 % organic matter content. The climate is Aw by the Köppen classification, with two distinct seasons: hotter and rainy (October to April) and colder and drier (May to September). The average annual precipitation for the region is between 1,100 and 1,700 mm. The highest monthly average temperature is 28.5 °C and the minimum average is 12 °C.

16.2.2 Fertilization Treatments and Soil Analyses

The field design consisted of four fertilization treatments and an unfertilized control replicated four times in twenty 15 m × 15 m plots separated by at least 10 m from each other. Treatments were randomly assigned to plots. The treatments were given as follows: +N (100 kg N ha^{-1} year^{-1} as $(NH_4)_2SO_4$), +P (100 kg of P ha^{-1} year^{-1} as $Ca(H_2PO_4)_2 + CaSO_4.2H_2O$), +NP (100 kg of N + 100 kg of P ha^{-1} year^{-1} as $(NH_4)_2SO_4$ plus $Ca(H_2PO_4)_2 + CaSO_4.2H_2O$) and +Ca (4,000 kg of dolomitic limestone and $CaSO_4.2H_2O$). An additional area of 1-m width surrounding the 15 m × 15 m plots was also fertilized. Nutrient treatments were applied twice yearly between 1998 and 2006, at the beginning and the end of the rainy season. Baseline variation in soil nutrient concentrations was low (Kozovits et al. 2007).

Soil samples were collected at 0–10 cm depth in 2007. Three samples were collected per plot and mixed to form a composite sample, resulting in four replicates per treatment. Analysis were performed to determine pH in water and $CaCl_2$ (0.01 M), total N (micro Kjeldahl method), available P and K (extraction with Mehlich), exchangeable Al, Ca, Fe and Mg (extraction with 1 M KCl) (EMBRAPA 1999). Soil organic carbon (C) was determined by the Walkley–Black method. Inorganic N concentrations were determined by colorimetry: N-NH_4^+ was analyzed through reaction with Nessler reagent and N-NO_3^- by UV absorption according to the method proposed by Meier (1991).

16.2.3 Data Collection and Data Analysis

Vegetation surveys were performed in April 2009 using the line-intercept method (Canfield 1941, 1950) to sample the floristic composition and the linear coverage of the species. Each plot (15 m × 15 m) was subdivided in 9 subplots (5 m × 5 m), of which 3 were marked for sampling, totaling 15 m per plot and 60 m for each treatment for the inventory of herbaceous-subshrub layer. Shannon's (H') index was adapted to evaluate alpha diversity by using absolute cover values per species (Munhoz et al. 2008). The diversity among the treatments was then compared according to Hutcheson's *t* test ($p < 0.01$).

Canonical Correspondence Analysis (CCA), using the program CANOCO for Windows version 4 (Ter Braak and Smilauer 1998), was used to ordinate soil characteristics and cover of plant species by direct gradient analysis. The species matrix included only the 44 species for which the sum of absolute cover in the four plots treatments equaled or exceeded 1.5 m. The environmental variables matrix originally included 14 soil variables in 20 plots. The variables Mg, organic matter (O.M) and pH (CaCl) presented a high redundance (Variance Inflation Factor > 20). Therefore, only the variables Al, K, P, N, pH (H_2O), Fe, organic C percentage, N, NO_3^-, N-NH_4^+ and N-min remained in the final analysis. A Monte Carlo (Ter Braak and Smilauer 1998) significance test was used to evaluate whether ordination axes were related to the environmental variables.

16.3 Results

Calcium (Ca) addition increased the pH in all the Ca fertilized plots (varying from 5.06 to 5.85), while the additions of N, NP and P decreased pH (ranging from 3.48 to 3.63 for the N treatment, 3.44 to 3.65 for the NP treatment and 3.71 to 3.96 for the P treatment). In the NP treatments, Al saturation varied from 1.35 to 1.45%, in P treatments, from 0.1 to 0.96%, in Ca treatments, from 0 to 0.1% and in N treatments from 1.45 to 1.73%. In control, Ca and N plots, available soil P did not exceed 3.5 mg dm^{-3}, while in P and NP plots, this concentration varied from 9.2 mg dm^{-3} to 114.2 mg dm^{-3}.

We sampled 95 species in the cerrado *sensu stricto* area. The species with higher absolute cover values are presented in Table 16.1. The floristic diversity was high in all treatments and significantly different between them ($p<0.01$) (Table 16.1). NP plots presented the lowest richness and the control plots showed the highest richness. *Melinis minutiflora* (exotic C4 grass) cover was high in NP and P plots. In the N treatment *Echinolea inflexa* (native C3 grass) increased but *M. minutiflora* was absent.

16.3.1 Correlation Species x Environmental Variables

Canonical correspondence analyses (CCA) showed correlations between species cover and the environmental variables. The eigenvalues for the two first ordination axes were 0.18 and 0.16, respectively, explaining 11.3 and 21.3% of the species variance and 18.5 and 35.1% of the cumulative variance of the relationship between species and environmental variables. Species x environment correlations were high for both axes, 0.98 and 0.97, respectively. In addition, species cover and environmental variables were correlated to axes 1 and 2 ($F=1.14$; $p=0.035$). The correlation between environmental variables with the first axis was, in decreasing order, with K, Al, and C. Calcium presented significant (>0.5) weighted correlations with Al and pH (H_2O). All NP treatments plots were positioned in the right quarter of CCA diagram (Fig. 16.1a). Cover of the exotic grass *Melinis minutiflora* was highly correlated with soil available P and NH_4-N and total nitrogen (Fig. 16.1b).

16.4 Discussion

The N fertilizer used in the present study was $(NH_4)_2SO_4$, which reduced soil pH and led to an increase in Al levels. Besides the effects on soil chemistry, fertilization of soils with low nutrient levels leads to a decrease in biodiversity (Willems et al. 1993; Tilman 1993), as found in our study.

The African grass *Melinis minutiflora* represents a threat to natural areas (Pivello et al. 1999). This species is highly flammable and can alter the cycles of fire in

Table 16.1 Total absolute cover (m^2) of the principal species of the herbaceous-subshrub layer at a Cerrado *sensu stricto* in four plots of each treatment of nutrient additions: Control (C) = P1, P5, P11, P21; Calcium (Ca) = P3, P12, P17, P20; Nitrogen (N) P2, P7, P10, P14; Nitrogen and Phosphorus (NP) = P6, P8, P13, P16 and Phosphorus = P4, P9, P15 ,P19

Species	Treatments				
	C	Ca	N	NP	P
Echinolaena inflexa (Poir.) Chase	13.7	2.8	16.1	9.0	8.1
Myrcia linearifolia Cambess.	13.8	7.6	7.7	4.7	13.3
Myrcia torta DC.	8.3	8.0	7.8	4.7	9.2
Bauhinia dumosa Benth.	3.3	4.2	7.8	4.2	3.9
Poaceae 1	7.0	3.8	4.4	1.2	6.3
Melinis minutiflora P. Beauv.[a]	–	1.4	–	7.5	7.8
Croton goyazensis Müll. Arg.	2.3	3.6	1.5	2.2	4.0
Axonopus cf. *marginatus* (Trin.) Chase	4.1	2.7	2.0	1.4	2.2
Cassytha filiformis L.	5.5	1.0	2.5	2.2	0.1
Axonopus barbigerus (Kunth) Hitchc.	2.9	3.8	1.1	1.4	0.6
Scleria scabra Willd.	1.4	1.4	0.8	2.6	3.3
Croton antisyphiliticus Mart.	0.4	5.0	1.0	1.0	1.5
Trachypogon sp. 2	1.4	3.7	2.0	0.2	0.8
Campuloclinium megacephalum (Martius ex Baker) R.M. King and H. Rob	1.4	2.0	1.0	0.3	2.9
Dalechampia caperonioides Baill.	2.7	1.2	0.4	–	2.5
Sebastiania ditassoides (Didr.) Müll. Arg.	1.5	3.2	0.2	–	1.6
Oxalis suborbiculata Lourteig	3.5	1.2	0.3	0.4	0.8
Pavonia rosa-campestris A. St.-Hil.	1.7	1.2	0.6	0.3	1.7
Ouratea hexasperma (A. St.-Hil.) Baill.	1.0	0.6	2.1	0.1	1.4
Jacaranda ulei Bureau and K. Schum.	0.8	1.1	1.0	0.2	1.8
Erythroxylum campestre A. St.-Hil.	0.2	1.0	2.6	0.7	0.4
Periandra mediterranea (Vell.) Taub.	1.6	0.1	2.4	–	0.3
Diplusodon villosus Pohl	1.2	0.5	0.1	0.1	2.0
Myrcia stricta (O. Berg) Kiaersk.	1.0	–	1.8	0.7	0.3
Protium ovatum Engl.	1.9	–	1.3	0.5	–
Anacardiaceae 1	0.1	–	1.7	0.6	1.2
Croton glandulosus Jacq.	0.9	1.4	0.7	0.1	0.6
Galactia stereophylla Harms.	1.8	1.1	0.3	0.2	0.1
Poaceae 3	1.1	0.8	–	0.2	1.3
Calliandra dysantha Benth.	1.2	–	1.6	–	0.2
Melinis repens (Willd.) Zizka[a]	–	1.8	–	–	1.1
Campomanesia pubescens (DC.) O. Berg	–	1.8	–	0.3	0.7
Staelia capitata K. Schum.	1.2	1.3	–	–	–
Bulbostylis sphaerocephala (Boeck.) C.B. Clarke	0.1	–	1.2	0.1	1.1
Eriope complicata Mart. ex Benth.	1.7	0.2	–	0.2	0.2
Eugenia myrcianthes Nied.	0.1	0.9	0.1	0.1	1.1
Chamaesyce caecorum (Mart. ex Boiss.) Croizat	2.0	–	–	–	–
Panicum cervicatum Chase	0.4	1.1	–	–	0.6
Manihot gracilis Pohl	0.7	0.9	0.1	–	0.3

Table 16.1 (continued)

Species	Treatments				
	C	Ca	N	NP	P
Senna rugosa (G. Don) H.S. Irwin and Barneby	–	0.5	0.9	0.4	–
Galianthe ramosa E.L. Cabral	1.5	–	–	–	–
Piriqueta sidifolia (A. St.-Hil. and A.Juss. and Cambess.) Urb.	1.3	–	0.2	–	0.1
Spiranthera odoratissima A. St.-Hil.	–	–	–	0.2	1.3
Chamaecrista desvauxii (Collad.) Killip	–	0.1	0.1	1.3	–
Species Number	72	58	55	42	56
H' (nats.cover-1)	3.42	3.42	3.06	2.85	3.19

[a] Alien species

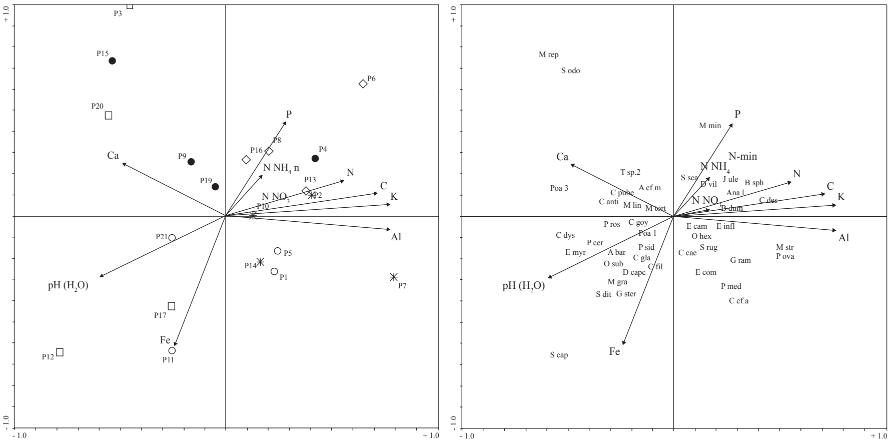

Fig. 16.1 Ordination diagram of the sampling units and environmental variables (**a**) and species and environmental variables (**b**) at the first two axes produced by the Canonical Corespondence Analyses (CCA) for absolute cover of the main 44 species (≥ 1.5 m) at a Cerrado *sensu stricto*, in the Ecological Reserve of the IBGE (Brazilian Institute for Geography and Statistics, www.recor.org.br), Brazil. Species are identified by the first letters of the binomial, see Table 16.1. *Empty circle* (○) are Control treatments; *square* (□) = Ca treatments; *star* (*) = N treatments; *diamond* (◊) = NP treatments and *full circles* in bold (●) = P treatments

areas where it establishes (D'Antonio and Vitousek 1992), in addition to negatively affecting the establishment of native plants (Hoffmann and Haridasan 2008). Competition, P and N limitation and shade restrict the establishment of *M. minutiflora* (Saraiva et al. 1993, Barger et al. 2003). In our study, it responded to both treatments: P and N + P, but was absent from the N alone plots, probably due to P limitation. The high cover showed by *M. minutiflora* in P and NP treatments agrees with Saraiva et al. (1993), who found that this species growth is limited by P and with Barger et al. (2003), who found that this plant responded to P addition only when it was coupled with N. The low cover of *M. minutiflora* in control plots may be due to competition with native species, since these plots had a high H' index for the herbaceous-subshrub layer, and probably also were P limited. Both factors, competition with native species and P limitation, apply also for the calcium treatment.

The cover of the native C3 grass *E. inflexa* was insensitive to *M. minutiflora* cover and had a higher cover than *M. minutiflora* in the NP, P and Ca plots, corroborating the Pivello et al. (1999) study on a Brazilian Savanna. However, the Ca and control treatments had the two highest densities in the woody layer (Jacobson 2009) and the shading effect favours C3 species (Klink and Joly 1989).The Ca treatment had the lowest cover of *E. inflexa*, irrespective of shading, possible due to changes in soil chemistry (increase in pH and Ca availability and decreased K availability).

The nutrient treatments had a strong negative effect on the distribution and species richness in the herbaceous-subshrub layer in the study area. The combination of N+P was especially detrimental, inducing the invasion by *M. minutiflora*. The invasion seems to be strongly limited by P and interespecific competition with native species.

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Chapter 17
Leaf Litter Decomposition and Nutrient Release Under Nitrogen, Phosphorus and Nitrogen Plus Phosphorus Additions in a Savanna in Central Brazil

Tamiel K. B. Jacobson and Mercedes M. C. Bustamante

Abstract The aim of this study was to determine leaf decomposition rates and nutrient release in a cerrado *sensu stricto* under nitrogen (N), phosphorus (P) and N plus P additions. The experiment was carried out in an area located in the Ecological Reserve of the Instituto Brasileiro de Geografia e Estatística, near Brasília (15° 56' S, 47° 53' W). Between 1998 and 2006, 100 kg ha^{-1} $year^{-1}$ of N (N treatment), P (P treatment) and N plus P (NP treatment) were applied to 16 225 m^2 plots, arranged in a completely randomized design. Litterfall was collected at the end of dry season (September 2006) and oven dried (60 °C) for 72 h. Litter bags with 10 g of leaf litter were incubated in situ for 453 days to determine decomposition rate. Nitrogen and P concentrations and mass loss were measured during the incubation process. Decomposition rates of leaf litter in N plots did not differ in relation to those in control plots. Leaf litter decomposition rates increased in P (+18.6%) and NP (+27.4%) plots, where there was a greater N (in NP plots) and P (in P and NP plots) initial concentration in litter relative to the control plots ($p<0.05$). Leaf litter in the N treatment had the highest N mass loss, and together with NP treatment, the smallest P mass loss. Nitrogen addition increased N mass loss, while the combined addition of N and P resulted in an immobilization of N in leaf litter. When the nutrients are supplied separately, there is greater mass loss of N with N addition, and greater mass loss of P with P addition compared to that observed when N and P are supplied together. The results indicate that if the availability of P is not increased proportionally to the availability of N, the losses of N are intensified during the decomposition process.

Keywords Biogeochemical cycling • Cerrado • Nutrient limitation • Woody plants

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17.1 Introduction

Ecosystem function is defined primarily by organic matter production, accumulation and decomposition. Nutrient cycling is one of the most important functions in the organization and maintenance of an ecosystem and include inputs (atmospheric deposition, biological fixation, rock weathering) and outputs (runoff, runoff water from rivers, leaching and gas losses). Nutrient transfer between plant and soil represents a key factor in ecosystem functioning and organization (Attwill and Adams 1993). Shifts in global biogeochemical cycles, due to human disturbance of environments, can affect biotic interactions and resource availability patterns in a range of different ecosystems (Vitousek 1997; Bobbink et al. 2010). Anthropogenic introduction of nutrients has amplified global nitrogen (N) and phosphorus (P) cycles by 100 and 400 % respectively, since the industrial revolution (Falkowski et al. 2000). Particularly in tropical systems, N cycling had been modified through urbanization and agricultural intensification (Filoso et al. 2006). In this way, cattle ranching expansion and mechanized agriculture since the 1970s has led to large conversion of Cerrado vegetation (one of world's biodiversity hotspots), with intensive fertilizer addition causing rapid loss of sensitive habitats (Klink and Machado 2005). In the Cerrado ecosystem, the seasonality of water supply and highly weathered soils with low nutrient content have probably acted as selection drivers for species with high nutrient retention. Nutrient storage mechanisms such as leaf scleromorphism, high resorption rates and low decomposition rates are common in Cerrado plant communities (Nardoto et al. 2006). Nutrient cycling, especially of N, has been shown to be conservative in this ecosystem. Changing patterns of rainfall distribution and nutrient pulses can disrupt the supply of and demand for nutrients, resulting in higher losses (Bustamante et al. 2006). In this context, the aim of this study was to determine how nutrient additions (N, P and N plus P) affect leaf litter nutrient concentration, decomposition and nutrient release in a cerrado *sensu stricto* area. We tested the following hypotheses: N and P additions will increase N and P leaf litter concentration, leaf decomposition and N and P mass loss. These changes will be more intense when N and P are supplied together.

17.2 Material and Methods

17.2.1 Study Area and Fertilization Treatments

This study was carried out in an area located in the Reserva Ecológica do Roncador, Brazilian Institute of Geography and Statistics (RECOR/ IBGE), near Brasília—Federal District, Brazil (15° 56' S, 47° 53' N, average altitude = 1,100 m) in a native cerrado *sensu stricto* area under nutrient additions. The soil is characterized as an Oxisols (Haplustox), which is acidic, with high Al levels and low cation exchange capacity (Haridasan 1994). Total precipitation was 1,667 mm in 2006 and 1,184 mm in 2007. Air temperature ranged from 10.1 and 31.9 °C during the study period. The vegetation is classified as cerrado *sensu stricto*, which is characterized by a continuous grass layer and a woody layer of trees and shrubs varying in cover from 10–60 %. This is the most common vegetation type of Cerrado region (Eiten 1972). The fertilization experiment began in 1998. The experimental design was completely randomized, with four nutrient addition treatments and four replicates randomly assigned to 16 plots of 225 m^2, separated by a 10 m buffer area. The treatments were: control (C; without fertilization), +N (single addition of ammonium sulfate $(NH_4)_2SO_4$), +P (single addition of 20 % superphosphate—Ca $(H_2PO_4)_2$ + $CaSO_4$ $2H_2O$) and +NP (simultaneous addition of ammonium sulphate/20 % superphosphate) applied to the litter layer without incorporation. Between 1998 and 2006, 100 kg ha^{-1} of N, P and N plus P, was applied twice a year (beginning and end of rainy season). The study area was burned accidentally two times, in 1994 (before the beginning of the treatments) and in 2005.

17.2.2 Leaf Litter Decomposition

Leaf litter was collected from the soil surface in the end of the dry season (September 2006) and oven dried at 60 °C for 72 h. Approximately 10 g (10.115 g, $sd = 0.209$) of mixed leaf litter was weighed into each bags (2 mm mesh). In October 2006, litter bags (2 mm; 20 cm × 20 cm) were placed randomly on the litter layer in each plot. A total of 576 litter bags were placed, 36 per plot (144 per treatment). At approximately 60 day intervals, we randomly collected four litter bags per plot ($n = 16$). Initial mass of each litter bag corresponded to time zero (T0). Collection dates were: December (61 days), February 2007 (125 days), April (189 days), June (248 days), August (309 days), October (369 days) and January 2008 (453 days). Litter from the recovered litter bags was oven-dried at 60 °C to constant weight, and ground in a Wiley mill (40 mesh sieve). A simple negative exponential model was used to determine decomposition rate (Olson 1963). We also calculated the half-life (T50 %) (required time for disappearance of 50 % of the litter mass), using the equation ln 2/k, and litter residence time, given by 1/k.

17.2.3 Leaf Litter Nutrient Concentration

Samples ($n = 4$) corresponding to T0 (initial mass, October 2006), T1 (61 days), T4 (248 days) and T7 (483 days) were analyzed for N and P concentrations. Extraction was performed using wet digestion method (nitric, perchloric and sulphuric acid; 10:2:1). Nitrogen was determined by distillation, using the Microkjeldahl method. Phosphorus was determined by colorimetric analysis with ammonium molybdate and ascorbic acid (EMBRAPA 1999). Litter N and P concentrations were used to calculate nutrient release through litter decomposition.

17.2.4 Statistical Analysis

Data were tested for normal distribution using Kolmogorov–Smirnov test. Regression was used to analyze the decomposition data. Decomposition constant (k), % of mass remaining, litter half-life and residence time were compared between treatments using ANOVA and Student-t test ($p<0.05$). Nutrient litter concentrations were compare across the time periods and treatments using repeated measures ANOVA, followed by Bonferroni adjustment for multiple comparisons and Dunnett test ($p<0.05$). The analysis was performed using SPSS 15.0 package for Windows (SPSS Inc. USA).

17.3 Results

After the end of the incubation period, percentage of litter mass remaining was 58.7% ($sd=7.82$) in control plots, 56.0% ($sd=10.88$) in N plots, 51.9% ($sd=9.11$) in P plots and 47.9% (sd=9.12) in NP plots. Leaf litter decomposition rate in N plots did not differ to that in control plots. Rates of mass loss were the same in the control and N plots whereas in the P plots the final mass was significantly less than in control plots. In NP plots, the mass remaining was significantly lower relative to control plots at 125 days, 309 days and 453 days. Litter residence time in control plots was 8.2% higher (2.32 years) than that observed in N plots, but this difference was not significant. Phosphorus and NP plots had significantly lower litter residence time, 18.7% (P) and 27.5% (NP) relative to that observed in control plots (Fig. 17.1).

The N concentration in leaf litter significantly increased (+50% in P and +66% in NP plots) during the decomposition process and was significantly higher in N plots (248 days), in NP plots (248 and 453 days) relative to control plots. A higher N (in NP plots) and P (in P and NP plots) initial concentrations in litter were also measured in comparison to control plots (Fig. 17.2).

Lower N loss was observed in P (−21.4%) and NP (−20.3%) plots while the highest N loss (−38.1%) was observed in N plots. Phosphorus and NP plots had the highest N immobilization rates and also increased P concentrations (+23% P and +70% NP) over the incubation period. These concentrations were significantly higher than those remaining in control plots for all sampling date incubation periods (with the exception of 61 days in the P plots). Higher P mass loss (45.1%), followed by P (35.6%), N and NP plots (both 18.7%) (Fig. 17.3) were measured in control plots during litter decomposition.

17.4 Discussion

Cerrado *sensu stricto* areas are associated with low decomposition rates (Peres et al. 1983). Although environmental characteristics control decomposition rates at the global scale, the initial nutrient content of the litter controls decomposition rates at

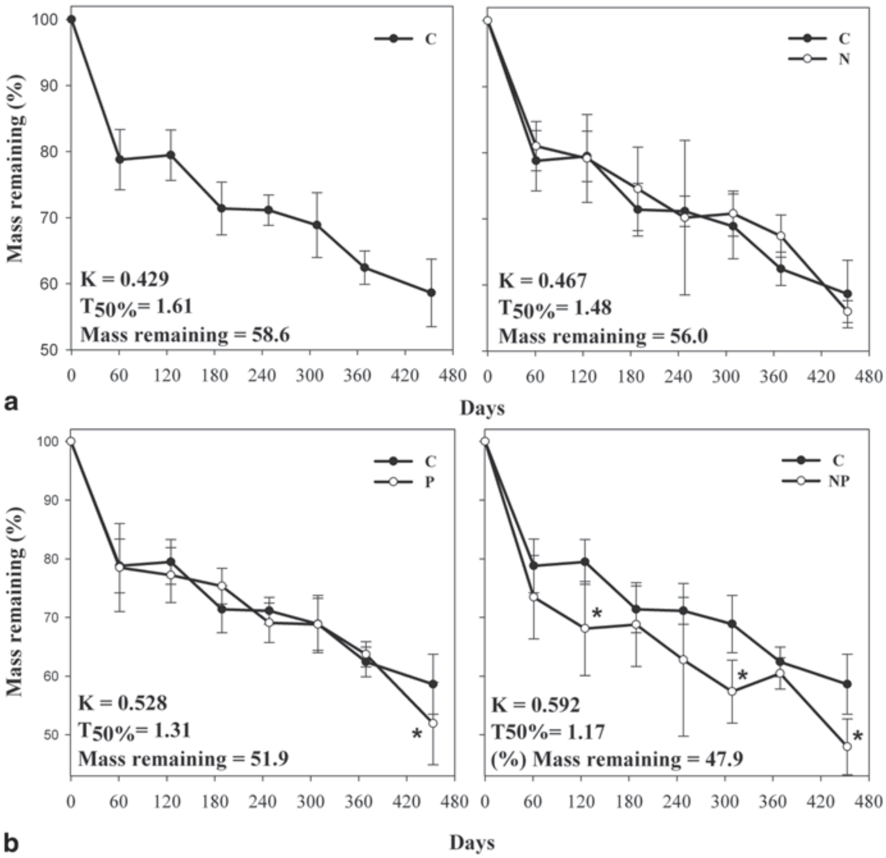
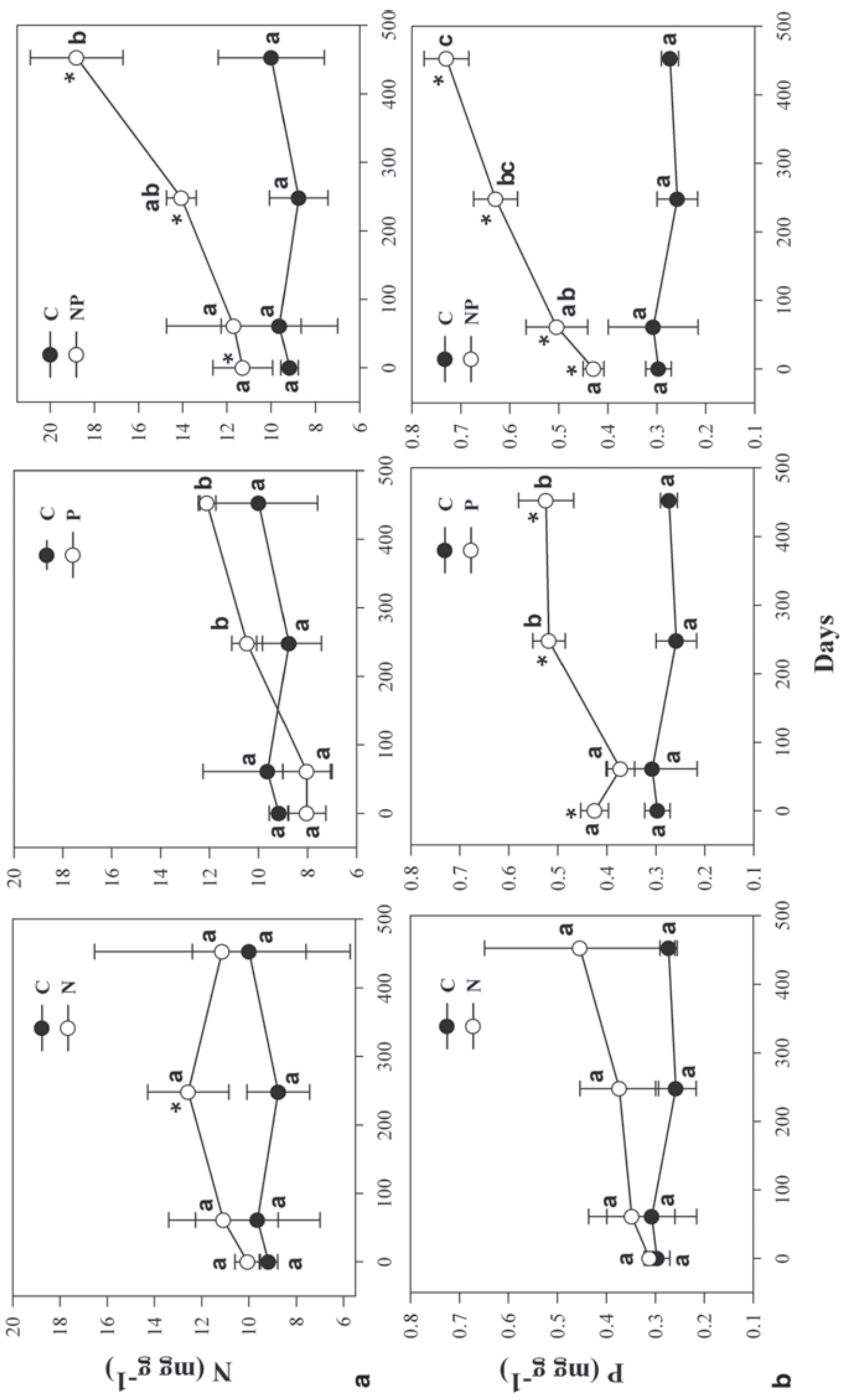


Fig. 17.1 k values, half-life (T 50 %) and % of mass remaining of leaf litter under nitrogen (N), phosphorus (P) and N plus P additions in a savanna in Central Brazil. *Bars* indicate standard deviation. * Indicates significant differences from control (F and t-test, $p < 0.05$). (Reprinted from Jacobson et al. (2011) with permission from Elsevier)

the ecosystem scale (Zhang et al. 2008). As expected, higher initial N and P concentrations in litter from the NP plots and higher initial P concentrations in litter from P plots increased decomposition rates. If nutrients (especially N and P) are more readily available, decomposers use less energy in nutrient acquisition, leaving more to invest in enzymes that degrade cellulose, hemicellulose and lignin (Weedon et al. 2009). At the global scale, N addition has had no significant influence on litter mass loss compared with other nutrients (Knor et al. 2005). However, Hobbie (2008) suggested that N addition increases C retention, since decomposition rates in grassland, coniferous forest and oak forest on sandy weathered soils were lowered by N addition. By contrast decomposition rates in tropical rain forest appear insensitive to P additions (Cleveland et al. 2006) although, decomposition rates in Australian Eucalyptus forest were increased by P addition (O'Connell 1994). In combination


a
N (mg g-1)
b
P (mg g-1)
C
N
P
NP
Days

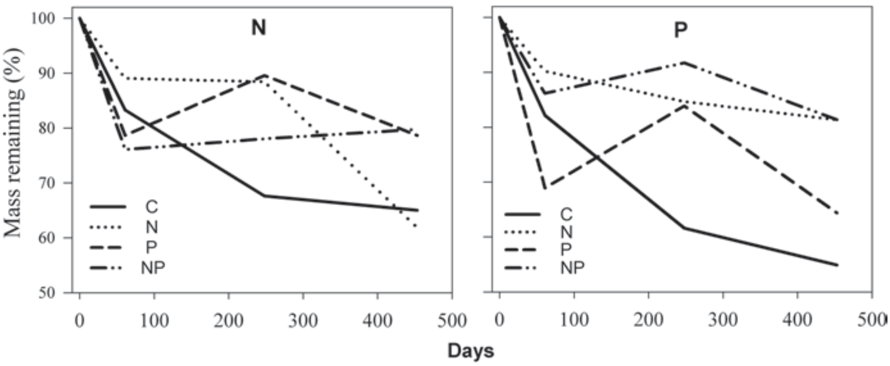


Fig. 17.3 Nitrogen and phosphorus mass remaining (%) during decomposition process. (Reprinted from Jacobson et al. (2011) with permission from Elsevier)

N and P additions produced synergistic positive effects on decomposition rates in Hawaiian rainforests (Allison and Vitousek 2004). These results indicate that decomposition responses, like most ecosystem responses to elevated N deposition, are preconditioned by the balance in N and P availability.

In our study, P addition (single or combined) increased decomposition rates, while N alone, despite increasing the initial N concentration of the litter, only accelerated decomposition when applied with P, indicating P co-limitation. According to Vitousek (2004), long-term fertilization experiments incorporate edaphic and plant chemical modifications. By contrast short-term experiments usually do not reproduce these effects because the communities of plant and soil organisms respond slowly to changes in nutrient availability. This can be verified when we compare our results with initial results from the same experimental area (Kozovits et al. 2007). Nine years after the first fertilization, control litter half-life (1.6 years) has not been modified. Decomposition rates in the NP plots are still significantly lower than those observed in the control, but with the effects are decreasing (−42 % in 1999 down to −27.4 % in 2007). Decomposition rates in the N plots increased 21.8 % over those observed by Kozovits et al. (2007). However, in the P plots decomposition rates were significantly increased, whereas in the early years of fertilization no effect of P had been seen. Nitrogen addition promoted greater N mass loss, while the combined P addition promoted P immobilization in litter. Nitrogen addition did not lead to N conservation in the litter in contrast to NP addition. Nitrogen mass loss increased by 9 % in N addition treatment while P and NP addition immobilized N in litter, decreasing, respectively, 39 and 42 % N mass loss. This may be due to nutritional limitation of the decomposer community, which immobilizes nutrients in litter in response to increased micro-organism activity (Allison and Vitousek 2004).

Fig. 17.2 Nitrogen (**a**) and phosphorus (**b**) concentration (mg.g^{-1}) in leaf litter during the decomposition process. *Bars* indicate standard deviation. * Indicates significant differences with control (Dunnett, $p<0.05$). Different letters indicate differences during litter incubation process (Bonferroni, $p<0.05$). (Reprinted from Jacobson et al. (2011) with permission from Elsevier)

Nitrogen and P litter retention patterns in fertilized plots indicate that the decomposer community appears to be limited by these nutrients. High N mass loss in N plots litter may be due to the fact that C microbial biomass limitation was reached earlier that N limitation. The initial immobilization of N seems to have been reversed due to rapid microbial turnover in response to increased N availability, as observed by Fisk and Fahey (2001). All treatments showed P immobilization relative to control plots, N addition with and without P (NP and N) reduced P loss ~58 but P alone (P) only reduced P loss by 21 %. Phosphorus fertilization has a major impact on the activity of litter decomposers, in some cases, exceeding N fertilization effects (Hobbie and Vitousek 2004). The results suggest that fertilization increases leaf litter N and P initial content, which results in higher decomposition rates in P and NP plots. Even with an acceleration in decomposition rate of higher nutritional quality material, soil N transfer (except for N plots) and P soil transfer via litter is not increased, indicating that the additional supply of nutrients is immobilized by microbial biomass.

17.5 Conclusions

Fertilization can increases leaf litter N and P concentrations, suggesting the withdrawl of these nutrients prior to litterfall is less efficient. Adding P and especially P+N increased decomposition rates (mass loss) in this ecosystem. The absence of a stimulatory effect of N addition suggests decomposition is limited primarily by P then N. The greater loss of N and P from litter in the N or P treatments provides evidence of this co-limitation. As hypothesized the combined NP addition had the greatest effect on decomposition, and conservation of these nutrients within the ecosystem. Even with an acceleration in decomposition rate of higher nutritional quality material transfers of both N and P remain unaffected indicating increased immobilization of these nutrients within the litter.

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Chapter 18
Diversity of the Shrub-tree Layer in a Brazilian Cerrado Under Nitrogen, Phosphorus and Nitrogen Plus Phosphorus Addition

Tamiel K. B. Jacobson and Mercedes M. C. Bustamante

Abstract The aim of this study was to compare the diversity of the shrub-tree layer in fertilized and unfertilized plots in a cerrado *stricto sensu* area in Central Brazil. The experiment was conducted in 16 plots of 15 m × 15 m arranged in a completely randomized design with tree fertilization treatments (+N, +P, +NP), and an unfertilized treatment (control) in the Ecological Reserve of the Instituto Brasileiro de Geografia e Estatística (RECOR-IBGE), Federal District, near Brasília. Treatments were applied from 1998 to 2006. Vegetation surveys were performed during January and July 2008 on all trees and shrubs with circumference > 5 cm at ground level. Indices of diversity of Shannon (H′), evenness of Pielou (J′) and similarity of Sørensen were calculated. Control plots contained 479 individuals of 47 species, belonging to 29 families. In the nitrogen (N) plots, 461 individuals were registered, belonging to 53 species and 34 families while 448 individuals of 54 species from 31 families were registered in phosphorus (P) plots and 336 individuals of 40 species, belonging to 24 families in nitrogen + phosphorus (NP) plots. The N (H′ = 3.20; J′ = 0.80) and NP (H′ = 2.89; J′ = 0.78) plots showed lower Shannon (H′) and Pielou (J′) indices relative to the control plots (H′ = 3.40; J′ = 0.88). The Sørensen floristic similarity was high between fertilized and control plots but decreased in the following order: P plots (0.81), N (0.78) and NP (0.76) plots. Fertilization shifted species density and dominance patterns in comparison to unfertilized plots. Nitrogen and NP addition decreased the evenness, species diversity and provided the least floristic similarity relative to the control plots. Density and dominance changes resulted in differences in species importance values among treatments. Simultaneous addition of N and P affected density, dominance, richness and diversity patterns more significantly than addition of N or P separately.

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18.1 Introduction

Cerrado is the second largest Brazilian biome and it is characterized by a vegetation mosaic ranging from grassland to forest formations (Eiten 1972) where fire is a common occurrence (Kauffman et al. 1994). The attributes of Cerrado vegetation were considered to be driven by seasonality of water availability (Warming 1908). Later, Rawitscher (1948) observed that soil water is available to deep roots throughout the year. Alvim and Araújo (1952) linked the distribution of vegetation to low soil pH and calcium (Ca) concentration. Goodland (1971) proposed that aluminium (Al) would have a toxic effect on Cerrado plants, which, together with low soil nutrient content, determine the scleromorphic characteristics of Cerrado vegetation. Furthermore, floristic composition were associated with nutritional differences between dystrophic and mesotrophic soils (Lopes and Cox 1977). In addition to variation among vegetation types, phytosociological and floristic variations also occur due to fertility gradients and soil physical characteristics (Haridasan 1987). Among the Cerrado plant adaptive strategies, economy of nutrients is a crucial point in the establishment in highly weathered soils (Meinzer et al. 1999). Thus, phenological groups have different root system and resource exploration strategies (Scholz et al. 2008). Currently, it is known that soil fertility significantly influences species composition (Ratter and Dargie 1992). Changes in global biogeochemical cycles due to anthropogenic emissions and increasing human disturbance have affected processes, biotic interactions and resource availability patterns in different ecosystems, with changes in vegetation structure and composition (Vitousek et al. 1997; Bobbink et al. 2010). Particularly in tropical systems, land use changes due to agricultural intensification and urbanization have altered the nitrogen (N) cycle (Filoso et al. 2006). In Cerrado, one of world's biodiversity hotspots, land conversion has been substantial over the last 40 years. More than half of vegetation has been converted into pastures and croplands, with intensive use of chemical fertilizers (Klink and Machado 2005). Changes in soil chemical properties may possibly result in changes between soil-plant and plant-plant interactions patterns. In addition to individual nutritional adaptations, competition is an important factor in community establishment under altered nutrient availability conditions. The aim of this study was to compare shrub-tree layer diversity in fertilized (+N, +P, +NP) and unfertilized plots in a cerrado *stricto sensu* area in Central Brazil. The following hypotheses were tested: fertilizer addition will change soil nutrient availability (N and P) and species richness and diversity will be lower in fertilized plots. Changes in analyzed attributes will be greatest when N and phosphorus (P) are applied in combination.

18.2 Material and Methods

18.2.1 Study Area and Fertilization Treatments

The study was carried out in an area located in the Ecological Reserve of the Brazilian Institute of Geography and Statistics (RECOR/IBGE), near Brasília—Federal District, Brazil (15° 56′ S, 47° 53′ N, average altitude = 1,100 m) in a cerrado *sensu stricto* area over dystrophic soil. RECOR-IBGE is part of environmental protection area Gama Cabeça de Viado, that has 10,000 ha of continuous protected native area. The climate is classified as Aw (Köppen's classification), with average annual rainfall varying between 1,100 and 1,700 mm. The average annual temperature is around 22 °C, daytime average relative humidity ranging from 80 % in rainy season and 55 % in dry season, with minimum values below 15 %. Cerrado *sensu stricto* vegetation type is characterized by a continuous grass layer and a woody layer of trees and shrubs varying in cover from 10 to 60 % and is the most common vegetation type, occupying approximately 43 % of Cerrado region (Eiten 1972). The study area burned accidentally on two occasions, in 1994 and 2005. Soil is classified as Haplustox, which is deep, well drained, with 1:1 clay minerals and predominance of iron and aluminum oxides. This soil type is very acidic with low levels of base cations (Ca, Mg, K) and plant available P (Haridasan 1994). The fertilization experiment began in 1998 and the experimental design was completely randomized, with four nutrient addition treatments and four replicates randomly divided into 16 plots of 225 m^2, separated by a 10 m buffer area. The treatments were: control (C; without fertilization), + N (single addition of ammonium sulfate $(NH_4)_2\ SO_4$), + 1P (single addition of 20 % superphosphate—Ca $(H_2PO_4)_2 + CaSO_4\ .2H_2O$) and + NP (simultaneous addition of ammonium sulfate/20 % superphosphate) applied in litter layer without incorporation. Each year, between 1998 and 2006, were annually added 100 kg ha^{-1} of N, P and N + P, applied two times by year (beginning and end of rainy season). At the beginning of the experiment, soil nutrient concentrations did not differ significantly among plots (Kozovits et al. 2007).

18.2.2 Soil Sampling and Analysis and Vegetation Survey

In October 2007, a composite soil sample (two sub-samples) was collected, in each plot, at five depths (0–10, 10–20, 20–30, 30–40; 40–50 cm). Analysis were performed to determine pH in water and $CaCl_2$ (0.01 M), total N (micro Kjeldahl method), P (extraction with Mehlich 1 and colorimetric determination) and Al (extraction with 1 M KCl and titration with NaOH) (EMBRAPA 1999). In January and July 2008, we performed vegetation surveys in all plots including all trees and shrubs with circumference > 5 cm at ground level. The phytosociological absolute and relative parameters of density, frequency and dominance were calculated for each species within each treatment. The phytosociological parameters were

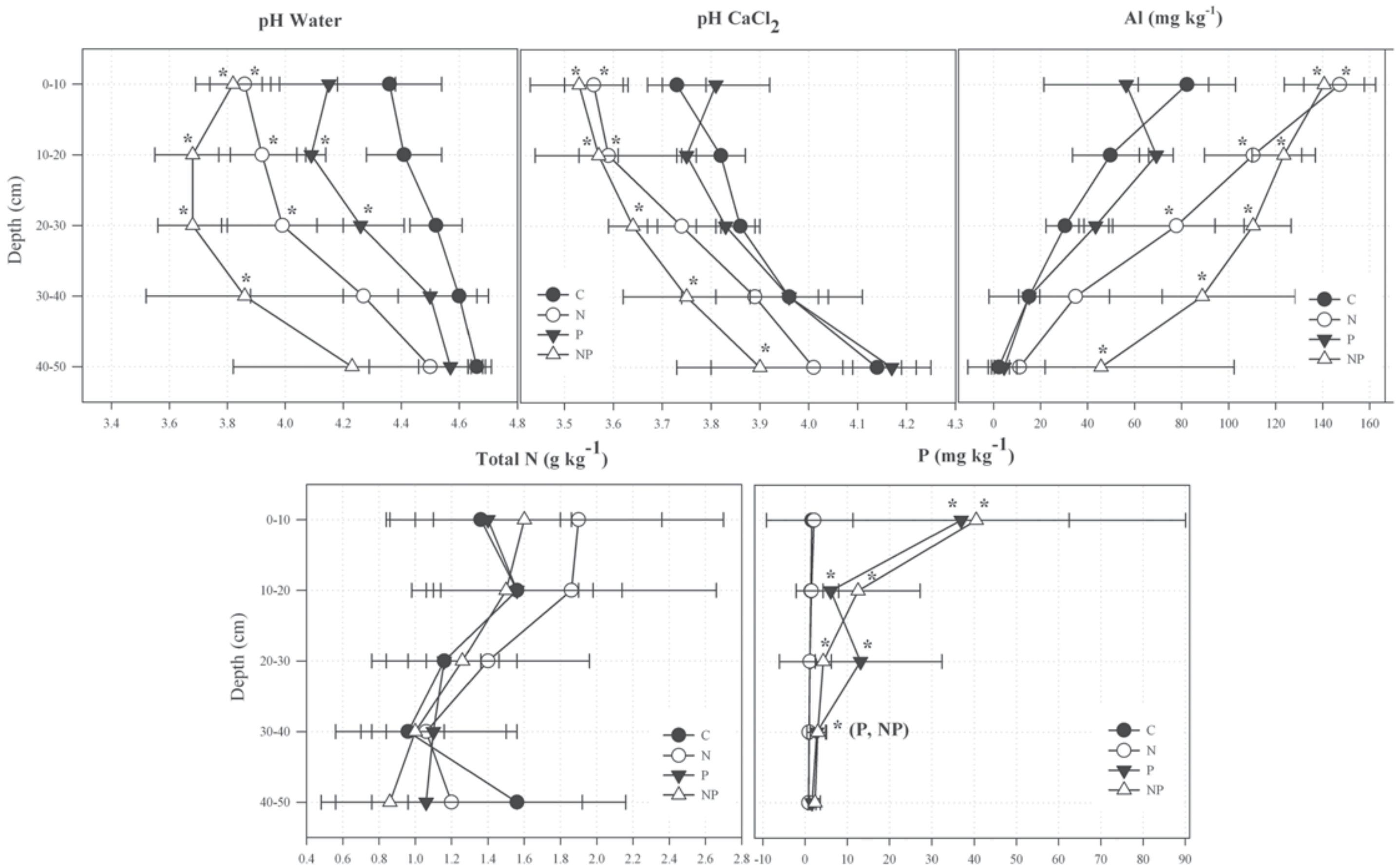

Fig. 18.1 Soil chemical characteristics (mean and standard deviation) at five depths (0–10, 10–20, 20–30, 30–40, 40–50) of a cerrado *sensu stricto* under fertilization treatments (+N, +P, +NP) ($n = 4$). *Indicates significant differences in comparison to control treatment (unfertilized) (t-test, * $p < 0.05$). Reprinted from Jacobson et al. (2011) with permission from Elsevier

calculated according to Mueller-Dumbois and Ellenberg (1974). The index of importance value (IVI) was calculated for each species within each treatment according to Kent and Coker (1992).

18.2.3 Statistical Analysis

Nutrient concentrations in each depth were tested for normality using Kolmogorov-Smirnov test ($p<0.05$) and tested with F and student t test ($p<0.05$). The data with no normal distribution even after transformation, were compared with Mann-Whitney nonparametric test ($p<0.05$). Comparisons were made relative to control for each depth ($n=4$). Woody vegetation diversity was tested with Shannon-Wiever (H′) diversity index and Pielou evenness index (J′) for each treatment. Floristic similarity between fertilized and control plots, was tested with the Sørensen similarity index (Kent and Coker 1992). Diversity indices among fertilized plots were compared with control plots using Shannon diversity t test ($p<0.05$). All tests (soil and woody vegetation) were performed using the statistical software PAST (Paleontological Statistics Software Package for Education and Data Analysis, UK).

18.3 Results

Nitrogen, P and NP plots showed lower soil pH values (water and $CaCl_2$) than those observed in control plots in the top 30 cm. Total soil N did not differ between fertilized and unfertilized plots, but available P concentrations were significantly higher in the P and NP plots at all depths. N and NP plots had higher exchangeable Al in comparison to control plots (all depths in NP plots and in the first 30 cm in N plots). Soil pH values (water and $CaCl_2$) increased with depth in all treatments, while total N, P and exchangeable Al showed the inverse pattern (Fig. 18.1).

Relative to species diversity, 479 individuals of 47 species belonging to 29 families were sampled in control plots, 461 individuals belonging to 53 species and 34 families in N plots, 448 individuals from 54 species and 31 families in P plots and 336 individuals of 40 species belonging to 24 families in NP plots. Nitrogen and NP plots showed lower Shannon diversity (H′) and evenness (J′) indices compared to control plots (Table 18.1). Sørensen floristic similarity index was high among fertilized and unfertilized plots, decreasing in P plots (0.81) to N plots (0.78) and NP plots (0.76). *R. montana* (Proteaceae) had the highest absolute density in N, P and NP plots, and in control plots while *B. salicifolius* (Myrtaceae) (34.9) presented the highest importance value, with 26.2% of relative dominance. *B. salicifolius* (39.05) and *R. montana* (22.89) were the most important species in N plots. In P plots, the most important species were *R. montana* (27.35) and *C. brasiliense* (Caryocaraceae) (17.22), and the most dominant were *C. brasiliense* (12.02%) and *R. montana* (9.48%). *B. salicifolius* (56.73) and *R. montana* (30.0) were the most important species in NP plots, and *B. salicifolius*, the most dominant (44.59%).

Table 18.1 Density, richness, number of genus and families, Shannon's diversity index (H′), Pielou's eveness index (J′) of the shrub-tree flora in fertilized (+N, +P, +NP) and unfertilized (C) plots in a cerrado *sensu stricto* of Brasília—Brazil. *Indicates significant differences with control plots (Diversity t-test, $p<0.05$)

Treatment	Density	Richness	Genus	Families	Shannon (H′)	Pielou (J′)
C	479	47	38	29	3.40	0.88
+N	461	53	43	34	3.20*	0.80
+P	448	54	41	31	3.39	0.85
+NP	336	40	34	24	2.89*	0.78

18.4 Discussion

Species with greater ability to grow and establish under high nutrient availability conditions and lower susceptibility to disturbance (in this case, the occurrence of fire in 2005), had a greater competitive advantage. In fertilized plots, the dominant mature, established species responded to fertilization by increasing their dominance (*B. salicifolius*) and regenerating species with increased recruitment and abundance (*R. montana*), changing the community composition relative to control plots. These composition changes implied a decrease in evenness and diversity, especially in the N and NP plots, where P and Al availability and pH values were significantly different. Soil acidification and increased Al concentration is common under ammonium sulphate addition and is considered a key mechanism in plant diversity loss in several ecosystems (Bobbink et al. 2010). Comparing our results with earlier studies in the same area (Kozovits et al. 2007; Saraceno 2006), fertilization changed pH and P availability in deeper soil layers, on the other hand, total N decreased in the surface layer, but increased with depth.

Species density decreased, especially in NP plots, where we also observed lower richness. Changes in N and NP plot densities and dominance patterns led to a lower resemblance to the unfertilized control plots. Moreover, in these plots, *R. montana* increased its density ~2-fold and, despite the similar density, *B. salicifolius* increased in relative dominance with respect to control plots. The increase in herbaceous layer biomass and increase in exotic grass invasive potential is common in many ecosystems where N availability is increased (Bobbink et al. 2010). *R. montana* significantly increases its' height in competition with the exotic grass *M. minutiflora* (Poaceae) (Hoffmann and Haridasan 2008) and increases vegetative reproduction rates after fire (Hoffmann 1998). *R. Montana*'s importance in the N and NP community can be explained by its high post-fire regenerative capacity by increasing height and vegetative reproduction rates (Hoffmann and Solbrig 2003). Moreover, species of Proteaceae family are associated with proteoid roots, which facilitate the uptake of P forms, not available forms to other species (Watt and Evans 1999; Turner 2008). Other studies showed that *B. salicifolius* is associated with plant communities in nutrients rich soils (Proença and Gibbs 1994) which might explain its increasing dominance under higher nutrient availability. However, observed changes in this study can be dynamic on a larger time scale as the relationship between adaptive strategies, competitive ability, composition and diversity have different rates of change over time. These results suggest that nutrient enrichment changes diversity and abundance patterns due to differences in individual species responses to fertilization. Simultaneous NP addition effects on density, dominance, richness and diversity patterns were more significant than those observed for N or P on their own. However, fertilization effects on diversity can be also influenced by other variables such as interaction with the herbaceous layer.

18.5 Conclusions

Our results indicated that nutrient addition decreased soil pH and increased exchangeable Al concentrations (N and NP plots) and increased available P concentrations (P and NP plots). Species richness was lower in NP plots, and N addition plots (single or combined) showed lower evenness and species diversity relative to control plots. Changes in species diversity were more intense in combined NP addition plots.

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Chapter 19
Model Predictions of Effects of Different Climate Change Scenarios on Species Diversity with or without Management Intervention, Repeated Thinning, for a Site in Central European Russia

Larisa G. Khanina, Maxim V. Bobrovsky, Alexander S. Komarov, Vladimir N. Shanin and Sergey S. Bykhovets

Abstract The EFIMOD-ROMUL soil-vegetation dynamic model of carbon and nitrogen cycles in forest ecosystems and a static ground vegetation model BioCalc were used for simulating the dynamics of forest ecosystem parameters and prognosis of plant species biodiversity under two management and two climate change scenarios. A large forested area occupying approximately 1,800 km^2 on the Central Russian Plain (in Kostroma administrative region) was taken as a case study. Natural forest development (forest reservation) and clear cutting regime were taken as the management scenarios. The most dramatic climate change based on HadCM3 model and A1Fi emission scenario and 'stationary climate' were taken as the climatic scenarios. The simulation results showed that clear cutting impacts on forest biodiversity are very strong in the study area and climate warming has minimal effect on biodiversity under the clear cutting regime but climate changes lead to a slight decrease in species diversity under the forest natural development.

Keywords BioCalc • Boreal forest • EFIMOD • Ground vegetation diversity • Plant functional groups

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19.1 Introduction

Forest understory vegetation can provide important information on forest biodiversity and ecosystem function. Some European soil-vegetation models used to predict plant species composition as a function of atmospheric deposition of nitrogen (N) and acidity have recently been reviewed (de Vries et al. 2010). The models SMART2 (-SUMO)-MOVE/NTM and MAGIC(-SUMO)-GBMOVE and ForSAFE-VEG were evaluated with respect to the effects of nitrogen deposition on plant species diversity.

The EFIMOD-ROMUL model system (Chertov et al. 2001; Komarov et al. 2003) is another soil-vegetation dynamic model of carbon and N cycles in forest ecosystems, while BioCalc (BIOdiversity CALCulator) is a static ground vegetation model describing plant species diversity based on the outputs of the EFIMOD (Khanina et al. 2007). A description of an approach to plant diversity estimation and prognosis realized in the BioCalc and an experience of a case study application are presented.

19.2 Case Study Area

Manturovsky forestry enterprise in Kostroma administrative region was selected for the case study. It is a large forested area with 21,637 stands (forest inventory compartments) occupying approximately 1,800 km^2 on the Central Russian Plain. The study area belongs to the Atlantic continental forest region of the temperate climatic zone defined as moderate continental with intensive atmospheric circulation and a strong seasonal cycle. Average monthly air temperatures of the warmest month (July) and of the coldest one (January) are 18.1 °C and −13.3 °C, respectively. Total annual precipitation is 620 mm. The area is located within flat and lightly undulating water-glacial sandy plains with large areas of waterlogged soils. Soils include podzols, podzolic, soddy-podzolic, pleats, and gleys.

The region belongs to the Southern Taiga forest zone. The vegetation is coniferous-broad-leaved forest dominated by Norway spruce (*Picea abies*), fir (*Abies sibirica*), and lime (*Tilia cordata*) in the overstory and boreal, nemoral, and nitrophilous herbaceous species and dwarf shrubs in the understory (Smirnova 2004). Intensive anthropogenic activity only began in the twentieth century due to the remoteness of the region from the big rivers and industrial centres. Clear cutting began there in 1930, and the cuttings have been very intensive and often accompanied by large fires. According to the forest inventory from 1997 (which was taken as input parameters for the simulations), forests with dominants of Scots pine (*Pinus sylvestris*), birch (*Betula* sp.), Norway spruce and aspen (*Populus tremula*) occupied 48, 36, 11 and 5 % of the simulated area, respectively. The stands were mainly mixed. Lime composed 8 % of the total tree stand biomass. The young stands (<40 years old) occupied 61 % of the simulated area, pre-mature stands (40–80 years old) occupied 35 %, and mature stands (older 80 years) cover 4 % of the area. All forest site classes (from extremely dry and poor to extremely wet and rich) were represented in the study area, but more than half of the area belongs to wet sites with poor and moderate soil fertility. Dwarf shrubs (*Vaccinium myrtillus*, *V. vitis-idaea*) and boreal and nemoral herbaceous species dominate the ground vegetation. Information on deadwood volume was practically absent in the inventory data.

19.3 Silvicultural and Climate Change Scenarios

The dynamics of ecosystem properties and biodiversity under the different climate change scenarios were estimated for two silvicultural scenarios: natural development (NAT) and clear cutting regime (LR). The influence of natural disturbances (e.g. fires, windfalls, plant pathogens) was not considered in these scenarios. The NAT scenario assumed that tree stands were conserved as a forest reserve without any silvicultural operations. The natural regeneration by seeds of the main tree species was modelled every 15 years, maintaining the specific proportions of the dominant tree species for each site class. The density after regeneration was 2,000 trees/ha. The LR scenario was authorized by Russian legislation clear cutting regime and assumed that tree stands were subject to four improvement fellings (at the stand age of 5, 10, 25, and 50), and then to clear cutting (at age of 80 years for birch and aspen, 100 years for spruce and lime, 120 years for pine, and 140 years for oak). The clear cutting included burning of the felling debris. An obligatory forest planting (10,000 trees/ha) was modelled the year following clear cutting. The proportion of tree species was the same as for the NAT scenario.

For the climate change simulations we used the set of climatic scenarios compiled by Mitchell et al. (2004) and available at the http://www.cru.uea.ac.uk/cru/data/hrg.htm. The scenarios set includes a gridded (0.5º x 0.5º) climatic dataset for the twentieth century, CRU TS 2.0 (a previous version of the dataset was detailed described by New et al. (2000)) and a set of climate change scenarios for the twenty-first century, TYN SC 2.0. The last is based on the simulation results from four Global Circulation Models (CGCM2, CSIRO Mark 2, HadCM3, and PCM) calculated for four greenhouse gases emission scenarios (A1Fi, A2, B1 and B2) taken from the IPCC Special Report on Emission Scenarios (IPCC 2000). A simplified technique of spatial and temporal interpolation (so called 'pattern scaling', Mitchell 2003) is used in TYN SC 2.0.

To estimate the maximum possible changes in ecosystem properties during the twenty-first century, we used two climatic scenarios for the simulations: 'most dramatic climate change' (_C) and 'stationary climate' (_S). Both scenarios were taken for the dataset grid box centered at 58º15′N, 44º45′E, which is the closest to the study area. In both cases the data from CRU TS 2.0 were used for the first three years of the simulations, because the simulation runs began from the first year after available forest inventory data, i.e., from 1998.

The _C scenario from 2001 to 2100 was based on HadCM3 model and A1Fi emission scenario. According to the scenario, average annual air temperature increased up to 10.2 °C at the end of twenty-first century (with an increment of 7.2 °C comparing with the climate norms of 3.0 °C for 1961–1990). Corresponding total changes in precipitation were not so significant. The total annual precipitation increased by 8 % for the most part owing to the increase of monthly totals in winter. The _S climatic scenario was compiled using the dataset CRU TS 2.0 from 1951 to 2000. It was repeated several times for the simulations (two times for the twenty-first century or four times for 200-year simulation span). The _S scenario was closer in average to the "standard" of 1961–1990 during the whole simulation span.

Thus, for the study area, we simulated four scenarios: (a) 200-year forest natural development under the stationary climatic scenario (NAT_S); (b) 103-year forest natural development under the most dramatic climate change scenario (NAT_C); (c) 200-year forest development with clear cuttings under the stationary climatic scenario (LR_S), and (d) 103-year forest development with clear cuttings under the most dramatic climate change scenario (LR_C).

19.4 EFIMOD Description

In our study, the EFIMOD model of the forest-soil system (Chertov et al. 1999; Komarov et al. 2003) has been used for simulating the dynamics of forest ecosystem parameters. The EFIMOD consists of the individual-based forest growth sub-model, the soil sub-model ROMUL (Chertov et al. 2001), and the soil climate sub-model SCLISS (Bykhovets and Komarov 2002). The forest growth sub-model describes tree-population-level dynamics consisting of a set of separate trees competing for light and soil nutrition with its nearest neighbour trees. The individual-based approach makes it possible to trace the population-based mechanisms of forest stand development (tree competition, tree mortality, etc.) and to assess the effects of various forestry practices (tree planting, cutting, etc.) on ecosystem and forest stand properties. The soil sub-model, ROMUL, being embedded into EFIMOD calculates the rate of tree litter and soil organic matter mineralization and humification and the corresponding release of carbon dioxide. It describes the decomposition of different components of litter fall (woody parts, roots, and leaves) in relation to soil temperature, moisture, N and ash contents in the litter fractions. ROMUL returns available N for plant growth accomplishing a feedback to the forest sub model. Soil temperature and moisture are the outputs of soil climate sub-model SCLISS which generates forest floor and soil temperature and moisture using long-term average meteorological data at monthly resolution. EFIMOD is not suitable for peaty soils and for extremely wet conditions due to not taking into account the anaerobic soil processes and the absence of special carbon pool of peat, which has specific dynamics.

To simulate forest ecosystem dynamics, the input data of the model system are as follows: (1) tree species composition and age structure of the stand, (2) the main dendrometric parameters (mean stand height, diameter at breast height) of each forest element (even-aged pure tree cohort), (3) trees (number per hectare), (4) deadwood (tons per hectare), (5) carbon and N pools in organic horizon and mineral soil, (6) monthly mean air temperature and precipitation sum, and (7) forest management scenarios. The first four parameters were taken from forest inventory data. Soil characteristics were taken from special database which has been collected from published data for each site class (Komarov 2007). Climatic data and forest management scenarios were taken from the described above two climatic and two management scenarios. The model outputs for every annual time step are as follows: (a) tree species composition, (b) dendrometric parameters of each forest element, (c) deadwood, (d) pools of carbon and N in the stand and soil, (e) Net Primary Production (NPP), and (f) CO_2 emission.

To simplify the calculations, the case study forest inventory data were generalized: they were grouped in relation to stand dominants, the dominant age group and forest site class; the area-weighted average values were recalculated for each input parameter according to the procedure described (Shanin et al. 2011). 194 'virtual' forest units were derived from 21,637 forest inventory compartments. Extremely wet forest sites were excluded from the simulation and residual 116 forest units were used for the modelling.

19.5 BioCalc Description

A static ground vegetation model BioCalc has been used for prognosis of biodiversity in the case study. A model BioCalc forecasts dynamics of ecosystem and plant species understory diversity for each forest unit along the EFIMOD simulation outputs on a base of standard forest inventory data linked with the results of detailed phytosociological research as it was described by Khanina et al. (2007). Ecosystem diversity is estimated by a number of forest types. The forest type is defined for each forest unit as a combination of a dominant tree species in the overstory and a dominant functional species group in the understory. The functional groups are presented by the ecological-phytocoenotic species groups which are available online (http://www.impb.ru/index.php?id=div/lce/ecg&lang=eng). Species diversity is estimated for each forest unit in the ranks of species richness which is calculated for the forest types from the phytosociological relevés as an average number of plant species per square unit.

The input data for the BioCalc included: (a) time series tables of stand-level forest ecosystem parameters as the results of the EFIMOD runs reflected dynamics of current forest units under two silvicultural and two climate change scenarios; (b) the correspondence table between the ecological-coenotic forest types and the ranks of plant species richness calculated from the FORUS database (Smirnova et al. 2006), and (c) the rules for changing the dominant ecological-coenotic group in ground vegetation in dependence on simulated outputs in the time series tables. The rules were composed according to the results of previous vegetation and soil investigations in the study area (Braslavskaya and Tikhonova 2006; Lugovaya 2008;

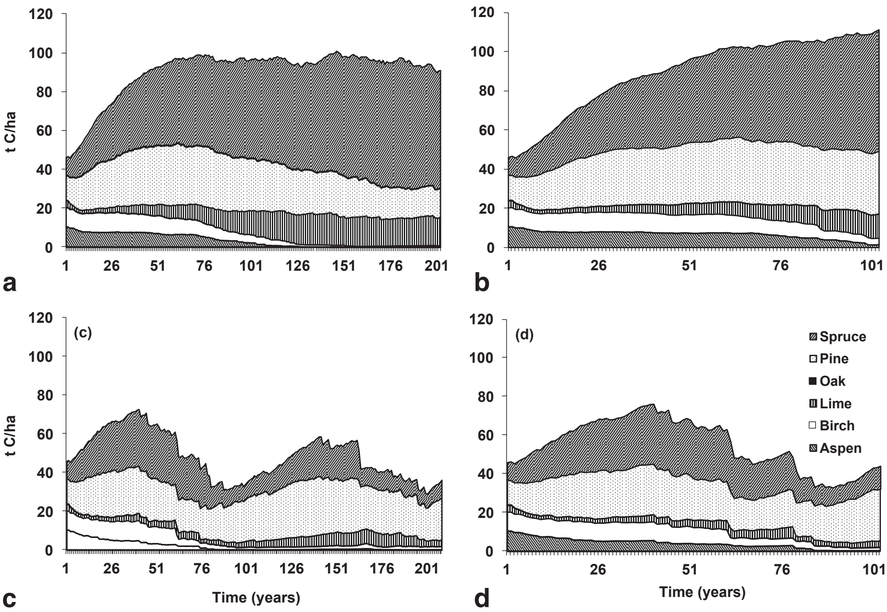

Fig. 19.1 Carbon dynamics in different tree species according to simulation results: (**a**) NAT_S, (**b**) NAT_C, (**c**) LR_S, (**d**) LR_C scenarios

Bobrovsky 2010) assuming that there were seeds of all plant species from the regional species pool. Note that any dynamic model output parameter can be used in the BioCalc for the changing dominant functional groups in ground vegetation. For the case study, we used tree dominants and deadwood volume, because these parameters define a structure of forest ecosystems on which depends species diversity as a whole (Scheller and Mladenoff 2002; Smirnova 2004). Output data of the BioCalc were time series tables and graphics of the following parameters: (i) ground vegetation functional groups, (ii) forest types, and (iii) ranks of species diversity.

19.6 Results

Simulated dynamics of the estimated parameters under two forest management regimes and two climate change scenarios are presented in the Figs. 19.1, 19.2, 19.3 and 19.4. At the NAT_S scenario, the birch, aspen and partly pine stands were gradually replaced by spruce and lime stands: the uneven-aged coniferous-broad-leaved forests with a large pool of deadwood and dominated by boreal, nemoral, and nitrophilous species in ground vegetation prevailed at the end of NAT_S scenario (Figs. 19.1a, 19.2a, 19.3). Simulated results on dynamics of all parameters under the NAT_C scenario were very similar to the results under the NAT_S scenario, but the

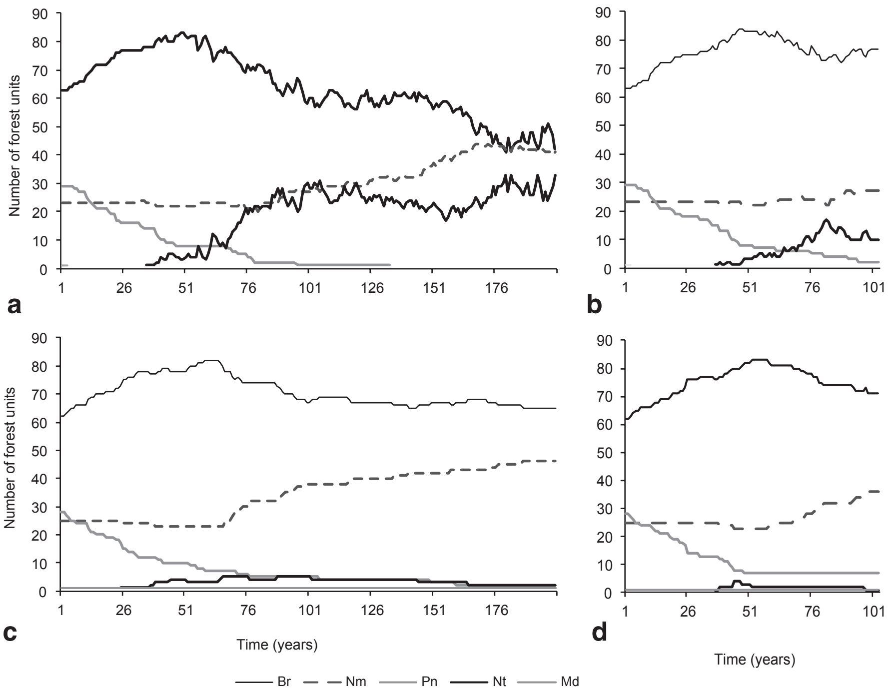

Fig. 19.2 Dynamics of the dominant ecological-phytocoenotic groups in ground vegetation according to results of simulations: (**a**) NAT_S, (**b**) NAT_C, (**c**) LR_S, (**d**) LR_C scenarios. *Br* boreal, *Nm* nemoral, *Pn* piny, *Nt* nitrophilous, and *Md* meadow groups

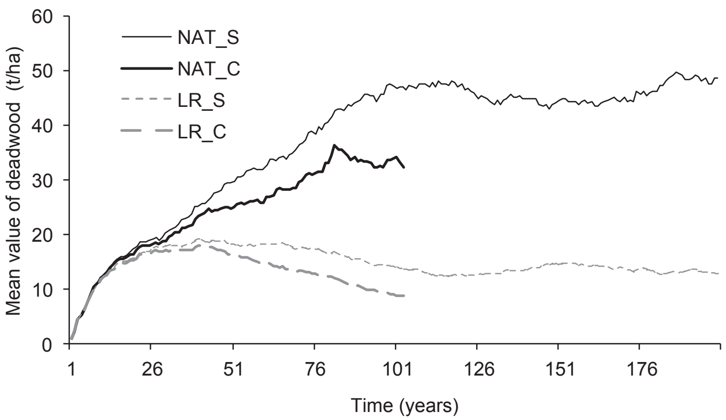

Fig. 19.3 Dynamics of deadwood pool according to results of simulations

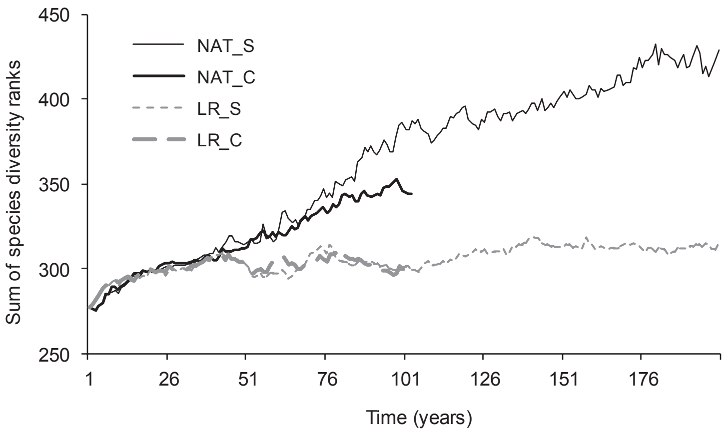

Fig. 19.4 Dynamics of species diversity ranks according to results of simulations

stand biomass was greater by 15 %, the deadwood volume was lower by 30 % than the same parameters under the NAT_S scenario, and the relatively lower proportion of nitrophilous and nemoral units together with the relatively higher proportion of boreal units were observed under the climate change (Figs. 19.1b, 19.2b, 19.3). The LR_S and LR_C scenarios led to a predominance of pine forests at the study area with a sharp oscillation of the tree species biomass due to thinning and clear cutting (Figs. 19.1c, 19.1d). Pools of deadwood were approximately four times lower than the pools observed under the NAT_S and NAT_C scenarios. The total stand biomass at the LR_C scenario was greater by 17 % and the mean deadwood volume was lower by 40 % than the same parameters under the LR_S scenario. The dynamics of the ground vegetation composition under the LR_S and LR_C scenarios was much more similar (Figs. 19.2c, 19.2d). Up to the 50th step, the dynamics were similar to the dynamics under the NAT_S and NAT_C scenarios, but then the nitrophilous units were practically lacking and a portion of the boreal units was slightly higher in the 'cutting' scenarios in comparison with the 'natural' scenarios. The difference between LR_S and LR_C scenarios in the ground vegetation composition was less than 2.7 %.

Dynamics of ecosystem and species diversity was estimated by the dynamics of the forest types. At the beginning of the simulations, there were 13 forest types in the study area, but 85 % of the area was occupied by species poor pine, birch, and aspen forests dominated by pine and boreal groups in the ground vegetation. Under the NAT_S and NAT_C scenarios, the number of forest types decreased gradually (to 12 and 8 forest types at 103rd and 200th steps, respectively), but species rich coniferous-broad-leaved forests began to prevail in the area and the total sum of species diversity ranks increased significantly (Fig. 19.4). Regimes with cuttings supported practically the present level of ecosystem and species diversity, which were practically equal to each other in the LR_S and LR_C scenarios and were slightly higher than the initial level.

19.7 Conclusion

The simulation results showed that clear cutting impacts on forest biodiversity are very strong in the study area and climate warming has minimal effect on biodiversity under the clear cutting regime but climate changes lead to a light decrease in species diversity under the forest natural development. Management regimes with cuttings can support a higher level of ecosystem diversity in the study area in comparison with the level observed with the natural development strategy. However, the protective regime leads to the highest species diversity in ground vegetation due to the development of species-rich coniferous-broad-leaved forests dominated by spruce and lime in the overstory and nitrophilous, nemoral and boreal groups in the understory.

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Chapter 20
Seasonal Changes in Photosynthetic Nitrogen of Tree Species Differing in Leaf Phenology in a South-eastern Brazilian Savanna

Sabrina R. Latansio-Aidar, Luciana D. Colleta, Jean P. H. B. Ometto and Marcos P. M. Aidar

Abstract Dominant tree species from a south-eastern Brazilian savanna showing different leaf phenologies (evergreen, semi-deciduous and deciduous) were characterized regarding photosynthetic potential (A), leaf nitrogen content (% N), specific leaf area (SLA), photosynthetic nitrogen (PN) and photosynthetic nitrogen use efficiency (PNUE). The ecophysiological traits evaluated seasonally (dry and wet season) characterized a gradient of strategies among three species: the evergreen species that dominates lower strata, showed low % N, SLA, Amax and Amass and high PNUE; the semi-deciduous species that dominates intermediate strata, showed medium leaf nitrogen and SLA and high Amax, Amass and PNUE; the deciduous species that dominates the canopy, showed high leaf N, SLA, Amax and Amass and low PNUE. Non deciduous species invested relatively more nitrogen in photosynthesis during the wet season, while the deciduous species maintained higher PN in the dry season. Photosynthetic N and PNUE appear to be the key to a better understanding of the relations among leaf traits, N content and photosynthetic potential in species with different leaf phenologies and subjected to climatic seasonality.

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20.1 Introduction

The Brazilian Savanna (Cerrado) is one of the richest and most threatened tropical savannas in the world and is considered to be a hotspot for biodiversity conservation (Myers et al. 2000). The Cerrado biome in Brazil covers 2 million km^2 representing 23 % of the country's area (Ratter et al. 1997). Savanna ecosystems are primarily controlled by the interactions between water and nutrient availability (Medina 1987) with a high influence of seasonality (Nardoto and Bustamante 2003). The basic environmental structure can be modified by changes in fire frequency and land-use (Bustamante et al. 2006). Despite the conversion of the native Cerrado in the recent decades to more intensive land use, few studies have focused on increasing the understanding of the Cerrado ecosystem functioning.

The impact of climatic seasonality on leaf phenology was well documented in the early 1990s. However, the response of trees, particularly trees differing in leaf phenology, to seasonal drought has barely received attention latterly (Eamus et al. 1999). This kind of study is important mainly due to three reasons: as part of climate change research, knowledge of the seasonality of tree behaviour is required to estimate annual carbon (C) fluxes in relation to seasonally dry ecosystems; to manage water resources in such ecosystems; and a complete understanding of any ecosystem can be attained only if the annual cycle is well studied (Eamus et al. 1999).

Phoenix et al. (2006) report substantial increases in nitrogen (N) deposition rates across the tropics over recent decades, as a consequence of fossil-fuel combustion and fertilizer use (Matson et al. 1999). The deposition over Brazilian Atlantic Coast (Galloway et al. 2004), including the Cerrado hotspot has been well documented (Phoenix et al. 2006). Lewis et al. (2004) highlighted several climatic change forces that can act together to modify the forested ecosystems around the world, including increasing CO_2 and N deposition, which can promote growth depending on water availability and temperature. But studies on how C and N will possibly interact and on the influence of vegetation on C and N cycles in savanna ecosystem remain scarce (Eamus et al. 1999). In this context, understanding the assimilation of N and C is pivotal to clarifying these interactions, and photosynthesis is one of the most important physiological processes where these elements interact in plants.

Shipley et al. (2006) showed a unique link between most of the covariation in some leaf traits, across a wide range of environmental conditions and taxonomic groups, such as maximum net photosynthetic rate (Amax), leaf respiration (Rd), leaf N concentration, specific leaf area (SLA), leaf dry matter and leaf life span (LL). Together, this set of leaf traits has been called the 'worldwide leaf economics spectrum' (LES) as defined by Wright et al. (2004), because this correlated suite of traits reflects the trade-off between the rapid acquisition of resources and the conservation of captured resources (Marino et al. 2010). The average values of these traits change predictably along major environmental gradients, but the patterns of covariation are largely (but not completely) unaffected (Marino et al. 2010). Leaf photosynthetic capacity is generally well correlated with leaf N content, but some variations between species occur, and are mainly related to specific leaf area (SLA), i.e. the projected leaf area per unit leaf dry mass (Harrison et al. 2009). In the present study we evaluate the seasonal dynamics of some of the leaf traits involved in the LES and analyze how they interact with N investment into photosynthetic apparatus in dominant tree species belonging to three different phenological groups occurring in a south-eastern Brazilian Savanna.

20.2 Material and Methods

20.2.1 Study Area and Species

The study area, known as Pé-de-gigante, is located in a Brazilian Savanna (Cerrado) over Red-Yellow Latosol (Pivello et al. 1998) inside the Vassununga State Park, Sao Paulo State, south-eastern Brazil, (21° 36–38'S, 47° 36–39'W; 590–740 m above sea level;1,225 ha), under a Cwag climate (Köppen 1948). A more detailed characterization of the study area can be found in Pivello et al. (1998, 1999). The species were chosen based on a previous phytossociological study (Latansio-Aidar et al. 2010), which identified and characterized the most important species in the area: *Anadenanthera falcata* (Leguminosae-Mimosoideae), a deciduous species; *Xylopia aromatica* (Annonaceae), a semi-deciduous species; and *Myrcia lingua* (Myrtaceae), an evergreen species.

20.2.2 Gas Exchange Measurements

Net photosynthesis and stomatal conductance were measured simultaneously using a portable photosynthesis analyzer system (Li-6200, LiCor Inc, Lincoln, NE, USA). Light and CO_2 response curves were made in leaves under controlled air temperature (25 °C), light and CO_2, a flow rate of 500 mmol s^{-1} and the relative humidity of air entering the leaf chamber maintained between 70 and 80 %. All measurements were performed from 07.00 to 11.00 h local time during late summer and winter in 2006. Photosynthetic rates were measured in ten fully expanded leaves of each species, ten individuals per species. Immediately after the gas-exchange measurements, each leaf was harvested, taken to the laboratory, and its area, dry mass and N concentration determined. From the data obtained, we calculated specific leaf area (SLA), leaf N content per unit mass (% N), net CO_2 assimilation per unit leaf area and mass (Aarea and Amass), instantaneous photosynthetic nitrogen (PN) and photosynthetic nitrogen-use efficiency (PNUE).

20.2.3 Leaf Analysis

Fresh leaf areas were measured using Leaf Area Measurement software (Version 1.3). Leaves were oven-dried at 65 °C to get the dry mass, then grounded separately in a ball mill to a fine powder and a 1.5–2 mg sub-sample were placed and sealed in a tin capsule and loaded into a ThermoQuest-Finnigan Delta Plus isotope ratio mass spectrometer (Finnigan-MAT; CA, USA) in line with an Elemental Analyzer (Carlo Erba model 1110; Milan, Italy) as described by Stewart et al. (1995). Light curves were fitted with a non-rectangular hyperbola and Rubisco activity was calculated according to Sharkey et al. (2007). The fraction of leaf N allocated to Rubisco or PN was inferred from the relationship between photosynthetic rate per unit leaf N and SLA according to von Caemmerer et al. (1994) using data from CO_2curves. Photosynthetic rate per unit N or Photosynthetic nitrogen-use efficiency [PNUE [μmol CO_2 mol^{-1} N s^{-1}] was calculated dividing the CO_2 assimilation rate per unit mass by the N content per unit leaf mass (Sharkey et al. 2007).

20.2.4 Statistics

The averaged data were analysed using the software packages Origin 5.0 (Microcal Software Corp., Northampton, MA, USA) and Winstat (R. Fitch Software, Cambridge, MA, USA, 2001).

20.3 Results

Figure 20.1a shows that the maximum photosynthetic rates based on area (Aarea) do not statistically differ between species neither in the wet, nor in the dry season, however the rates decreased in the dry season to more than half of the wet season values. By contrast, photosynthetic rates based on mass (Amass), shown in Fig. 20.1b, are clearly higher in the wet season for the semi-deciduous species, followed by the deciduous species and evergreen species. In the dry season, values were higher in the deciduous species, followed by the semi-deciduous and evergreen species. All species presented a decrease in photosynthetic rates in the dry season.

In the semi-deciduous and evergreen species, SLA did not change from the wet to the dry season, and the deciduous species presented a rise in this parameter due to the decrease in leaf mass, typical of deciduous species in senescence period (Fig. 20.1c). Decreases in N invested in photosynthesis (PN) were observed in the evergreen and semi-deciduous species from the wet to the dry season (Fig. 20.1d):

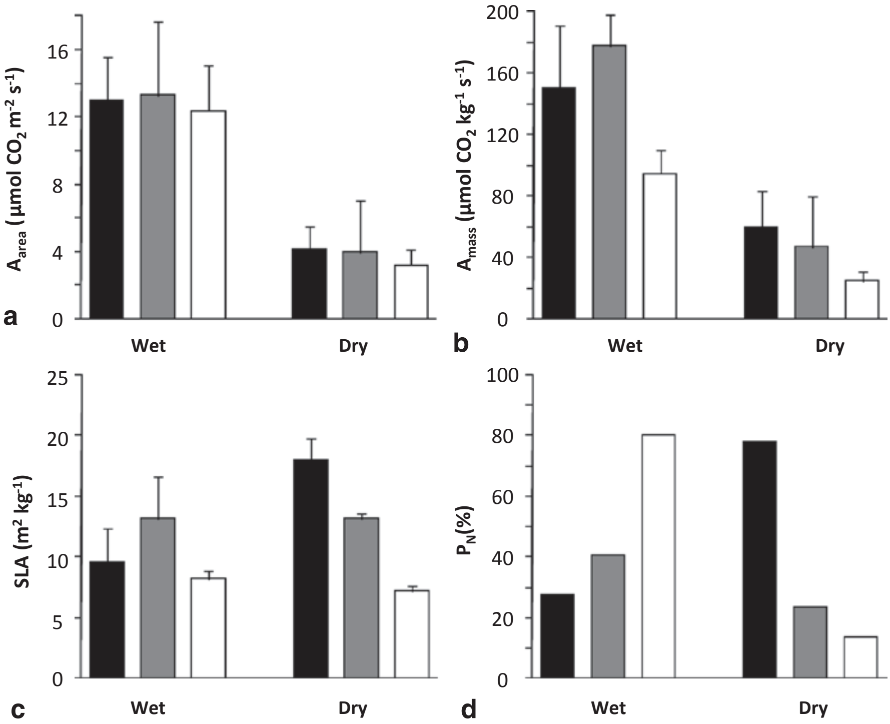

Fig. 20.1 **a** Photosynthetic rate per leaf area (A_{max}, µmol CO_2 m^2 s^{-1}). **b** photosynthetic rate per leaf mass (A_{mass}, µmol CO_2 kg^{-1} s^{-1}). **c** specific leaf area (SLA, m^2 kg^{-1}) and **d** photosynthetic leaf nitrogen (P_N, %) in the wet and dry season of the phenological groups studied in the Brazilian Savanna. Dark bars represent the deciduous species *Anadenanthera falcata*; *grey bars* represent the semi-deciduous species *Xylopia aromatica*; and *open bars* represent the evergreen species *Myrcia lingua*. *Error bars* denote one standard error of the mean

X. aromatica PN reduced from 40 to 24 % of total leaf N, and *M. lingua* PN reduced from 80 to 14 %, following a slight decrease in % N. By contrast, the deciduous species presented an increase in PN amount, rising from 27 % in the wet season to 78 % in the dry season but % N fell substantially between seasons (Table 20.1).

The PNUE value was lower in the deciduous species and higher in the semi-deciduous species in the wet season. The tendency was reversed in the dry season on the deciduous species that presented higher values just before leaf shedding, when compared with the other species (Table 20.1).

Based on the phenological and ecophysiological traits, it was possible to characterize a gradient of strategies among species: the evergreen species *M. lingua* dominating the lower strata, showing low SLA, N content, Amax and Amass; the semi-deciduous species *X. aromatica* dominating the intermediate strata, and showing intermediate SLA and N content and high Amax and Amass; the deciduous species *A. falcata* dominating the canopy and showing high SLA, Amax and Amass.

Table 20.1 Total leaf nitrogen content per leaf mass (% N) and photosynthetic nitrogen-use efficiency [PNUE [μmol CO_2 (mol N)$^{-1}$ s^{-1}]] of the phenological groups studied in the Pé-de-Gigante Brazilian savanna: evergreen species *Myrcia lingua*, semi-deciduous species *Xylopia aromatica* and deciduous species *Anadenanthera falcate*

	Evergreen	Semi-deciduous	Deciduous
% N			
Summer	1.47	2.34	2.47
Winter	1.23	2.19	2.07
PNUE μmol CO_2 (mol N)$^{-1}$ s^{-1}			
Summer	64.48	75.97	61.03
Winter	20.23	21.48	28.71

20.4 Discussion

The results indicate that semi-deciduous and evergreen species invested more nitrogen in photosynthesis in the summer, in agreement with higher photosynthetic assimilation in this season, but they did not change SLA. The increased investment in PN in the winter observed in the deciduous species, even with the lower Amass, suggests that, in spite of the absolute decrease in total leaf N, the remobilization of compounds (including N compounds) preceding senescence, somewhat preserved PN from being withdrawn before leaves started to fall. This result supports the world pattern found by Wright et al. (2004) when describing the LES: deciduous species have high Amass rates, SLA, % N and low LL. Here we have showed that the deciduous species retain some leaf N as PN goes up until leaf abscission.

According to Harrison et al. (2009) PN tends to decrease as SLA decreases because a smaller SLA is associated with greater leaf longevity. Field and Mooney (1986) suggested that there is maybe a trade-off between investing N in photosynthetic proteins such as ribulose1,5-bisphosphate carboxylase/oxygenase (Rubisco) versus compounds required for longevity (Harrison et al. 2009). Our study shows that this relation between PN and SLA is true for the deciduous species but not applicable to the semi-deciduous and evergreen species, which showed similar SLA in both seasons and decreased PN in the dry season, suggesting N reallocation to other functions than photosynthesis, probably to maintain the leaf structure during the dry season, investing in leaf anatomy to protect against water loss. This hypothesis is plausible if we consider the need to cope with water loss imposed by seasonality changes. A study conducted in the same area by Coletta et al. (2009) found that the seasonality of water availability plays a major role in N uptake.

Harrison et al. (2009) found no trade-off between N associated with cell walls and the N allocated to ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco) and variation in PNUE could not be explained by variation in cell wall N. But the comparison between evergreen and deciduous *Quercus* species (Takashima et al. 2004) revealed a clear trade-off between N invested in Rubisco and cell wall proteins. Leaves from evergreen *Quercus* had greater leaf mass per unit area (LMA, the reciprocal of SLA) and allocated a greater proportion of leaf N to cell wall protein than leaves from deciduous *Quercus*. Onoda et al. (2004) studying leaves of *Polygonum cuspidatum* also found a greater proportion of leaf N allocated to cell walls as LMA increased. Ellsworth et al. (2004) calculated that the proportion of N allocated to Rubisco declined as LMA increased in 16 species with LMA ranging from 50 to 300 g m^{-2}. They suggested that this was related to the need for greater investment in structural N. Clearly, there is a need for more data on cell wall N. Still, our results suggest that the semi-deciduous and evergreen species are probably allocating N in the dry season to processes other than photosynthesis. However, we cannot be sure at this time, that investing more N on cell walls, for improvements in leaf structure, is an adaptation to surviving throughout the dry season and low water availability, even with no changes in SLA or total leaf N between the seasons. Further data are needed for a better understanding on the relations among leaf phenology, leaf N content, PNUE and PN in tree species from the Brazilian Savanna.

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Chapter 21
Atmospheric Nitrogen Deposition can Provide Supplementary Fertilization to Sugar Cane Crops in Venezuela

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Abstract Acidic rain, loaded with ammonium is characteristic of Central Northern Venezuela, a region dominated by sugarcane plantations. Nitrogen (N) inputs in precipitation are crucial to the N economy of natural ecosystems; in agro-systems these inputs are of less importance. However, in some polluted areas, atmospheric deposition loaded with N as a consequence of industrial and agricultural activities can contribute significantly to crop nutrition. The N and other nutrients present in both precipitation and dry deposition can originate from a variety of natural and anthropogenic sources, including air pollution. Canopies of forest and agricultural crops can modify the chemistry of rainfall in different ways: through uptake, leaching and removal of ions from the canopy in throughfall. In this contribution we analyzed the chemical changes in N enriched acid rain as it passed through a sugarcane canopy. The study site was located on a sugarcane farm near San Felipe, Yaracuy state, Venezuela. Four plots of 300 m^2 within an experimental area of 4.5 ha, planted with *Saccharum officinarum* had rain and throughfall collectors installed. The study corresponds to the analysis of the second and third ratoons of two sugarcane varieties. Rain water was quite acidic ranging from 3.54 to 4.52, a situation that is common in Northern Central Venezuela as a consequence of the high industrial and agricultural activities. The pH of the acid rain in the sugar cane system

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increased after passing through the canopy. The magnitudes of the changes were important and related to the significant amount of cations leached from the leaves or washed out from dry deposition to the leaves and cane stems. Ammonium was the dominant N form in wet deposition. N inputs for wet and dry deposition in the agro-system were high compared with other ecosystems (26.3 kg ha^{-1} $year^{-1}$, mostly in the ammonium form). This is probably due to: the high agricultural activity in the area, the local burning of the sugarcane before cropping, and the location of the experimental area close to petrochemical industrial activities and fertilizer producer industries. Although nitrates were leached and wash out in throughfall, the balance accounted for a significant N fertilization of the canopy through ammonium uptake.

Keywords Nitrogen requirements • Nutrient inputs • Pollution • Prescribed fire • Throughfall inputs

21.1 Introduction

Acidic rains enriched with ammonium are characteristic of Central Northern Venezuela, a region currently supporting sugarcane plantations where significant agricultural and industrial activities take place.

Nitrogen (N) inputs (ammonium and nitrate) in precipitation are considered of great importance in the N economy of natural ecosystems (López-Hernández et al. 2012); on the contrary, in agro-systems those inputs are of lesser importance when compared with the N requirements of crop production (Stevenson 1982; Thorburn et al. 2005). However, in some areas N enriched deposition, as a consequence of industrial and agricultural activities, can contribute a significant proportion to crop nutrition through foliar absorption.

The N and other nutrients present in precipitation and dry deposition can originate from a variety of natural and anthropogenic sources, including air pollution (Rodrigo et al. 2003). Canopies of forest and agricultural crops can modify the chemistry of rainfall in different ways: via uptake and retention of elements by the canopy, removal and leaching of ions or when the throughfall waters are enriched by the wash out of dry deposition to the canopy (Tukey 1970; Rodrigo et al. 2003; Perez–Marin and Menezes 2008). The magnitude of the foliar leaching depends on a variety of factors: plant age, physiological state, plant composition and canopy morphology, but also on the frequency, duration intensity and chemical composition of the rainwater. In polluted areas the actual composition of the washout depends on the contamination source (Rodrigo et al. 2003). This chapter describes the chemistry of the N enriched acid rain after passing through a sugarcane canopy. We hypothesized that because of the significant N-requirement of sugarcane, and the volume of its canopy (high biomass production), a large proportion of the N contained in the N enriched rain will be retained by the canopy.

21.2 Material and Methods

21.2.1 Study Site

The study site was located in a sugarcane farm near San Felipe, Yaracuy state, Central Venezuela (10°29′44′′N and 68°31′44′′W), the experimental site corresponds to a tropical humid climate region (1400–1700 mm of precipitation) affected by marine aerosols.

Four plots of 300 m^2 within an experimental area of 4.5 ha cropped with *Saccharum officinarum* were selected for the installation of rain and throughfall collectors. The study corresponds to the analysis of the second and third ratoons of two sugarcane varieties (Puerto Rico (PR) 1028 and Venezuela (V) 58–4). The soil is a Mollisols, Haplaquoll (fine loam, isohiperthermic, muscovite, montmorillonitic, kaolinitic) with a pH of 7.4, moderate to high effective cation exchange capacity (ECEC) and N content 0.1–0.2 %.

21.2.2 Collection of Rain and Stream Waters and Analysis

Bulk precipitation for chemical analysis was sampled during 1 year from five gauges located in the plots. Bulk precipitation (i.e. wet plus dry) was collected with plastic funnels (PVC polyvinyl chloride) attached 4.5 m above soil surface and above the sugar cane canopies. The funnels were connected to 2 l plastic bottles (PET, Polyethylene Terephtalate) which were first acid-washed and then rinsed with demineralized water. Throughfall waters were collected in twenty PVC funnels attached 0.3 m above soil surface within the canopies connected to PET bottle collectors. After one day of the collection, the samples were taken to the laboratory where pH was measured with a glass electrode. Water samples were then filtered through 0.45 µm pore size Millipore filters and phenyl mercury acetate (1 ml l^{-1}) was added as preservative. Rain and throughfall waters were analyzed individually and averaged for monthly inputs. Monthly element flux to the sugarcane ecosystem is taken as the product of monthly precipitation and/or throughfall volumes and the average chemical concentration.

Samples were rejected when contaminated by debris.

More details of the collectors for precipitation and throughfall waters are presented in Infante et al. (1993) and López-Hernández et al. (2005); the total precipitation measured was 1752 mm, whereas the water volume estimated from the throughfall was 1124 mm which corresponds to 64 % of the total precipitation.

Nitrate and ammonium in the waters were analyzed in a Technicon Auto Analyzer II.

Cations were analyzed by atomic absorption in a Varian Techtron AA6.

Table 21.1 Monthly average pH and sum of cation concentrations (μ eq l^{-1}) in bulk deposition and throughfall in a sugar cane agro-system

Month	pH Rain water	pH Throughfall	Σ cations Rain water	Σ cations Throughfall
April	4.52	5.50	227	138
May	3.70	5.26	177	105
June	3.97	4.99	209	271
July	3.97	4.90	156	145
August	4.22	5.45	83	134
September	3.67	5.20	113	225
October	3.54	4.50	66	198
November	4.12	5.76	126	210
December	4.20	5.29	103	251

Table 21.2 Monthly average of cations concentrations (μ eq l^{-1}) in bulk deposition (BD) and throughfall (T) in a sugarcane agro-system

Month	Na BD	Na T	K BD	K T	Mg BD	Mg T	Ca BD	Ca T
April	155	87	37	16	28	32	7	4
May	127	70	29	10	17	16	5	9
June	139	109	26	62	39	88	6	12
July	66	44	56	54	28	41	6	6
August	33	27	28	59	15	42	7	6
September	57	28	42	102	12	78	3	16
October	40	50	20	68	6	68	0	12
November	23	30	83	78	12	81	9	22
December	68	75	13	58	19	100	9	18

21.2.3 Statistical Analyses

Analyses were carried out with t-tests for paired samples on the difference between monthly concentration of NH_4-N in precipitation and throughfall waters.

21.3 Results and Discussion

Precipitation pH ranged from 3.54 to 4.52 (Table 21.1), a situation that is common in Northern Central Venezuela as a consequence of the high industrial (petrochemical and fertilizer production plants) and agricultural (crop fertilization and cattle rearing) activities (Lewis and Weibezahn 1981; Sequera et al. 1991). In the rest of Venezuela, even in the absence of anthropogenic influence, precipitation is still fairly acid (5.1–5.8, Montes et al. 1985; López-Hernández 2008). Data in Table 21.2 for cations (μ eq l^{-1}) includes monthly average values and followed the order Na > K > Mg > Ca, the dominance of Na in precipitation reflects the deposition of marine aerosols.

Table 21.3 Monthly average concentrations (mg L^{-1}) and monthly input (kg $ha^{-1}yr^{-1}$) of N-ammonium and N-nitrate in bulk deposition and throughfall in a sugar cane agro-system. Mean followed for different letters differ statistically $p<0.05$. n.d. not detectable

Month	$N\text{-}NO_3$ BD	$N\text{-}NO_3$ T	$N\text{-}NO_3$ T input	$N\text{-}NH_4$ BD	$N\text{-}NH_4$ BD input	$N\text{-}NH_4$ T	$N\text{-}NH_4$ T input
April	n.d.	0.19	0.31	0.52a	0.90	0.63a	1.04
May	n.d.	0.14	0.17	1.13a	1.74	1.10a	1.30
June	n.d.	0.28	0.05	3.08b	1.03	1.75a	0.32
July	n.d.	0.39	0.17	2.46b	2.75	1.05a	0.47
August	0.02	0.28	0.39	3.10b	7.17	1.09a	1.53
September	0.01	1.05	0.80	3.28b	4.80	1.00a	0.76
October	n.d.	0.38	0.50	1.06a	2.45	0.89a	1.18
November	n.d.	0.75	0.65	1.59b	1.82	0.70a	0.61
December	n.d.	0.40	1.10	0.71a	2.53	0.76a	2.09
Total	–	–	4.14	–	25.19	–	9.30

21.3.1 Changes in pH and Bases in the Throughfall Waters

The pH of the bulk precipitation in the sugar cane agro-system increased as it passed through the canopy (Table 21.1), the magnitude of the changes were important since it corresponded from 0.93 to1.64 pH units (Table 21.1). Those last results are in accordance with the significant amount of cations leached from the leaves or wash off from materials deposited on the leaves and cane stems (Table 21.2). Thus, throughfall waters were, in general, enriched in bases compared with bulk precipitation, particularly after the month of June (peak of the rain season) when the sum of base cations in the throughfall waters surpassed the values of the bulk precipitation (Table 21.1).

Similar information is presented by Rodrigo et al. (2003) for Mediterranean forests which receive African red rains responsible for most of the inputs of alkalinity and base cations in bulk deposition. However, the precipitations in the Mediterranean environment were more enriched in Ca and Mg compared with this tropical site. Pérez-Suárez et al. (2008) in two polluted forest sites in the México City air basin reported also a net positive throughfall deposition of Ca, Mg and K, where Perez-Marin and Menezes (2008) in an agroforestry system with *Gliricidia sepium* in the semi-arid northeastern Brazil reported important K inputs to the soil from the throughfall waters.

21.3.2 Changes in Nitrogen Forms

Ammonium was the dominant N form in bulk deposition with a mean value of 1.29 mg l^{-1} (Table 21.3); nitrate-N was not detectable in the majority of months.

The N inputs for wet and dry deposition in the agro-system were high compared with other ecosystems (26.3 kg ha^{-1} $year^{-1}$), mostly in the form of ammonium

(25.19 kg ha^{-1} $year^{-1}$, Table 21.3). This is probably due to the high agricultural activity in the area, the local burning of the sugarcane before cropping, and the closeness of the experimental area to petrochemical industrial activities and fertilizer production industries. In other Venezuelan sites, mineral N inputs in precipitation ranged from 2.2 kg N ha^{-1} $year^{-1}$ in savannas of Calabozo to 6.2 kg N ha^{-1} $year^{-1}$ in a predominantly rural community at Estación Experimental, La Iguana (López–Hernández et al. 2012). Similar precipitation inputs of N are presented for savannas of *Loudetia* located at comparable geographical latitude at Lamto, Ivory Coast, Africa (1.3–2.3 kg NO_3 ha^{-1} $year^{-1}$ and 3.0 kg NH_4 ha^{-1} $year^{-1}$) according to Villecourt and Roose (1978).

Although nitrates were leached (increased concentration in throughfall) (Table 21.3), the N balance indicated a substantial amount of ammonium uptake by the canopy, i.e. fertilization. Similarly, Pérez-Suárez et al. (2008) in two polluted forest sites in the México City air basin also found significant removal of nitrate and ammonium inferred from their lower concentrations in throughfall under fir and pine canopies. By contrast Rodrigo et al. (2003) for Mediterranean forests reported a much smaller annual removal of N, of 1.64 and 1.61 kg ha^{-1} $year^{-1}$ of NO_3 and NH_4, respectively, possibly reflecting temporal differences in rainfall, the volume of rain and morphological species traits, i.e. the potential for uptake and the species of trees (*Quercus ilex* L.).

21.3.3 Nitrogen Foliar Absorption and Nitrogen Requirement

Based on a detailed evaluation of the N budgets of the agro-system, López–Hernández et al. (2005) reported that major N export from the system include crop removal and loss of ash from post crop fires which account for 72 % of the annual N accumulation (210 kg ha^{-1} $year^{-1}$) in the aerial biomass. In general, the annual nitrogen budget derives from fertilization and bulk precipitation (235 kg ha^{-1} $year^{-1}$ + 26.3 kg ha^{-1} $year^{-1}$) and output through stem cropping (120 kg ha^{-1} $year^{-1}$) and N volatilization by fire (30.7 kg ha^{-1} $year^{-1}$), therefore the N input of rain water (26.3 kg ha^{-1} $year^{-1}$) represents around 12 % of the N requirement (226 kg ha^{-1} $year^{-1}$) for biomass production of the sugarcane plantation.

21.4 Conclusions

Ammonium, not nitrate is the main source of N in bulk precipitation for sugarcane crops. Approximately 12 % of the annual N balance is supplied by anthropogenic deposition of reactive N. This uptake was balanced by exchange with base cations leached from the canopy and some dry deposition of alkaline dusts.

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Chapter 22
Competition Alters Responses of Juvenile Woody Plants and Grasses to Nitrogen Addition in Brazilian Savanna (Cerrado)

Viviane T. Miranda, Mercedes M. C. Bustamante and Alessandra R. Kozovits

Abstract The Cerrado, Brazilian savanna, is characterized by high radiation and dystrophic soils. Seedlings of woody species must compete effectively for resources belowground in order to establish in the herbaceous matrix. Few studies focus on the dynamics of herbaceous and woody juvenile plants and their competitive strategies, especially under increasing nitrogen (N) availability. In the present study, seedlings of three woody species, *Eugenia dysenterica, Magonia pubescens* and *Enterolobium gummiferum* were grown with or without the dominant grass in Cerrado areas of central Brazil, *Echinolaena inflexa*. Half of the pots were exposed to N additions equivalent to a deposition of 20 kg N-NO_3NH_4 ha^{-1} $year^{-1}$. The N induced responses of plants growing under intra and interspecific competition were analyzed, with special attention to plasticity of root biomass and morphology. One year after the beginning of the experiment, the fresh and dry biomass of roots and shoots were weighted. Before drying, total length, surface area and diameter of roots were determined. Interspecific competition tended to reduce root and shoot biomass of all plants. However, effects of competition with *E. inflexa* were more obvious on root morphology, being total root and fine root length diminished in two of the woody species in the absence of N addition. The enhancement of N availability, in general, minimized the effects of competition, increasing the potential competitiveness of some woody species due to changes in total fine root length

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and biomass. The results provide indication that competition between saplings of woody plants and grasses could be an important factor driving plant allometry and morphology during the first stages of development in Cerrado environments. The responsiveness of plants to N deposition seemed to depend, in part, on the type of competition (intra- or interspecific), what should be taken into account in models of vegetation dynamics in response to nutrient deposition.

Keywords Native savannah plant species • Nitrogen deposition • Root morphology • Sapling growth • Woody plant and grass competition

22.1 Introduction

Savanna ecosystems are characterized by the coexistence of a shrub-tree layer and a grass layer. In Brazil, about 2,000,000 km^2 of land was originally occupied by the Brazilian savanna (Cerrado), although large areas have already been converted into pastures and agricultural fields. Integrated in the herbaceous matrix, seedlings of woody species must compete effectively for resources in order to establish. The Cerrados are characterized by high radiation and dystrophic soils. Below-ground competition for nutrients appears to play a major role in community structure compared with competition aboveground. Plasticity in root morphology and physiology might therefore be important traits, hitherto little researched in such ecosystems (Grams and Andersen 2007). Despite the obvious importance of the undergrowth layer in grassland areas of the Cerrado, few studies focus on the dynamics of herbaceous and woody juvenile plants and their competitive strategies. Changes in the distribution of these plant life forms due to differential responses to variations in nutrient availability might have several consequences that affect ecosystem function.

In the last century, native ecosystems have been involuntarily fertilized with nitrogen from atmospheric deposition. It is estimated that the deposition of nitrogen (N) has increased by about 4.5 times from 1843 to the present (Goulding et al. 1998), and will continue to rise due to the expansion of pasture and nitrogen-fixing crop legumes, increased use of N fertilizers, burning of plant biomass and industrial activities (Vitousek et al. 1997). The main N forms emitted by human activities (NO, N_2O, NH_3, NO_2) and their products of reaction (NH_4^+, NO_3^- and HNO_3) are highly mobile in the atmosphere and can be deposited hundreds of miles from their sources (Asman et al. 1998; Fabian et al. 2005). Thus, the dichotomy between anthropogenically altered ecosystems and wild areas, free of human influence, begins to fade.

The enhancement of N availability for vegetation can cause increases in N concentration in plant tissues and reduce C:N ratios, increase foliar N:P ratios, change biomass allocation to shoots or to storage organs, reduce scleromorphy features e.g. low specific leaf area and increase photosynthetic rates of all species (Harmens et al. 2000; Zak et al. 2000) and thus, alter the competitiveness of different species. In the northern hemisphere, changes in structure and composition of plant communities as a function of elevated atmospheric N deposition have been observed, with an increase in nitrophilous species at the expense of N sensitive species (Bobbink et al. 1998).

In an N addition experiment in native Brazilian savanna (Cerrado), grasses responded rapidly to fertilization, increasing their biomass, whereas dicotyledons did not respond to fertilization. Comparing different grasses, a C_3 species was favoured over diverse C_4 species (Luedemann 2001), especially under the combination of N and phosphorus (P) fertilization. Considering the tree layer, the increased N availability alone or in combination with P amendment led to higher stem relative growth rates (Simpson 2002), higher concentrations of leaf N, reduced N resorption rate during senescence and acceleration of leaf litter decomposition at the community level (Kozovits et al. 2007). However, the magnitude of these responses varied widely between species and there were no information about root responses. The consequences of long-term changes in the ecophysiology of individual species and of functional groups of plants to the structure and composition of the community of Cerrado are still unknown. It is especially unclear how the seedlings of woody species and grasses, coexisting in the understory layer, will respond to increased N availability, and how these responses will affect the relative competitive ability of these two plant functional groups.

The objective of this study was to evaluate N induced responses of juvenile woody plants and the dominant C_3 grass in Cerrado areas of central Brazil, growing under intra and interspecific competition. Special attention was given to responses involved in competition, in terms of root biomass and morphology.

22.2 Methodology

The experiment was conducted under greenhouse conditions at the Experimental Station of the University of Brasília, Brasília, Brazil. Seeds of native Cerrado woody plants, including two non-leguminous—*Eugenia dysenterica* (Myrtaceae) and *Magonia pubescens* (Sapindaceae) and a legume species, *Enterolobium gummiferum* (Leguminosae-Mimosoideae) were germinated in agar.

About 20 days after germination, the seedlings were transferred to plastic bags filled with a mixture of Cerrado soil and washed sand (2:1 ratio), and were taken to the greenhouse to acclimate. Within ~30 days, the seedlings were transplanted into 18 L polyethylene pots filled the same substrate described above. The mixture of soil and sand was added over a layer of gravel for better drainage. Three individuals of the same species of woody plants were placed in each pot to grow in the absence of grass (intraspecific competition) or in the presence of grass (see below, interspecific competition) in February 2008.

Rhizomes of the C_3 grass *Echinolaena inflexa* were collected in natural field sites close to Brasília, selected by similar size and transplanted into pots. Each pot received two to four rhizome parts for a total of approximately 5 g fresh biomass per pot. Seventy pots were prepared, 20 for each species of woody plants (10 in monoculture and 10 in mixed culture with grass) and 10 for the grass monoculture.

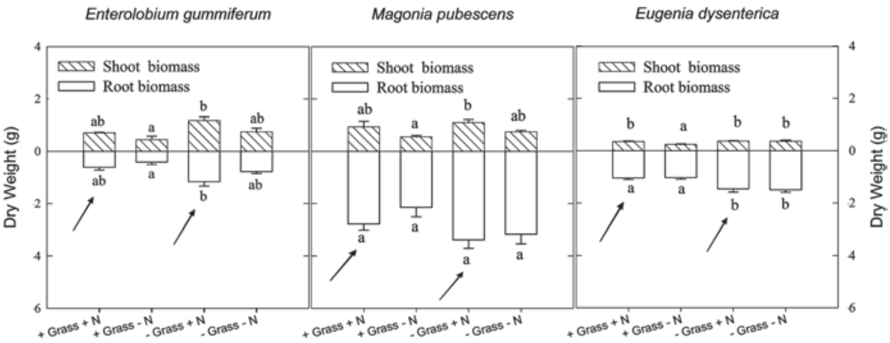

Fig. 22.1 Dry weight of shoots and roots of three woody species growing in monoculture (−Grass) and in the presence of grass (Grass+), without (−N) and with (+N) fertilization. Different letters indicate significant differences among treatments ($p<0.05$). *Arrows* ↑ indicate treatments with N addition

To determine the effect of enhanced N availability on sapling development and on their competitive abilities, half of the pots received addition of 0.0171 g of N in the form of NO_3NH_4, divided into five monthly applications (from September 2008 to January 2009), amount equivalent to a deposition of 20 kg N ha^{-1} $year^{-1}$. Fertilizer was dissolved in distilled water and applied over the soil. The pots were randomly divided between three benches in the greenhouse at the Experimental Station Biological UnB and rotated every 20 days throughout the experimental period.

Five months after transplanting to pots, plants presented yellowish spots on the leaves indicating nutrient deficiency. Thus, Hoagland solution was applied (1/2 strength in the first two applications and 1/3 strength in the last two). 45 ml of nutrient solution were applied per pot every two weeks between July and August 2008.

One year after, the individuals were collected the fresh and dry biomass (after drying at 60 °C for 48 h) of root, shoot non-photosynthetic (stem and branches) and leaves were determined. Grasses were also collected and weighed separately as roots and shoots. Before drying, the root system of each individual was scanned (Epson Perfection V700 Photo) and the images analyzed with the software Win-Rhizo 2008a for determination of the total length, surface area, mean diameter and length of fine roots (up to 0.5 mm in diameter).

Data distribution was tested by Kolmogorov–Smirnov test. Differences between means were tested by ANOVA< and post-hoc test and were considered significant at $p<0.05$.

22.3 Results and Discussion

Interspecific competition tended to reduce root and shoot biomass of juvenile woody plants and grasses (Figs. 22.1 and 22.2). However, significant effects were found, mainly, on root length (Fig. 22.3). The higher N availability minimized the nega-

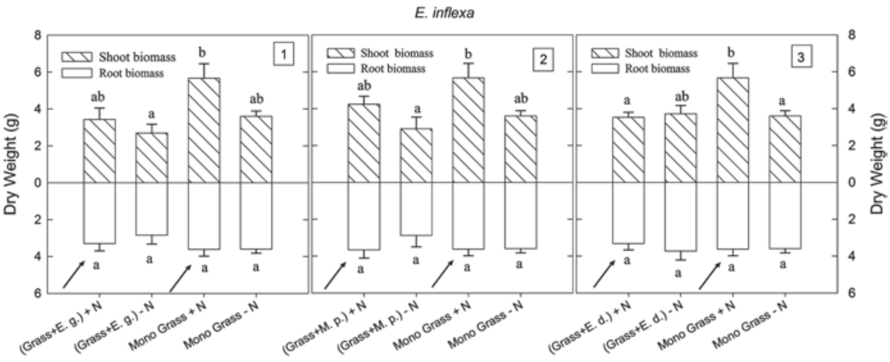

Fig. 22.2 Dry weight of shoot and root system of the grass *E. inflexa* in monoculture (mono. Grass) and in competition with woody species, (*1*) grass + *E. gummiferum* (Grass + *E.g*), (*2*) grass + *M. pubescens* (Grass + *M.p*) and (*3*) grass + *E. dysenterica* (Grass + *E.d*). Different letters indicate significant differences among treatment means, $p < 0.05$. *Arrows* ↑ indicate treatments with N addition

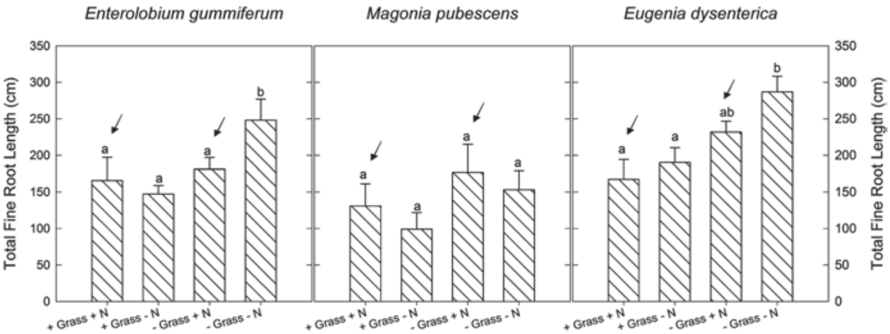

Fig. 22.3 Mean of total length of roots (cm) in *E. gummiferum*, *M. pubescens* and *E. dysenterica* growing in monoculture (−Grass) and in the presence of grass (+Grass, *E. inflexa*), without (−N) and with (+N) fertilization. Different letters indicate significant differences between treatment means, $p < 0.05$. *Arrows* ↑ indicate treatments with N addition

tive effects of interspecific competition, especially in the juvenile woody plants, increasing root biomass to levels similar to those found in the monocultures.

The effect of interspecific competition with the grass (*E. inflexa*) was even more obvious in the root morphology of the saplings, which were on average 12 and 28 % shorter in the presence of the grass without N addition (Grass − N) compared with the monocultures of *E. gummiferum* and *M. pubescens*, respectively. On the other hand, roots of *E. dysenterica* were about 14 % shorter in the treatment Grass + N (Fig. 22.3). In general, the addition of N counterbalanced or reduced the effect of competition (Fig. 22.3).

Under interspecific competition, the total root length and total fine root length diminished in two of the woody species and in the grass. *E. dysenterica* and *E. gummiferum* had higher total length of fine roots (up to 0.5 mm diameter) in the absence

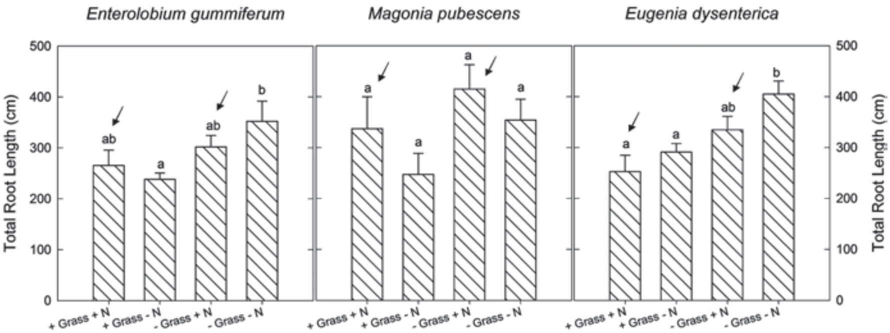

Fig. 22.4 Mean of total length of fine roots (up to 0.5 mm in diameter) in the three woody species growing in monoculture (−Grass) and in the presence of grass (+Grass), without (−N) and with (+N) fertilization. Different letters indicate significant differences between treatment means, $p<0.05$. *Arrows* ↑ indicate treatments with N addition

of the grass and without N addition (−Grass −N) (Fig. 22.4). *M. pubescens* presented the highest total length of fine roots in −Grass +N, without significant differences between the other treatments (Fig. 22.4). Root biomass was also reduced but only in one of these woody species.

22.4 Conclusion

The results provide an indication that competition between saplings of woody plants and grasses could be an important factor driving plant allometry and morphology during the first stages of development in Cerrado environments.

Our results also suggest that the responsiveness of plants to N deposition, as observed for other atmospheric nutrients or pollutants (Kozovits et al. 2005) depends in part on the type of competition (intra- or interspecific) occurring, and that this needs to be take into account in models of vegetation dynamics in response to nutrient deposition.

The enhancement of N availability might, in some cases, minimize the effects of competition, increasing the potential competitiveness of some woody species due to changes in total fine root length. The consequences of such changes in the competitive ability of plants in a long term, however, still have to be evaluated.

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Chapter 23
Pigment Ratios of the Mediterranean Bryophyte *Pleurochaete squarrosa* Respond to Simulated Nitrogen Deposition

Raúl Ochoa-Hueso, Cristina Paradela, M. Esther Pérez-Corona and Esteban Manrique

Abstract Nitrogen (N) deposition alters ecosystem structure and functioning. To study potential impacts on Mediterranean ecosystems, we designed a field fertilization experiment where NH_4NO_3 was added at four rates (0, 10, 20 and 50 kg N ha^{-1} year^{-1}). The terricolous moss *Pleurochaete squarrosa* was sampled and pigments extracted in spring-autumn 2008 and spring 2009. Simulated N deposition increased lutein and *VAZ* pigments to chlorophyll ratios in autumn 2008; β-carotene to chlorophyll ratio was reduced in spring 2009; (neoxantin + lutein) to β-carotene increased with N supply and this was explained as higher investment in light-harvesting complexes than in reaction centres. Response of carotene to chlorophylls and of (neoxantin + lutein)/β-carotene to N enrichment were only evident when soil NH_4 and Mn, respectively, were used as covariates. Thus, covariance analyses are highly recommended to detect N fertilization effects on terricolous species when field experiments are set up in highly heterogeneous environments.

Keywords Bryophyte • Mediterranean • Nitrogen deposition • Pigment ratios

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23.1 Introduction

The extent to which nitrogen (N) deposition has already affected European Mediterranean ecosystems and the level of impact are un-certainties that need to be urgently addressed (Bobbink et al. 2010). Vourlitis et al. (2009) proposed using experimental evidence from Californian Mediterranean-type ecosystems to predict potential N impacts. However, the environmental problems and hysteresis of both areas are not the same. In addition, their soil fertility, which could determine potential responses to N addition, is usually different; e.g. Californian soils are richer in phosphorus (P) (Hobbs and Richardson 1995). Mediterranean mosses from herbaria collections, particularly the drought-tolerant and relatively abundant species *Pleurochaete squarrosa* (Brid.) Lind., have been shown to accumulate deposited N in tissues, which makes it a good potential bio-indicator (Peñuelas and Filella 2001). However, studies using mosses as indicators of N pollution are only common in temperate and boreal areas. In these areas, mosses affected by elevated N deposition have declined and shown altered pigment composition and ratios (Arróniz-Crespo et al. 2008). This decline is assumed to operate via N to P imbalance or because of direct N toxicity (Arróniz-Crespo et al. 2008), yet the importance of other nutrients, including micro-nutrients, has not been evaluated.

The first goal of this study was to determine the effects of simulated N deposition on pigment ratios (chlorophyll *a/b*, carotenoids to chlorophylls, and (neoxantin + lutein) to β-carotene) of the Mediterranean moss *P. squarrosa*. If proved to be sensitive enough, these ratios could be used to predict N deposition loads at national and international scales, given the wide distribution within the Mediterranean Basin of this moss species. A second goal was to identify which soil variables best explain pigment ratios and if they condition responses to N fertilization through N deposition. We hypothesized that, being a terricolous species in tight contact with soil surface, responses of pigment ratios will be related not only to N enrichment but also to the heterogeneous spatial and temporal distribution of certain soil nutrients. Based on previous work, we also hypothesized an increase of pigments forming part of light-harvesting complexes (involved in photo-protection mechanisms) in relation to those of reaction centres (Arróniz-Crespo et al. 2008).

23.2 Methods

23.2.1 Study Area

This study was conducted in a semi-arid Mediterranean thicket located within the Nature Reserve El Regajal-Mar de Ontígola (Central Spain, 40° 00′ N, 3° 36′ W; mean altitude ~ 500–600 m asl). Annual rainfall is ~ 425 mm, confined to the period between October and May (mainly in winter months). Annual plants are absent most of the year and a diverse and well-developed late-successional biological soil crust composed by terricolous lichens and mosses (predominantly *P. squarrosa*) is characteristic of the interspaces between shrubs. The relief is hilly and the thicket is located at the high and middle parts of the hills. Soils are rich in calcium carbonate and with a slightly basic pH (8.01 in spring 2009); nitrate is the dominant inorganic N form in soils (~2-fold greater than ammonium in spring 2009) (Ochoa-Hueso and Manrique, unpublished data); phosphate in soils is usually below 1 mg kg^{-1} and higher values are related to animal activity, mainly rabbits and partridges. Temporal variation (seasonality) of nutrients in soil is high, independent of simulated N deposition treatments, corresponding to this type of seasonal ecosystems (Ochoa-Hueso and Manrique, unpublished manuscript).

23.2.2 Nitrogen Fertilization Experiment

24 plots (2.5 × 2.5 m) were established in October 2007 within the thicket in a 6-block design. Each plot in each block was randomly assigned to one of four N treatments (0, 10, 20 and 50 kg N ha^{-1} $year^{-1}$) over the background deposition (~22 kg N ha^{-1} $year^{-1}$; Ochoa-Hueso and Manrique 2011). All treatments, excluding the latter, are within the predicted deposition scenarios for the Mediterranean Basin by 2050 (Phoenix et al. 2006) or in the range of N deposition loads measured in other Mediterranean regions (Fenn et al. 2003). Nitrogen was applied monthly as wet deposition (2 L NH_4NO_3 solution, providing 0, 19, 37 and 93 mM (NO_3^- + NH_4^+) concentrations). During the dry period (July-August) treatments were not added and the 3-month N load was applied in September, simulating the peak of N availability with the onset of rain (Fenn et al. 2003).

23.2.3 Pigment Analyses

Three fragments from different clonal individuals of *P. squarrosa* were taken in spring and autumn 2008 and spring 2009 from each plot. Samples from 2008 were air-dried and stored in paper bags (we did so taking into account that individuals of this species remain dry a high proportion of the year and after Esteban et al. 2009). Samples from 2009 were deep-frozen with liquid nitrogen and stored at −20 °C. Chlorophylls (*a* and *b*), β-carotene, neoxanthin, lutein, and VAZ cycle pigments (violaxathin, anteraxanthin, and zeaxanthin) were separated by HPLC (Waters, U.S.A.) as described in Martínez-Ferri et al. (2000). Pigment reports are expressed as pigment ratios.

23.2.4 Soil Sampling and Chemical Analysis

Soil samples 4 cm deep were seasonally removed (from autumn 2008 to summer 2009) from each plot. Samples were then air-dried and stored at room temperature in the dark. Soil pH was measured in water; organic matter and organic N were assessed by acid digestion and oxidation; extractable P (5 g of soil in 25 ml 0.001 M $CaCO_3$, 0.001 $MgCO_3$, 0.04 M CH_3COOH, 0.003 M H_2SO_4 extractant solution), extractable base cations (Ca, Na, Mg and K; 2.5 g of soil extracted in 25 ml of M CH_3COONH_4 at pH 7), and extractable non-base cations (Fe, Mn, Zn, Cu and Al; 2.5 g of soil extracted with 0.5 M $CH_3COOHNH_4$, 0.5 M CH_3COOH and 0.02 M EDTA) were analysed by ICP-OES at the Unit of Analysis of the Centre for Environmental Sciences (CSIC, Madrid, Spain) as extensively described in Campos-Herrera et al. (2008). Soil nitrate (NO_3^-) and ammonium (NH_4^+) were colorimetrically evaluated after extraction in deionised water. Gravimetric soil water content was also calculated.

23.3 Data Analysis

Analysis of variance (ANOVA) for repeated measures (RM) was used for the effects of N supply (fixed factor) and sampling season (repeated factor). Repeated measures approximation was used because of the clonal nature of the selected moss species and given the high probability of sampling the same individual in different sampling seasons. One-way ANOVA was also used for the effects of N treatments by season. LSD tests were used for post-hoc comparisons. When tests were non-significant, we used soil variables as covariates (current season, four-season average, and seasonal values) by ANCOVA procedures. Seasonality of soil parameters was assumed to be reflected by standard deviation to a certain degree. Stepwise linear regressions were used for the effects of soil variables (current season, average and seasonal values) on pigment ratios. When necessary, data were transformed to fit tests' assumptions. SPSS17.0 package was used and statistical significance was established at $P=0.05$.

23.4 Results

Nitrogen effects on pigment ratios and their seasonal variation are reported in Table 23.1 and Fig. 23.1. Carotenoids to chlorophyll ratios were highly seasonal. When analysing by season, lutein to chlorophyll and *VAZ* to chlorophyll ratios were significantly increased by N supply in autumn 2008, and carotene to chlorophyll was marginally decreased by N in spring 2009 when current season ammonium was the covariate. Chlorophyll *a/b* ratios seasonally changed, but overall season-based effects of either N fertilization or the interaction between N and season were non-significant. (Neoxantin + lutein) to β-carotene ratio was seasonal and there was a significant effect of N when Mn seasonality was used as covariate; the interaction N x season was not significant for this ratio. Sorted by season, this ratio was not affected by N in spring 2008, affected in autumn 2008 when current season Mn was used as covariate, and affected in spring 2009. Results from the stepwise linear regression analyses are shown in Table 23.2.

Table 23.1 Univariate *F*-tests for *P. squarrosa* pigment ratios after one-way ANOVAs for repeated measures (N treatment as fixed and time as repeated factors) and one-way ANOVAs for each sampling season. When appropriate, ANCOVA results are presented instead of those from ANOVA analyses

	Neoxanthin/chl $a+b$			Lutein/chl $a+b$			β-carotene/chl $a+b$			*VAZ*/chl $a+b$			Chlorophyll a/b			(Neox + lut)/carot		
	df	*F*	*P*	df	*F*	*P*	df	*F*	*P*	df	*F*	*P*	df	*F*	*P*	df	*F*	*P*
Nitrogen	3	0.51	0.68	3	2.31	0.11	3	0.73	0.55	3	0.48	0.70	3	0.04	0.99	3	10.01	0.01
Season	2	157.1	**<0.01**	2	694.2	**<0.01**	2	555.7	**<0.01**	2	743.8	**<0.01**	2	100.5	**<0.01**	2	39.9	**<0.01**
N x season	6	0.55	0.77	6	0.54	0.78	6	1.92	0.10	6	1.09	0.38	6	0.86	0.53	6	1.04	0.41
Manganese[a]																1	4.82	0.01
Spring 2008																		
Nitrogen	3	1.52	0.24	3	1.17	0.35	3	0.95	0.44	3	0.15	0.93	3	0.32	0.81	3	0.40	0.75
Autumn 2008																		
Nitrogen	3	0.17	0.92	3	4.06	**0.02**	3	0.96	0.43	3	3.76	**0.03**	3	0.52	0.67	3	3.30	**0.04**
Manganese[b]																1	3.43	0.08
Spring 2009																		
Nitrogen	3	0.84	0.49	3	0.78	0.52	3	3.00	0.06	3	0.85	0.48	3	0.61	0.62	3	4.45	**0.02**
Ammonium[b]	1						1	7.24	**0.01**									

Significant effects ($P<0.05$) are in bold
df (degrees of freedom)
Covariates: [a]seasonal, [b]current season values

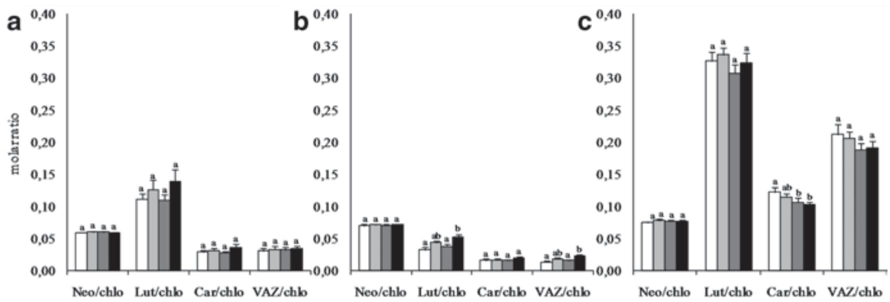

Fig. 23.1 Nitrogen fertilization effects on carotenoid to chlorophyll ratios in **a** spring 2008, **b** autumn 2008, and **c** spring 2009. Same letter above SE bars indicates no significant differences ($P > 0.05$) between treatments. Neo (neoxanthin), lut (lutein), chlo (chlorophyll $a + b$), carot (β-carotene), VAZ (VAZ cycle pigments). *Open* (0N), *light-grey* (10N), *dark-grey* (20N), *dark* (50N)

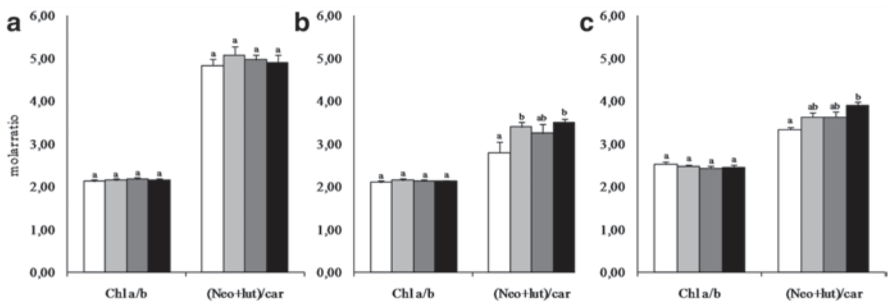

Fig. 23.2 Nitrogen fertilization effects on chlorophyll *a/b* and (neoxantin + lutein)/β-carotene ratios in **a** spring 2008, **b** autumn 2008, and **c** spring 2009. Same letter above SE bars indicates no significant differences ($P > 0.05$) between treatments. Neo (neoxanthin), lut (lutein), chlo (chlorophyll $a + b$), carot (β-carotene), VAZ (VAZ cycle pigments). *Open* (0N), *light-grey* (10N), *dark-grey* (20N), *dark* (50N)

23.5 Discussion

Photosynthetic pigments and pigment ratios provide good complementary indicators of N pollution effects and of physiological recovery (Arróniz-Crespo et al. 2008). In temperate areas, decreased chlorophyll *a/b* and increased (neoxanthin + lutein) to β-carotene ratios after N fertilization have been related to higher proportions of light-harvesting complexes compared with reaction centres. We have proved the latter to be also true in Mediterranean ecosystems subjected to N enrichment.

Increased pigment concentrations (usually chlorophylls) are a typical consequence of N deposition in mosses and lichens (Sánchez-Hoyos and Manrique 1995; Arróniz-Crespo et al. 2008; Ochoa-Hueso and Manrique, unpublished manuscripts) but a reduction has also been reported in lichens fumigated with nitric acid (Riddell et al. 2008). Thus, pigment responses to N enrichment may depend on the dominant

Table 23.2 Stepwise linear regressions with *Pleurochaete squarrosa* pigment ratios and soil traits as dependent and independent variables, respectively. Only significant models are included

	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P
Spring 2008																				
Chlorophyll a/chlorophyll b	Ca^s	–	0.298	<0.01	$C:N^a$	+	0.425	<0.01												
Neoxantin/chlorophyll a+b	NH_4^s	–	0.535	<0.01																
Lutein/chlorophyll a+b	Ca^a	+	0.358	<0.01	Na^s	–	0.555	<0.01	WC^s	–	0.655	<0.01	pH^a	+	0.727	<0.01	Mn^s	–	0.815	<0.01
Carotene/chlorophyll a+b	$Ca:Al^s$	+	0.365	<0.01	N_i^a	+	0.526	<0.01												
VAZ/chlorophyll a+b	pH^a	+	0.324	<0.01	WC^s	–	0.521	<0.01	$Ca:Al^s$	+	0.639	<0.01								
(Neox + lutein)/carotene	Mn^s	–	0.305	<0.01																
Autumn 2008																				
Chlorophyll a/chlorophyll b	–																			
Neoxantin/chlorophyll a+b	Ca^s	+	0.338	<0.01	K^a	–	0.513	<0.01												
Lutein/chlorophyll a+b	NH_4^a	+	0.278	<0.01	$C:N^c$	–	0.381	<0.01	Ca^s	+	0.541	<0.01								
Carotene/chlorophyll a+b	Mn^a	+	0.271	<0.01	Al^a	+	0.499	<0.01	Mg^s	–	0.643	<0.01	Cu^a	+	0.774	<0.01				
VAZ/chlorophyll a+b	NH_4^s	+	0.225	<0.01	$C:N^c$	–	0.417	<0.01												
(Neox + lutein)/carotene	N^c	–	0.169	0.046	pH^s	–	0.317	0.018												

[a]Average, [c]Current season, [s]Seasonality

Table 23.2 (continued)

	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P	Var.	Sign	R^2	P
Spring 2009																				
Chlorophyll a/chlorophyll b	pH^s	+	0.195	0.03																
Neoxantin/chlorophyll a+b	N^s	+	0.293	<0.01																
Lutein/chlorophyll a+b	N^s	+	0.164	0.05	Mn^c	+	0.396	<0.01												
Carotene/chlorophyll a+b	$NH_4{}^a$	–	0.200	0.03	Mn^c	+	0.412	<0.01	Al^c	+	0.535	<0.01	Fe^s	–	0.648	<0.01				
VAZ/chlorophyll a+b	Mn^c	+	0.214	0.02	N^s	+	0.353	0.01												
(Neox + lutein)/carotene	–																			

[a]Average, [c]Current season, [s]Seasonality

N form (wet vs. dry and oxidized vs. reduced), pollution load and also on the plant species (Sánchez-Hoyos and Manrique 1995; Arróniz-Crespo et al. 2008; Riddell et al. 2008). In contrast, other pigments such as β-carotene can remain un-alterered, or just show small responses (increasing or decreasing) at different rates (Ochoa-Hueso and Manrique, unpublished manuscript). Thus, the alteration of pigment ratios will be related to impaired responses of different pigments, which should reflect physiological priorities either for photosynthesis or protection against photo-oxidation.

Additionally, terricolous moss species, in close contact with the soil surface, are usually micronutrient-limited (Bowker et al. 2005; Ochoa-Hueso and Manrique, unpublished manuscript); particularly, this study suggests that soil NH_4^+ and Mn^{2+} influence responses of *P. squarrosa* to N enrichment. The positive (and masking) relationship between β-carotene to chlorophylls with soil NH_4^+ (data not shown) could be reflecting the need for protection against excessive photo-oxidation if high soil NH_4^+ levels are damaging cellular machinery. The increase of carotene in relation to (neoxanthin + lutein) when Mn^{2+} increases is, in turn, most likely linked to the importance of Mn^{2+} for carotene formation (Blaya and García 2003).

23.6 Concluding Remarks

Responses of terricolous mosses to N enrichment may be mediated by existing soil environmental conditions and micronutrient demand and thus direct statistical comparisons with samples taken from low-replicated field experiments in highly heterogeneous environments may not be powerful enough to detect significant effects of treatments; therefore, covariance analysis are highly recommended in such cases. Finally, (neoxanthin + lutein)/β-carotene seems to consistently respond to N enrichment across biomes (temperate and Mediterranean), suggesting its potential use as a bio-indicator.

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Chapter 24
Calibrating Total Nitrogen Concentration in Lichens with Emissions of Reduced Nitrogen at the Regional Scale

Pedro Pinho, Maria-Amélia Martins-Loução, Cristina Máguas and Cristina Branquinho

Abstract The impact of nitrogen (N) on ecosystem functioning and biodiversity is currently recognized to be increasing worldwide. For that reason, there is an urgent need for strategies aimed at identifying and mitigating N mediated effects. Most studies undertaken at a regional scale regarding N deposition are based on models. However, there is a missing link between the predictions made by N emission models at broad spatial scales, and the actual atmospheric N deposition. Our aim was to use biomonitors to provide that link. More specifically our objective was to present clear evidence that N concentrations measured in lichen thalli can be used as an ecological tool to assess the deposition of atmospheric reduced N in ecosystems. To do so we have related N concentrations measured in lichens thalli to ammonia emissions estimated from cattle numbers and the cover of agricultural land. This was done in two areas with a Mediterranean climate in south-west Portugal. The results have shown that N concentrations in lichens could be significantly correlated with reduced-N emissions. There was a very close relationship between N concentrations in lichens and the main regional sources of reduced nitrogen. This lichen variable can thus be used as an ecological tool to map with high resolution and at a regional scale, N deposition in ecosystems. Measurement of lichen thallus N concentration will help identify areas of high N deposition where further monitoring may be required to help safe-guard against Critical Load exceedance and Biodiversity impacts.

Keywords Agriculture • Atmospheric pollution • Biomonitoring • Ecological indicators • Eutrophication

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24.1 Introduction

Pollution by nitrogen (N) was recently recognized not only as a major threat to biodiversity and ecosystem functioning but also a threat that is expected to increase worldwide (SCBD 2006). Moreover, N pollution, together with biodiversity loss and climate change, is considered one of the three global drivers whose changes have already passed the threshold beyond which unacceptable environmental change could occur (Rockstrom et al. 2009). In fact, the negative impact of N on ecosystem functioning and biodiversity has been confirmed in numerous works (Aber et al. 2003; Bobbink et al. 2010; Erisman et al. 2003; Kleijn et al. 2009; Krupa 2003; Phoenix et al. 2006; Purvis et al. 2003; Suding et al. 2005).

The main anthropogenic sources of reduced N, ammonia, are associated with agricultural activities, mainly intensive farming applying fertilizer and intensive animal husbandry (EPER 2004; Galloway et al. 2003). The studies dealing with the deposition of this form of N at a regional scale mostly rely on data derived from models (Phoenix et al. 2006). However, because models work at very broad spatial scales and the effects of atmospheric ammonia are very local (Pinho et al. 2009), there is often a mismatch between modelled deposition and actual deposition at the local scale. To improve our understanding of the effects of deposition we need more reliable means of quantifying it in the absence of effective measuring networks (Phoenix et al. 2006).

Lichens can be use to validate the predictions made by models to the actual N deposition on ecosystems. Lichens are organisms with particular physiological characteristics that make them well suited to acting as biomonitors. These characteristics include the absence of a cuticle and roots (Honegger 2009), allowing lichens to take up water and dissolved nutrients directly from the atmosphere. Lichens have been shown to accumulate a large number of pollutants (Augusto et al. 2010; Augusto et al. 2004; Branquinho et al. 1999; Branquinho et al. 2008). However, N is a special case being a macro-element essential for life. Despite this, some authors have shown that N can be accumulated in inorganic and organic forms in relation to N deposition (Branquinho et al. 2010; Gaio-Oliveira et al. 2001). For this reason, the N concentration in lichens has been used in local-scale studies dealing with N impact or deposition. However, these studies were mostly undertaken close to point sources such as cattle barns (Branquinho et al. 2010; Frati et al. 2007; Olsen et al. 2010). Here we have assessed the relationship at a regional scale between N concentrations measured in lichens and ammonia emissions.

Our objective was to provide evidence to support the use of N concentrations in lichens as an ecological tool to assess, at a regional scale, the deposition of atmospheric reduced N. Specifically we wanted to address the following questions: (i) Are N concentrations in lichens related to potential sources of reduced N at a regional scale? (ii) Can N concentration in lichens be used to estimate ammonia emissions with high spatial resolution?

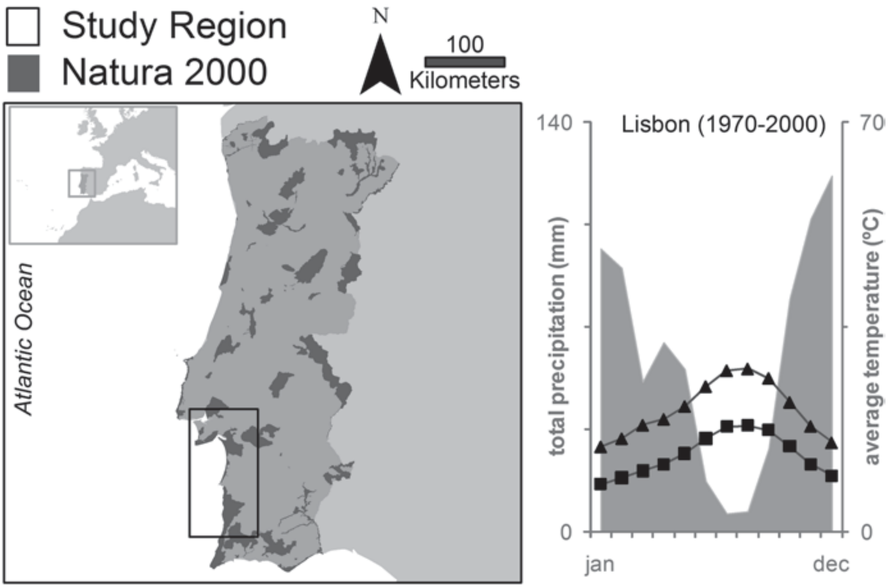

Fig. 24.1 Location and climatic characterization of the studied region. The Natura 2000 sites in mainland Portugal are also shown. In the climatogram the *lower* axis corresponds to months (from January to December), *left* axis average monthly total precipitation (mm) represented by the filled shape, *right* axis monthly temperature (ºC) using averages of the maximums (*triangles*) and minimums (*squares*). Values are averages from 1971–2000. (IM 2000)

24.2 Methods

This study was carried out in a region with a Mediterranean climate located in south-west Portugal (Fig. 24.1). The region has diverse land-use types including urban, industrial, agriculture and semi-natural vegetation as well as a large number of Natura 2000 sites (Fig. 24.1). Two large areas were studied in which the N concentrations in lichens growing at a number of sampling sites were determined. Sampling sites were distributed in the two areas at an average minimum distance of 3,360 m of each other. Selection of sampling sites avoided direct pollution sources, in order to reflect background conditions. In each area we also estimated potential ammonia emissions using two approaches: (i) land-cover information in order to estimate the N emissions from all agriculture activities; and (ii) animal census data in order to estimate N emissions from cattle only.

Using Corine LandCover 2000 (Caetano et al. 2009) the area occupied by agriculture in the neighbourhood of each sampling site was determined (Pinho et al. 2008a). Several agricultural types were considered: (i) permanent agriculture—orchards and olive groves (Corine class 22), (ii) heterogeneous agriculture—small

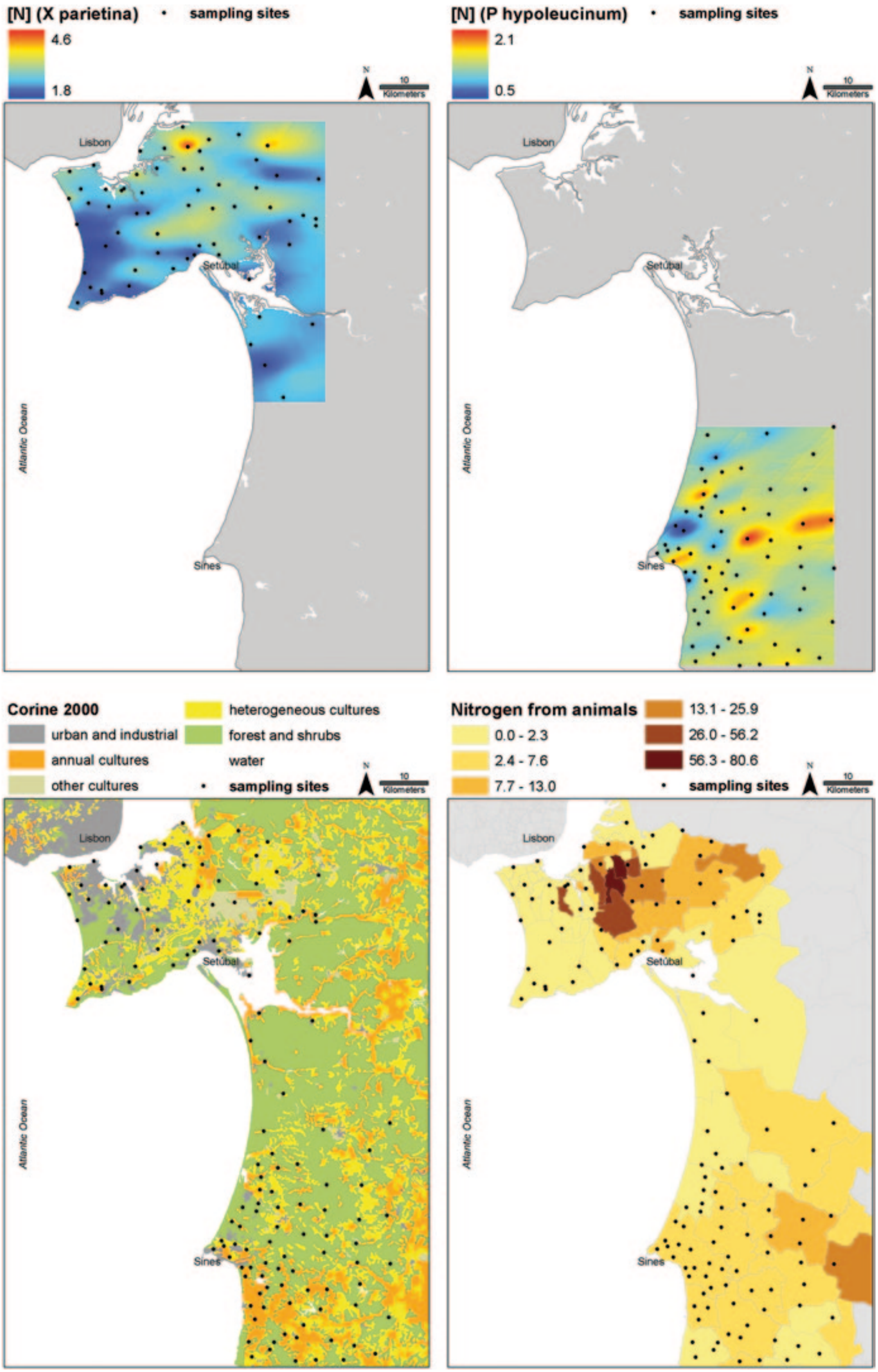

Fig. 24.2 *Top*: mapping of N concentrations measured in lichens, in % (N) for *Xanthoria parietina* (*left*) and *Parmotrema hypoleucinum* (*right*). *Bottom*: Corine land cover 2000 map (*left*) and

farms with animals and vegetables (Corine class 24) and (iii) annual agriculture—large areas with grain cultures (Corine class 21).

Nitrogen emissions from cattle were estimated from agricultural censuses at a civil-parish level (INE 1999), the most detailed level available. All types of cattle were considered in the calculations, using atmospheric ammonia emission factors available for each animal type (IPCC 2006). Total annual values were then divided by civil-parish area. Only civil-parishes containing one or more sampling sites were included in the correlation analysis.

Nitrogen concentration was measured in the lichen thallii of *Parmotrema hypoleucinum* (J.Steiner) Hale (south area, 71 sites) and *Xanthoria parietina* (L.) Th.Fr. (north area, 64 sites): 3 determinations from a composite sample of 15 g.

For the correlation analysis, the N concentration in the lichens was used in two different ways: Firstly, for correlating with neighbouring land-cover, each sampling site was considered independently and correlated to the area occupied by agriculture. This was done in a spatially explicit way using moving correlation analysis (Pinho et al. 2008b). Secondly, the lichen N concentration values were interpolated within each of the two study areas using ordinary kriging after variogram analysis, and the average value for each civil-parish was determined. This average value for each civil-parish was then correlated with the ammonia emissions estimated from cattle data. Using the interpolated values derived from kriging ensured the average values were very robust regarding any distortion on the spatial distribution of sampling sites within each civil-parish, ensuring that the parish lichen-nitrogen values were representative of the entire parish.

24.3 Results

The mapping of N concentration in lichens has shown that this variable had some spatial continuity (Fig. 24.2, top). Several hotspots of higher concentration were detected for both studied areas. Land cover mapping (Fig. 24.2, bottom) revealed that the region represents a typical Mediterranean landscape, with semi natural-land-cover mixed with agriculture and scattered urban areas. Mapping of ammonia-N emissions from cattle (Fig. 24.2, bottom) has shown a large emission gradient, including rather high values (~80 kg N ha^{-1} $year^{-1}$). The highest emissions occurred in the northern civil-parishes due to higher cattle densities.

Using local correlation analysis (Pinho et al. 2008b) a large number of significant and positive correlations were found between N concentration in lichens and the neighbourhood area occupied by agriculture (Fig. 24.4). The higher the areas occupied by annual and by heterogeneous agriculture, the higher the N concentration measured in lichens.

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atmospheric ammonia N emissions from cattle estimated from agriculture census at a civil-parish level, in kg ha^{-1} $year^{-1}$ (*right*)

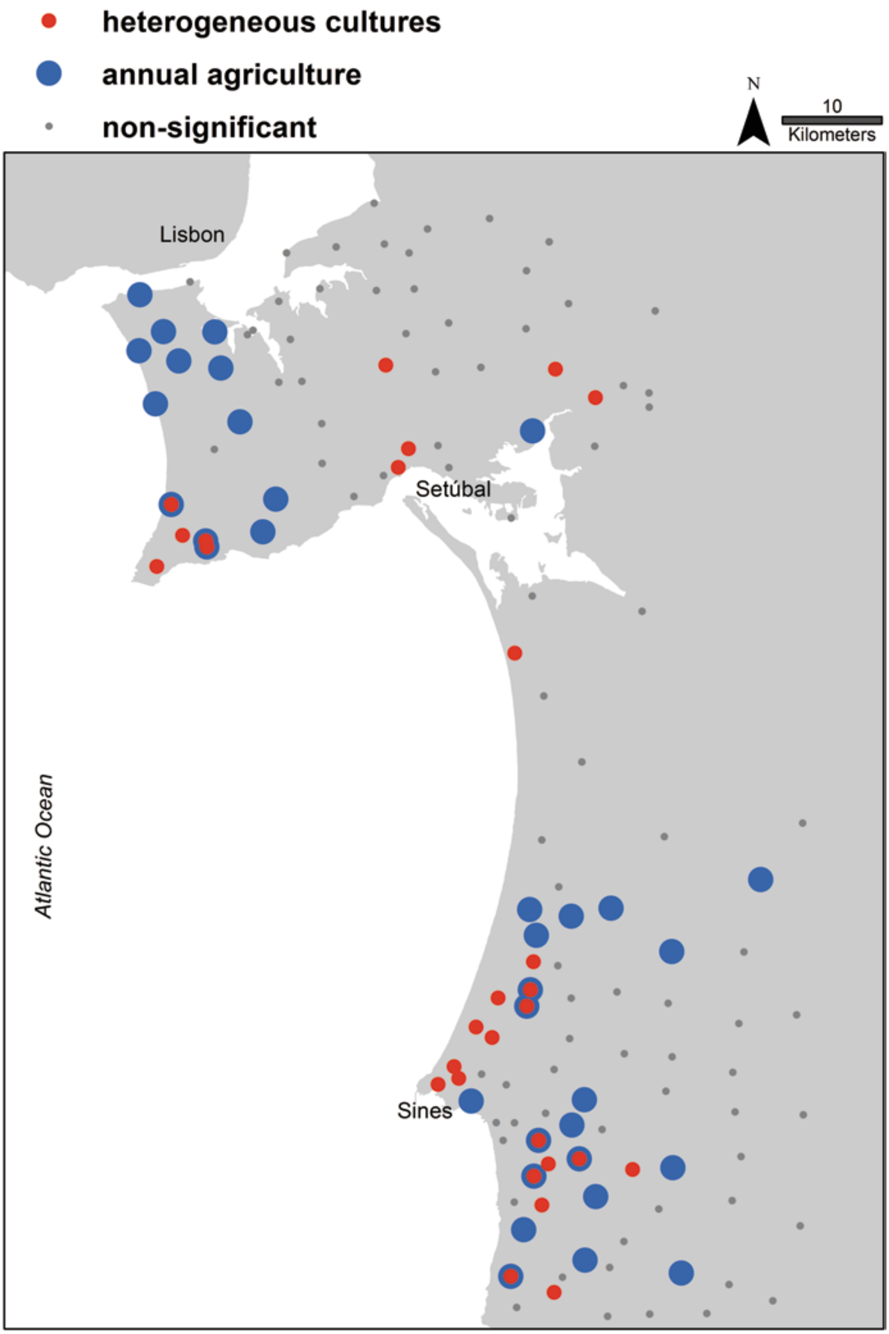

Fig. 24.3 Mapping of a correlation analysis between N concentrations in lichens and neighbouring land-cover. This is the result of a moving window analysis that correlates two variables, using as samples all sites at a distance of 10 km from each sampling site (Pinho et al. 2008b). A significant correlation indicates that, within a 10 km radius neighbourhood, the two variables are

Significant and positive correlations were also found between ammonia emissions estimated from cattle and N in lichens (Fig. 24.4). The civil-parishes with higher N emission from cattle presented the highest average N concentration measured in lichens. This was found for both studied areas.

24.4 Discussion

Nitrogen concentration values differed between the species with the highest values observed for the northern area in *Xanthoria parietina*. This species was expected to contain the highest concentration, because it is a nitrophytic species (Nimis and Martellos 2008). Nitrophytic species are known to contain higher N concentrations than non-nitrophytic ones (Gaio-Oliveira et al. 2001). However, this difference did not influence the correlation analysis because it was performed independently for each area.

The observed values fell within the nitrogen concentrations previously measured in *Xanthoria parietina*, between 1.34 and 3.34% (Gaio-Oliveira et al. 2001) or 1.66 and 2.35% (Frati et al. 2007). Concentrations measured in *Parmelia* spp between 0.5 and 2.1% (Palmqvist et al. 2002) and between 1.55 and 2.56% in *Flavoparmelia caperata* (Frati et al. 2007). In this study *Parmotrema hypoleucinum* has shown a similar range, whereas *Xanthoria parietina* has reached higher maximum values, 4.6%. This probably reflects the fact that, unlike the cited studies, the lichens used in this work, were *in situ* lichens, with prolonged exposure to ammonia deposition favouring N accumulation, leading to higher N concentrations. Another hypothesis may be related to the fact the studied areas had higher atmospheric N deposition than used in previous studies, and that lichens can reflect the higher deposition. Thus, lichen thalli N concentrations not only reflect ammonia N deposition in a given local area, but also can be used as tools to study large gradients of environmental N deposition.

24.4.1 Were Nitrogen Concentrations in Lichens Related to Potential Ammonia Sources at a Regional Scale?

Significant and positive correlations were found at a regional scale between the N concentrations in lichens and ammonia emissions, estimated both from annual and heterogeneous agricultural areas (Fig. 24.3) and from cattle census data (Fig. 24.4). Annual and heterogeneous agricultural types are the most intensive agricultural types, and include farming with fertilizer use, and also complex agricultural areas with cattle barns interspersed with greenhouses. All these agricultural activities,

significantly correlated. In the maps, non-significant correlations ($P>0.05$) are marked with small dots, significant ones with larger circles. The two regions were correlated separately (because N concentration was determined in two different lichens species) but were plotted together. Land-cover was determined from Corine Land Cover 2000 and a number of neighbouring distances were tested, the one with the highest correlation was plotted (Pinho et al. 2008b). All significant correlations were positive

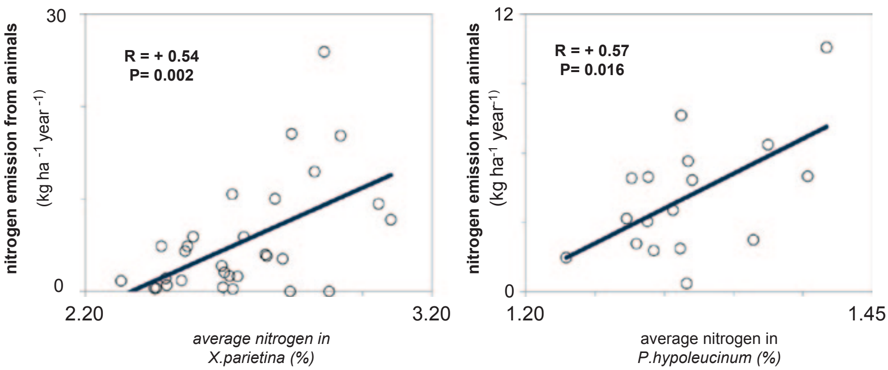

Fig. 24.4 Relationship between reduced-N emissions calculated from cattle census data and N concentration in lichens, for the two studied areas. Lichens used were *Xanthoria parietina* (*left*) and *Parmotrema hypoleucinum* (*right*). The correlation was calculated for the civil-parish level using all parishes with at least one sampling site within and the average N concentration in lichens within that civil-parish. $n=17$ (*left*) and $n=30$ (*right*)

including cattle husbandry and farming, are known sources of ammonia-N (EPER 2004; Galloway et al. 2003). Once emitted from agricultural fields or barns, N can be taken up by vegetation. It has been shown that lichens (Branquinho et al. 2010; Frati et al. 2007) and bryophytes (Pitcairn et al. 2003) located near cattle barns, and plants located in forests near fertilized agricultural fields (Pocewicz et al. 2007), have higher N concentration in the thalli. Nitrogen accumulation in lichens has therefore been used to monitor N deposition in local studies (Branquinho et al. 2010; Frati et al. 2007; Olsen et al. 2010). However, those monitoring surveys were performed at a local level, not at a regional one, such as here.

24.4.2 Can Nitrogen Concentrations in Lichens be Used to Estimate Nitrogen Emissions at High Spatial Resolution?

Nitrogen concentrations in lichens were significantly related to the main sources of atmospheric reduced N (Fig. 24.3 and 24.4). This correlation was found at a regional scale, using two separate ways of calculating reduced N-emissions: area occupied by agriculture and ammonia emitted by cattle. Additionally, the plotting of the significant correlations between N concentration in lichens and agricultural land-cover areas (Fig. 24.3) identified the areas under the influence of each agricultural type within the given neighbourhood. Therefore, mapping of N concentration in lichens may help locate areas with the highest N atmospheric deposition, identifying areas for monitoring potential exceedance of Critical Loads and Biodiversity impacts.

24.5 Conclusion

Nitrogen concentrations measured in lichens were shown to be significantly correlated with the main regional sources of reduced N, ammonia. They can therefore be used as an ecological tool to map, with high spatial resolution, the areas experiencing higher deposition of ammonia and evaluate impacts on ecosystem functioning and biodiversity.

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Chapter 25
The Impact of the Rural Land-Use on the Ecological Integrity of the Intermittent Streams of the Mediterranean 2000 Natura Network

Cristina Branquinho, Carla Gonzalez, Adelaide Clemente, Pedro Pinho and Otília Correia

Abstract The main objective was to understand the impact of the neighbouring land-use and of water pollution on the integrity of the riparian vegetation in intermittent Mediterranean streams of the 2000 Natura network in a rural area. The ecological integrity of the riparian vegetation of intermittent streams in the Mediterranean was negatively associated with the aquatic NH_4^+ concentration, which might a consequence of direct and indirect effects. There was a significant increase in frequency of exotic shrub species with increasing PO_4^{3-} concentration in stream waters and high NO_3^- concentrations in stream waters did not affected the QBR index or its components. Despite occupying a large area, pastures were not a source of eutrophication elements to the stream waters. Agricultural prac-

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tices close to streams i.e. <200 m, should be avoided. When the latter is not possible a well established native vegetation buffers should surround such areas.

Keywords Agriculture • Exotic plants • Montado • QBR • Water quality

25.1 Introduction

Today, eutrophication is one of the major problems in running waters in the Mediterranean region and it is dependent upon supplies of nitrogen (N) and phosphorus (P). Water managers need to understand the effects of eutrophication in stream ecosystems and be able to identify the most important eutrophying aquatic pollutants. Since the introduction of the European Water Framework Directive, in which member states are stipulated to reach good ecological quality for their surface waters by 2015, tools are needed to predict the effects of decreases or increases in nutrient levels on the stream and on riparian ecosystem. Knowledge of these effects is still limited, because most attention has been focused on nutrient transport through rivers, rather than on the effects on the river ecosystem itself.

The effects of eutrophication in streams and rivers can be diverse. Direct, as well as, indirect effects occur. Toxicity is one aspect of eutrophication that has a direct effect on the functioning of organisms in the ecosystem (Nijboer and Verdonschot 2004; Vieira et al. 2009). In many cases increasing nutrient levels result in indirect effects causing shifts in the species composition, for example in the benthic algal layer or among the higher plant communities, by altering the competitive balance between species (Lyon and Gross 2005; Mainstone and Parr 2002; Pinho et al. 2009). There is now a strong effort in the US and EU to include biotic criteria and to relate pollution abatement to ecological integrity (Novotny et al. 2005). The community and population response parameters represented by the Indices of Biotic Integrity (IBIs) are considered the main response indicators.

Plant-based Integrity Biotic Indices have been increasingly used and recognized for their capacity to inform about the overall ecological condition of riparian habitats (Ferreira et al. 2005; Miller et al. 2006; Reiss 2006; Salinas et al. 2000). The maintenance of ecosystem integrity, interpretable as ecosystem 'health' (Barkmann and Windhorst 2000), is seen as a way of retaining ecosystem resilience (and functional diversity) and therefore of mitigating 'ecological risk'. A deterioration in system integrity results in a reduction in the ecosystem provision of services and goods available for human society (Nunneri et al. 2007).

Riparian plant communities perform an array of important ecosystem functions, including stream bank stabilization, thermal regulation of streams, filtering and retention of nutrients, provision of critical wildlife habitat, and maintenance of ecosystem stability. Given their unique attributes, characterizing the composition and structure of riparian vegetation is an integral component of riparian protection and conservation effort (Lyon and Gross 2005; Mainstone and Parr 2002).

The complex vegetation and plant species distributions within riparian corridors influence plant species diversity patterns at both local and regional scales and further reflect both anthropogenic and natural disturbances (Lyon and Gross 2005; Mainstone and Parr 2002). Because of these characteristics, riparian zones are often the ecosystem component most sensitive to changes in the surrounding environment; they provide early indications of environmental change and can be viewed as the focal point of watersheds (Decamps 1993; Lyon and Gross 2005; Mainstone and Parr 2002). To fully understand vegetation patterns in these unique systems, the interactions between riparian vegetation, landscape position, abiotic factors and disturbance need to be ascertained.

Nutrient concentrations can reach high levels in waters that run through urbanised or agricultural areas. Surpluses of N and P in streams originate from different sources, such as: chemical fertilizers, animal manure, waste water effluent, and atmospheric deposition (Becher et al. 2000).

The study area is amongst the richest hydrological networks in the Alentejo, South Portugal under Mediterranean climate. Furthermore, this is an area which experiences conflicting land uses between conservation and farming: (i) it is a Natura 2000 site and has several aquatic habitats and species of priority conservation, listed in the EU Habitat Directive and (ii) most of the area ($>95\,\%$) is privately owned and the main socio-economic activities are extensive cork exploitation combined with large-scale, extensive livestock production and agriculture activities, which result in a diversity of organic pollutants entering the water system and consequently eutrophication (Gonzalez et al. 2009).

In this area the pressures on stream ecological function are: (i) natural torrential water flow regime, (ii) removal of water for cattle use and agriculture irrigation, (iii) change in precipitation regimes over time, (iv) pollution runoff from extensive and intensive livestock, (v) landholder's stream management practices i.e. stream damming (Gonzalez et al. 2009).

The main objective of this work was to understand the impact of the neighbouring land-use and of water pollution on the integrity of the riparian vegetation in intermittent Mediterranean streams of the 2000 Natura network in a rural area.

25.2 Material and Methods

25.2.1 Study Area and Selection of Sampling Sites

The study area, the Monfurado (Natura 2000 network) in Alentejo, Portugal (Fig. 25.1), is among the richest hydrographic networks in the Alentejo, in southern Portugal, a region characterized by sub-humid Mediterranean climate and dominated by cork-oak and holm-oak "montado" landscape. Thirty-eight sampling sites were selected from streams of the Monfurado (the site's total area is 23,946 ha) (Fig. 25.1). Sites were selected in order to: (i) include both intermittent and perma-

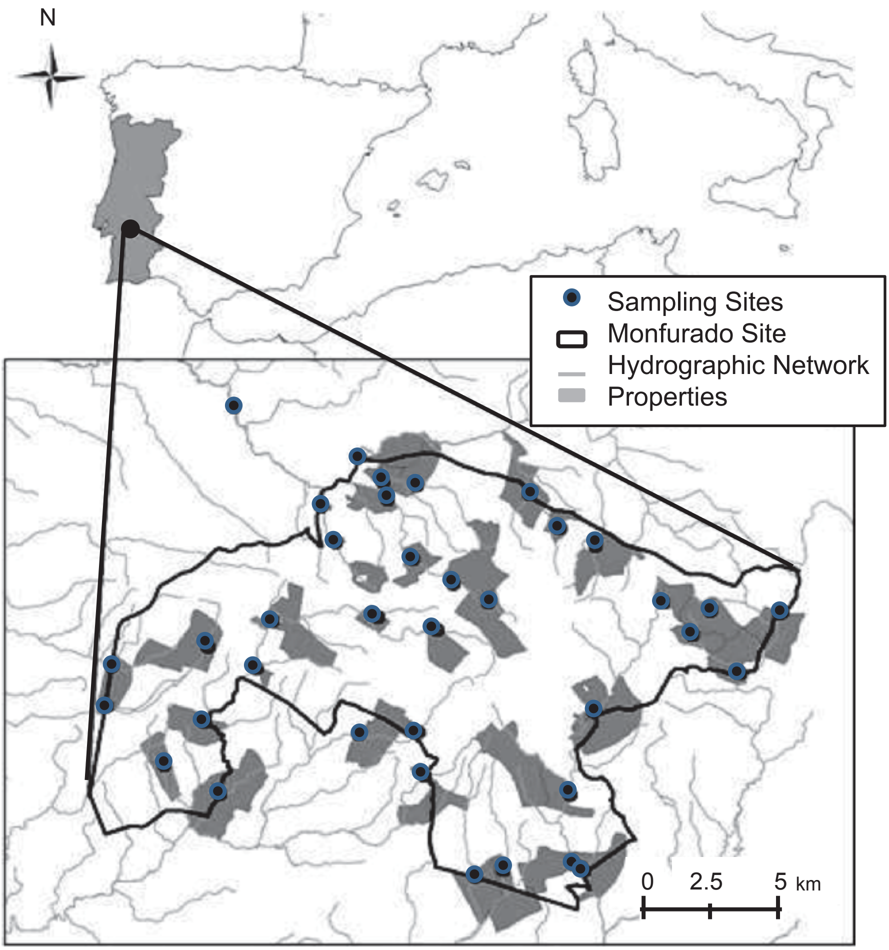

Fig. 25.1 Location of streams and 38 sampling sites and private properties in the Natura 2000 area of the Monfurado, located in Alentejo, Portugal (Gonzalez et al. 2009)

nent streams; (ii) have homogeneity amongst the several streams and areas of the site; (iii) represent different distances from point and diffuse pollution sources (i.e. involving land use); (iv) utilise existing information about the streams' conservation status (Gonzalez et al. 2009).

25.2.2 QBR Index

The IBI applied in this case study, for the assessment of riparian habitat quality in Iberian rivers, was the Index *Qualitat del Bosc de Ribera* (QBR) (Munne et al. 2003). This Index ranges from 0–100 % and is the sum of four components

Table 25.1 Descriptive statistics of the area occupied by different classes of land-use in a square of 2 km placed at each sampling site towards the direction of head waters (m^2), for details see Fig. 25.2. $N=38$

	Mean	Minimum	Maximum	Std. dev.
Pasture (m^2)	474,629	25,994	1,588,372	425,930
Annual agriculture (m^2)	358,388	23,991	1,254,011	257,727
Permanent agriculture (m^2)	153,850	0	1,131,719	283,416
Dwellings (m^2)	22,320	0	355,037	57,688

(0–25 %): Total Riparian Cover (the proportion of well established vegetation in the riparian area, including tree and shrub strata existing in the margins of streams); Vegetation Cover Structure (the relative proportions of tree and shrub strata); Cover Quality (the proportion of native and non-native species and communities expected from the geology of the river bed) and River Channel Alteration (the level of human intervention along the river channel). At all the sampling sites, the QBR Index was applied to 50 m lengths of river at each site: sampling was conducted between March and June 2006. The QBR index and its four components were correlated with measurements of water quality related to eutrophication: NH_4^+, NO_3^- and PO_4^{3-} concentration and pH.

25.2.3 Land-Use

Each sampling site was characterized according to the area occupied by different land-cover types in the adjacent neighbourhood, at 50, 100, 200, 300, 400, 500, 750, 1,000 m from the sampling site (Pinho et al. 2008). For each distance we calculated the relative cover of each land-cover class based on the Corine classification and other classes with potential for emitting eutrophying pollutants, namely: *Pasture, Annual Agriculture, Permanent Agriculture* and *Dwellings* (Table 25.1).

Only the percentage of land-cover located upstream, was considered likely to affect the sampling site (Fig. 25.2). This was determined from a line drawn perpendicular to the stream direction evaluated in the sampling site; areas downstream from that line were ignored (Fig. 25.2). A manual photo-interpretation of real-colour aerial photography (year 2005) with a work-scale of 1:1,000 in ArcMap (ESRI 2008) was used for this characterization. Classification was then verified through random field assessments.

25.2.4 Concentration of Pollutants in Stream Water

Water was collected at all sampling sites in December 2006, March 2007 and July 2007. The water was transported to the laboratory under cooling conditions (4 °C) and frozen or immediately analyzed for NH_4^+, NO_3^- and PO_4^{3-} concentrations and pH measurements. The concentration of NH_4^+ was measured through a colorimetric

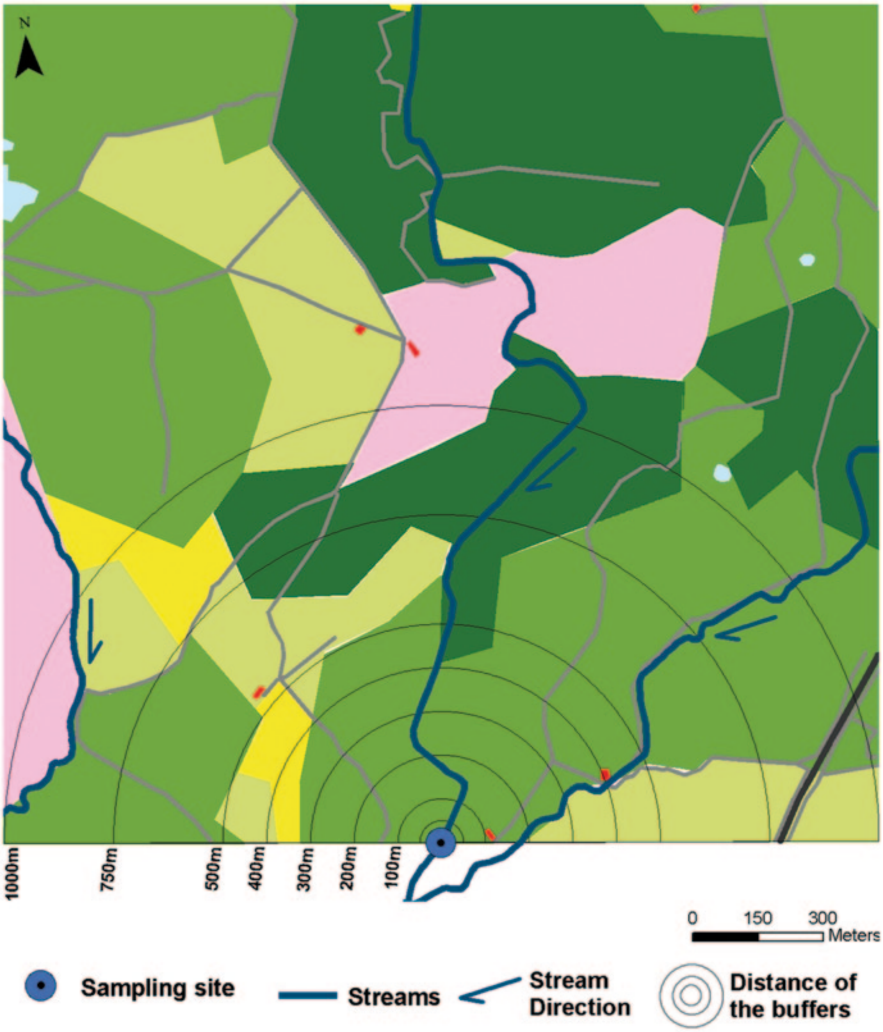

Fig. 25.2 Example of land-cover classes (different colours) analysed in the upstream surroundings of each sampling site (*blue dot*) with arcs representing the buffer areas at 50–1,000 m

method based on the Berthelot reaction measuring the absorbance at a wavelength of 665 nm. The concentration of NO_3^- was based on the colorimetric method (Matsumura and Witjaksono 1999), measuring the absorbance at 410 nm. The PO_4^{3-} concentration was performed based on the colorimetric test (Fiske and SubbaRow 1925) measuring the absorbance at 700 nm. All standards were prepared with deionised water.

Table 25.2 Correlation coefficient of Pearson *r* between QBR index and its four components, Total Riparian Cover, Cover Structure, Cover Quality and Channel Alteration with measurements of NH_4^+, NO_3^- and PO_4^{3-} concentration and pH measures in stream waters. Water nutrient concentration values and pH were the average of three different measures for each of the sampling sites (December 06, March 07 and July 07)

	NH_4^+	NO_3^-	PO_4^{3-}	pH
n	33	39	37	38
QBR	−0.45*	0.06	0.29	−0.1
Total riparian	−0.18	−0.02	0.28	−0.07
Cover structure	−0.37*	0.05	0.07	0.06
Cover quality	−0.39*	0.10	0.29	−0.12
Channel alteration	−0.27	−0.08	0.15	−0.19

*$p<0.05$

25.3 Results

25.3.1 Water Quality Versus Riparian Ecological Integrity

The decrease in QBR index and its components Cover Structure (CS) and Cover Quality (CQ) was significantly correlated with the increase in NH_4^+ concentration in stream waters but not with: NO_3^-, PO_4^{3-} or pH (Table 25.2).

The significant correlations were plotted in Fig. 25.3. The QBR index, CS and CQ showed a decrease with increasing NH_4^+ concentrations in water (Fig. 25.3). Interestingly we observed a decrease in variability with decreasing water NH_4^+ concentrations, showing that changes in riparian habitat quality at that level are more probably related with this environmental factor, whereas for higher stream water NH_4^+ concentrations other factors might be responsible for the higher variance observed (Fig. 25.3).

25.3.2 Water Quality Versus Neighbouring Land-Use with Potential for Causing Eutrophication

Indicators of water eutrophication (pH, NH_4^+, NO_3^- and PO_4^{3-} concentrations) were correlated with the potential of neighbouring land-use to release eutrophying pollutants (Table 25.3). The results show that Annual Agriculture is a source of NH_4^+ concentrations in stream water and that significant changes in water pH occur as the proportion of Annual Agricultural areas increased (Table 25.3). Permanent Agriculture did not affect the water eutrophication indicators (no significant correlation). The number of plots with this type of agriculture was probably too small in the studied region to evaluate the impact of nutrient release from this land-use type. The area of dwellings was shown to be related to the presence of PO_4^{3-} in stream waters

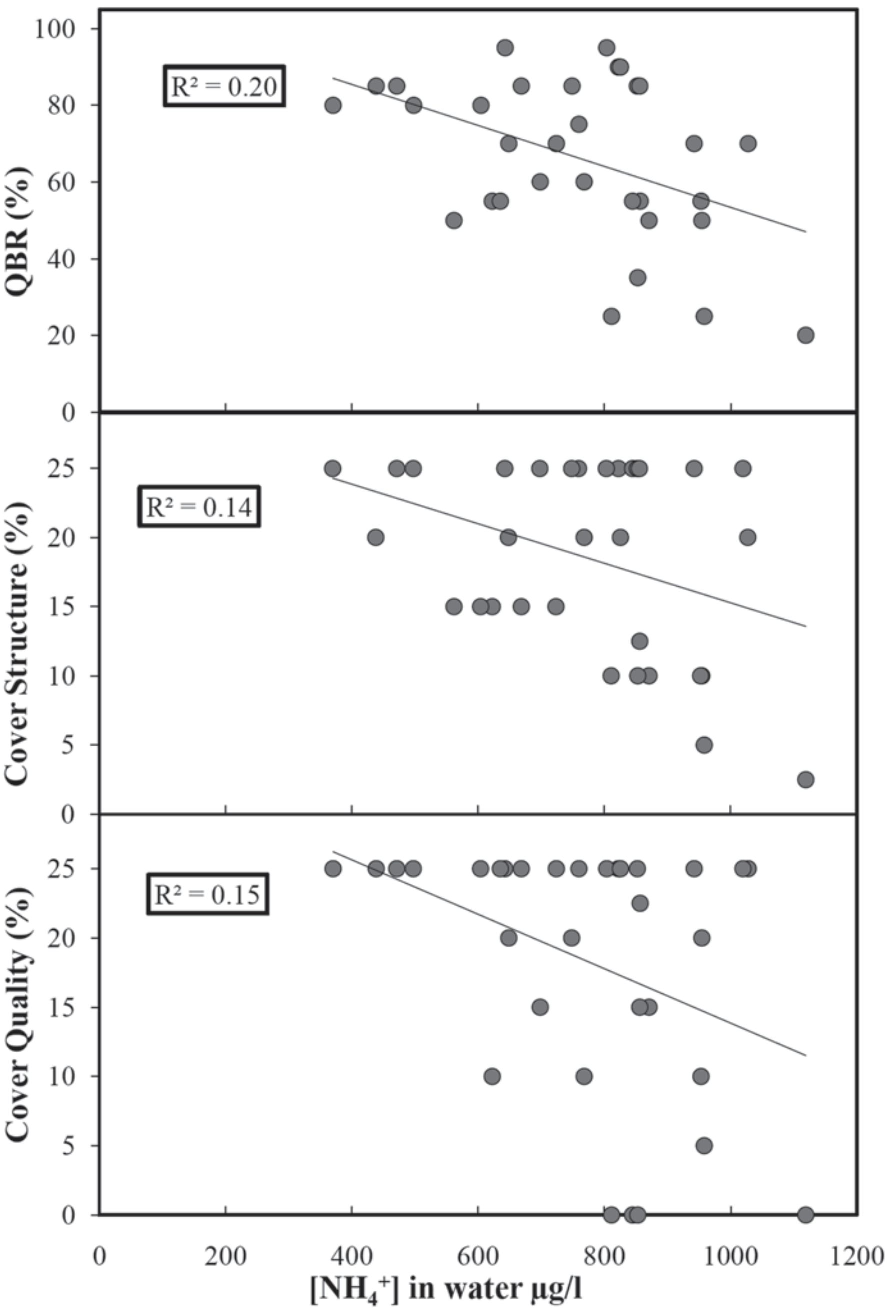

Fig. 25.3 QBR index (%), Cover Structure (%) and Cover Quality (%) plotted with average NH_4^+ water concentrations measured in three different periods (December 06, March 07 and July 07) in 33 streams

Table 25.3 Correlation coefficient of Pearson *r* between the area occupied by each land-use type in a certain buffer with measurements of NH_4^+, NO_3^- and PO_4^{3-} concentration and pH measures in stream waters, (average of three different measures December 06, March 07 and July 07). Sample numbers for each correlation shown in brackets

	NH_4^+	NO_3^-	PO_4^{3-}	pH
Annual agriculture (200 m)	0.60* (15)	−0.13 (18)	0.08 (17)	0.58* (17)
Permanent agriculture (400 m)	0.58 (10)	0.48 (12)	0.05 (11)	0.30 (10)
Dwellings (400 m)	−0.46 (16)	0.17 (19)	0.59* (18)	0.03 (19)
Pastures (400 m)	−0.49* (22)	−0.41* (24)	−0.23 (23)	0.07 (24)

*$p<0.05$

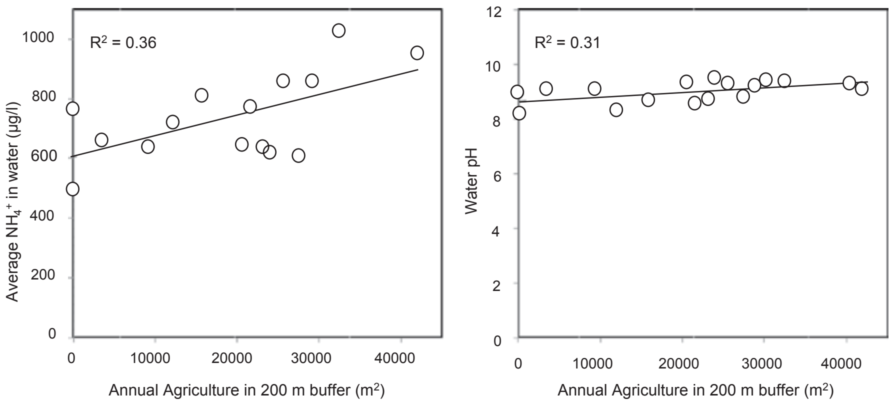

Fig. 25.4 Area occupied by Annual Agriculture (m²) measured in a land-use buffer of 200 m with average NH_4^+ water concentrations and Water pH, measured in three different periods (December 06, March 07 and July 07). $n=15$ and $n=17$, respectively

(Table 25.3). Pastures were not a source of eutrophication for the stream water, on the contrary the greater the area of pasture the lower the concentrations of both NH_4^+ and NO_3^- in stream waters (Table 25.3).

Significant sources of eutrophication indicators by land-use type are plotted in Figs. 25.4 and 25.5. An increase in NH_4^+ concentration in stream waters was observed with increasing Annual Agriculture areas. The same land-use type also resulted in the increase in water pH (Fig. 25.4). These results are in accordance to other data where total nitrogen, total phosphorus, faecal coliforms, conductivity and pH increased as the area under agriculture increased (Tong and Chen 2002).The area of dwellings, mainly residential houses and animal barns (pigs and cows), were related to increasing PO_4^{3-} concentrations in the stream waters (Fig. 25.5).

There was a significant correlation between both NH_4^+ and PO_4^{3-} in stream water and the increasing number of non-native shrub plant species at the same sampling sites (Table 25.4).

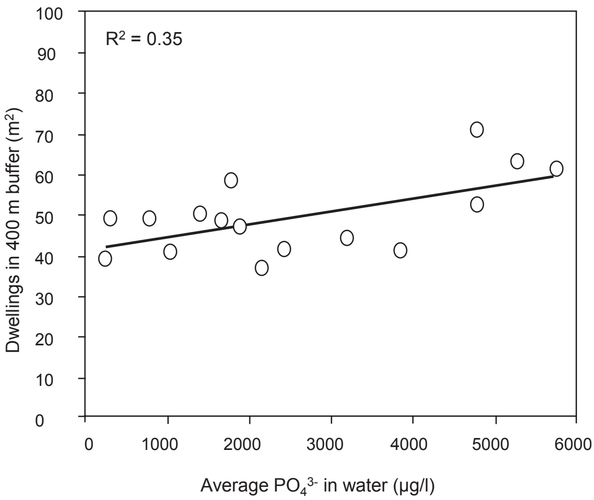

Fig. 25.5 Area occupied by Dwellings (m^2) measured in a land-use buffer of 400 m with average PO_4^{3-} concentrations in water, measured in three different periods (December 06, March 07 and July 07), $n=15$

Table 25.4 Pearson *r* correlations with concentration of eutrophication pollutants in water (NH_4^+ and PO_4^{3-}) with the number of non-native shrub species ($n=38$)

	NH_4^+	PO_4^{3-}
Number of non-native shrub species	0.459*	0.472*

*$p<0.05$

25.4 Discussion

The ecological integrity of the riparian vegetation of intermittent streams in the Mediterranean was negatively associated with the aquatic NH_4^+ concentration rather than with PO_4^{3-} and NO_3^- in water. The release of NH_4^+came mostly from the area covered by Annual Agriculture located close (200 m) to the stream. Ammonium is a product of the metabolism of organic nitrogen and the biological conversion, by bacteria, of NO_3^- to NH_4^+ in anaerobic waters and sediments. Inadequately treated municipal wastewater, agricultural runoff, groundwater contamination by fertilizer, storm waters, and feedlots are potential sources of NH_4^+ to streams. We suggest that the decrease in ecological integrity given by the QBR might be a consequence of direct or indirect effects of NH_4^+ on the vegetation.

Indirect effects of eutrophication shift the species composition, by altering the competitive balance between species (Dias et al. 2011; Mainstone and Parr 2002). In fact, the components of the QBR that seemed to be most affected by the NH_4^+ concentration are CQ and CS (Table 25.2). In the case of CS the decrease in this component is related to the loss of the tree component or the shrub layer of the riparian ecosystems with increasing NH_4^+ in streams. The changes in CQ were mostly due to the presence of exotic plant species. In fact, there is a significant correlation between both NH_4^+ and PO_4^{3-} in stream water and increasing numbers of non-native shrub plant species at the same sampling sites (Table 25.4). In accordance with what we found in this work, other authors (Lyon and Gross 2005; Mainstone and Parr 2002) have shown that the shrub layer appeared more prone to invasion by non-native species than the tree layer, demonstrated by the relatively high non-native species presence. They suggested that the shrub layer might be more susceptible to common disturbances, such as anthropogenic activity, grazing, low-intensity flooding and wildlife impacts. This is in accordance with the generally accepted fact that the increase in nutrients can promote increases in fast growing exotic species with invasive characteristics. This could explain the fact that QBR components such as total riparian cover did not change with increasing eutrophication gradient (Table 25.2): rather it was the species that changed. Other authors have also shown that very few native species have managed to survive in areas of the riparian zone adjacent to agricultural land (Meek et al. 2010).

In addition, direct toxic effects have also been reported. Reduced N is present in water in two forms: as a gas (NH_3) and ionized (NH_4^+) which exist in an equilibrium that is controlled by pH and temperature. In this work the NH_4^+ concentrations ranged from 369.9 to 1,027.5 μg l^{-1}. Ammonium, NO_3^- and PO_4^{3-} concentration can be toxic to plants and to aquatic life (Britto and Kronzucker 2002; Vieira et al. 2009): toxicity is restricted to combinations of extremely high nutrient concentrations and oxygen depletion. Thus toxicity is unlikely to explain much of the effect of NH_4^+ on the QBR index.

Concentrations <10 μg l^{-1} PO_4^{3-} can lead to nutrient limitation of aquatic organisms and P is often shown to be a limiting factor (Elwood et al. 1981). The values obtained here, were on average five times higher than the ones that were shown to be limiting (51.5 ± 16 μg l^{-1} of PO_4^{3-}). Thus there were no negative effects on the QBR index or its components (Table 25.2). However, there was a significant increase in frequency of exotic shrub species with increasing PO_4^{3-} concentration in stream waters (Table 25.4).

The values obtained here for NO_3^- (4.57 ± 0.56 mg l^{-1}) exceed the world average in natural rivers (~0.1 mg l^{-1}), but are in the range measured in streams running through areas of intensive agriculture in industrialized countries, which can reach 10 mg l^{-1} (Nijboer and Verdonschot 2004). However, in this study, high NO_3^- concentrations in stream waters did not affect the QBR index or its components. Nitrate does exert a fertilizing effect at this concentration (Britto and Kronzucker 2002), but this does not appear to be detrimental.

Within the studied land-use types the most abundant (Table 25.1) was pasture, due to the use of these areas for extensive livestock production which is hugely important economically. Despite occupying a large area, pastures were not a source of eutrophication elements to the stream waters (Table 25.2). In these rural areas, domestic housing and intensive livestock facilities could be a direct source of effluent for streams and an indirect source of disturbance (roads, air pollution, walk over, etc). However, houses and animal barns were only related to PO_4^{3-} pollution in streams, with no adverse impacts on riparian vegetation.

Ammonium released from Annual Agricultural areas located <200 m from the stream was shown to be associated with low ecological integrity of the riparian vegetation. The number of non-native shrub plant species increased with increasing NH_4^+ in stream water, together with other factors related to stream management such as, shrub removal. No recovery of native structure and functions has been found. Thus, agricultural practices close to streams i.e. <200 m, should be avoided. When the latter is not possible and where there is annual agriculture production within 200 m distance from the stream, well established native vegetation buffers should surround such areas. Preferably these should be connected to the riparian vegetation band, which should occupy a minimum of 30 m from the stream, as defined by the directions present in the management plan of this 2000 Natura Network (CMMN 2010).

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Chapter 26
Biodiversity of Acid Grasslands in the Atlantic Regions of Europe: The Impact of Nitrogen Deposition

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Abstract Reduction in the species richness of acid grasslands along a gradient of atmospheric nitrogen (N) deposition has previously been demonstrated in the UK (Stevens, Dise, Mountford, Gowing, Science 303:1876–1879, 2004). Further surveys of acid grasslands in the UK confirm this relationship. This chapter reports an examination of the relationship across the Atlantic region of Europe. Examining the cover of functional groups across this gradient reveals that forb cover is strongly reduced along the gradient of N deposition.

Keywords Atmospheric nitrogen deposition • Functional group cover • Grass: forb ratio • Plant species richness • *Violion caninae* grassland

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Table 26.1 Location of grasslands surveyed

Country	Number of grasslands surveyed
Belgium	9
Denmark	3
France	25
Germany	12
Eire, Ulster and Isle of Man	11
Netherlands	7
Sweden	4
Norway	9
Great Britain	73

26.1 Introduction

In 2004, Stevens et al. demonstrated a strong negative relationship between the level of ambient nitrogen (N) deposition and the species richness of acid grasslands across Great Britain, after accounting for other variables that affect diversity. Since then, negative correlations between N deposition and species richness have been reported in heathland and other grassland communities (Maskell et al. 2010). These findings corroborate experimental evidence gathered over many years showing the potential for declines in species richness and changes in composition in a broad range of habitats (e.g. Bobbink et al. 1998; Mountford et al. 1993; Clark and Tilman 2008). Despite strong experimental evidence, until now there has been little evidence at an international scale of how chronic N deposition is actually affecting the species richness and species composition of habitats. The BEGIN (Biodiversity of European Grasslands—Impact of Nitrogen deposition) project set out to address this knowledge gap with an international survey of acid grasslands.

26.2 Methods

153 acid grasslands belonging to the *Violion caninae* alliance were surveyed within the Atlantic biogeographic zone of Europe. Table 26.1 gives the locations of the grasslands. These were selected to cover the range of ambient N deposition in Europe and to give a distribution of sites at different latitudes and longitudes for different deposition values. The grasslands surveyed were not agriculturally improved and were managed by grazing or cutting. A full description of each site was made including latitude, longitude, aspect, slope, extent of grassland, soil depth and surrounding plant communities. At each site, five randomly located 2 m × 2 m quadrats were surveyed and all vascular plants and bryophytes were identified to species level. Cover was estimated using the Domin scale, to reduce the error associated with different people estimating cover by eye. To obtain the cover of functional groups, average values for Domin scores were used. Because Domin scores are ordinal, the average values can only be used to show relative changes. In order to calculate a grass: forb ratio, Domin scores were converted to percent cover by taking

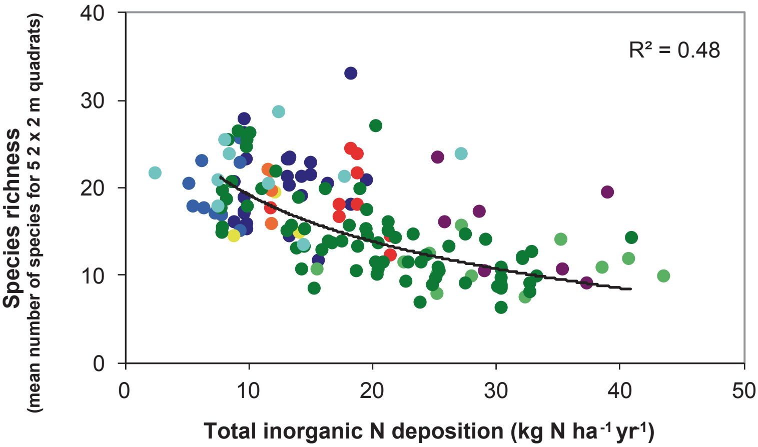

Fig. 26.1 Graph to show decline in species richness with increasing N deposition in 153 acid grasslands in the Atlantic biogeographic region of Europe. *Red*—Belgium, *yellow*—Denmark, *dark blue*—France, *dark green*—Great Britain, *light green*— Germany, *turquoise*—Ireland, Northern Ireland and Isle of Man, *purple*—Netherlands, *light blue*—Norway and *orange*—Sweden

the middle value in each cover grouping. These were then added together to give a total cover for each group in each quadrat and a mean was calculated for each site.

For each site, N deposition data were modelled using the EMEP-based IDEM model (Pieterse et al. 2007) or national deposition models depending on which were available in each of the countries surveyed. National models were used for Germany (Gauger et al. 2002), the Netherlands (Asman and van Jaarsveld 1992) and Great Britain (NEGTAP 2001; Smith et al. 2000). Comparisons between the models found good agreement in most regions, although uncertainty in the estimates produced is likely to vary between models.

Simple regression was conducted using SPSS v17. All variables were checked for normality and corrected if necessary.

26.3 Results

Earlier data from Great Britain (Stevens et al. 2004) showed a strong linear decline in species richness with increasing N deposition in 68 grasslands along the N deposition transect. The survey of ten additional sites in the UK confirmed this relationship giving a highly significant decline in species richness with increasing N deposition ($r^2=0.44$, $p<0.001$ with new sites; $r^2=0.55$, $p<0.001$ without new sites). The results also showed clear declines in species richness across Europe ($r^2=0.36$, $p<0.001$, Fig. 26.1) (Stevens et al. 2010).

Examining this relationship in more detail for the whole data set across the Atlantic zone by looking at the cover of functional groups (Fig. 26.2) gives a clearer

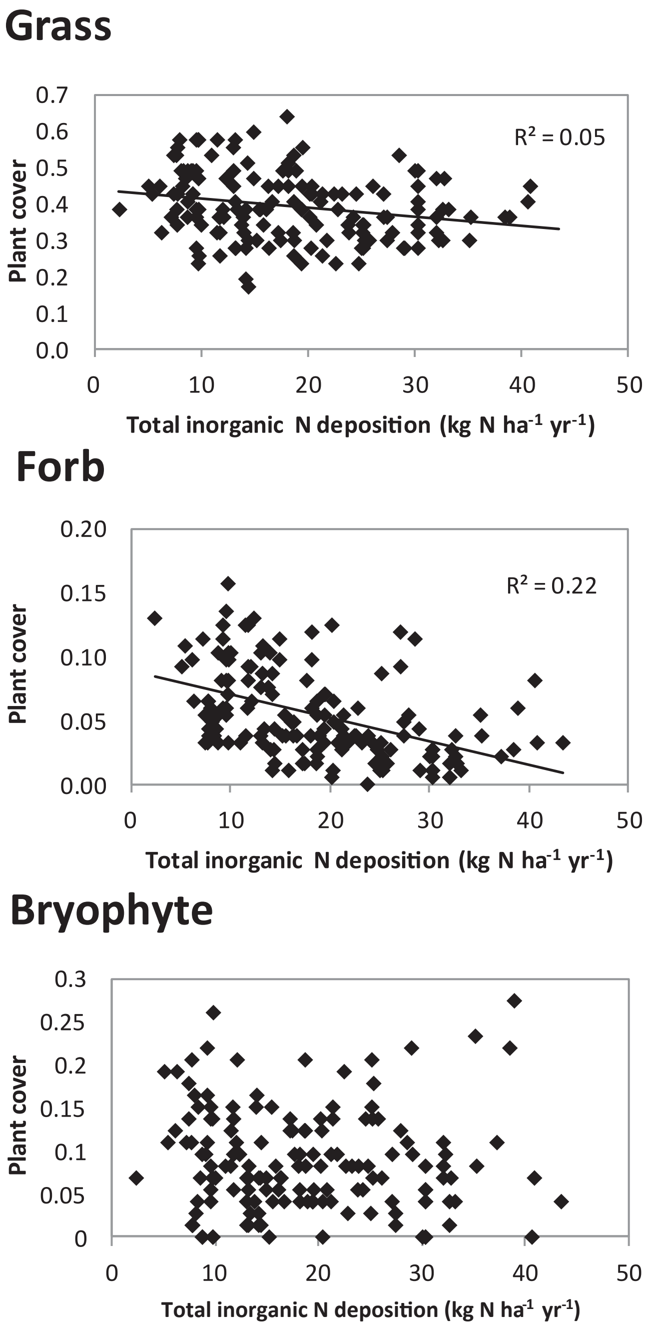

Fig. 26.2 Change in cover of functional groups with increasing N deposition in 153 acid grasslands in the Atlantic biogeographic region of Europe. Plant cover is calculated using a mean Domin score and can be considered relative cover

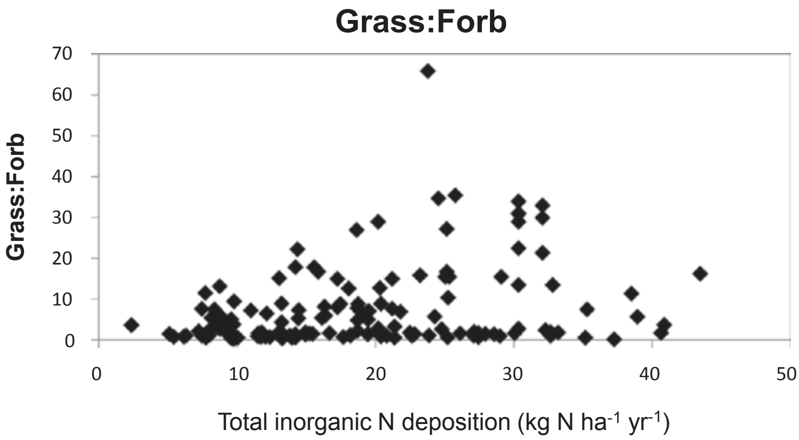

Fig. 26.3 Change in grass: forb ratio (based on estimated cover) with increasing N deposition in 153 acid grasslands in the Atlantic biogeographic region of Europe

idea of the changes that are occurring in the *Violion caninae* alliance. Grasses show a slight, but significant, decline in their cover, however the relationship is weak and the change in cover is very small. Forbs show a strong decline in cover along the N deposition gradient. The cover of bryophytes shows no significant relationship with N deposition but there is a slight decline in total cover with N deposition. Other variables, such as climate, have not been considered in this analysis. For further analysis of functional groups see Stevens et al. (2010).

The grass: forb ratio (Fig. 26.3) shows a tendency to be low at low deposition sites, but to become more variable at high deposition sites but this relationship is not significant.

26.4 Discussion

The results from this survey confirm the relationship between N deposition and species richness previously found in the UK by Stevens et al. (2004) and demonstrate it at an international scale (Fig. 26.1). The reduction in species richness in countries other than the UK show very similar results to those observed in the UK. These losses of species richness do not mean that species become locally extinct, or even that species are consistently lost from the grassland, although this is sometimes the case. A loss of species richness represents a reduced occurrence of species in five 2 m × 2 m quadrats placed within an area of one hectare.

The loss of species richness can be examined in more detail by looking at changes in the cover of the three functional groups of grasses, forbs and bryophytes. Grasses showed a small decrease in cover. This relationship is also very weak. Conversely, forbs show a very clear decline in cover with increasing N deposition. For the UK alone relationships were analysed using percentage cover and showed much clearer declines in cover of forb species, an increase in the cover of grasses and no change in bryophytes (Stevens et al. 2006). Comparison between the two methods of cover estimation is problematic but the direction of change in the results can be compared. The results show similar trends for forbs and bryophytes between the two analyses whereas grasses show the opposite result. Further work would be needed to determine if this is a consequence of the cover estimation used in the later survey or if this is a genuine difference between the UK response of vegetation and the response observed in the larger survey.

There are a number of potential reasons for the decline in forb and grass cover. Acidification may be causing a reduction in the occurrence and cover of species less able to tolerate acidic soil conditions (Tyler 2003). Eutrophication could lead to an increase in productivity of competitive species resulting in the suppression of less competitive species (Bobbink et al. 1998) but this is not consistent with the overall drop in cover values at high deposition sites. N deposition can also increase sensitivity to secondary stressors, both abiotic such as frost (e.g. Carroll et al. 1999) and biotic such as phytophagy (e.g. Brunsting and Heil 1985).

Bryophytes do not show any change in cover with N deposition although examining the abundance of individual species may reveal trends with some species increasing and others decreasing in relations to N deposition.

Because cover was estimated using the Domin scale, there is some loss of detail in the information. If percentage cover had been used, the trend for grasses may have been clearer. However, estimation of percentage cover varies between surveyors, so using percent cover would have increased error within the data set.

The grass: forb ratio has been shown to be a good indicator of N deposition in acid grasslands (Stevens et al. 2009). The use of Domin values for plant cover meant that the grass: forb ratio had to be estimated. There is a trend in the data for high grass: forb ratios to only occur at high deposition sites. This relationship is clearly driven by the strong decline in forb cover.

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Chapter 27
Effects of Increased Nitrogen Availability in Mediterranean Ecosystems: A Case Study in a Natura 2000 Site in Portugal

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Abstract Nitrogen (N) enrichment has been pinpointed as a main driver for biodiversity change. Most of our knowledge of effects of increased N availability on ecosystems comes from northern Europe and America. Most other ecosystem types have been neglected. Although Mediterranean ecosystems are N-limited biodiversity hotspots, very little is known about the effects of N enrichment in these systems. In contribution to filling this gap, our study examined the short-term effects of N enrichment in a N-manipulation (doses and forms) field study of a severely nutrient-limited Mediterranean ecosystem located in a Natura 2000 site in Portugal. N availability (dose and forms) was modified by the addition of 40 and 80 kg N ha^{-1} $year^{-1}$ as NH_4NO_3 or 40 kg N as NH_4^+ ha^{-1} $year^{-1}$ (control plots are not fertilized) since January 2007. The studied ecosystem was highly N responsive, i.e., visible changes were seen within one year of N additions: vascular plant and soil microbial diversity (soil bacteria and arbuscular mycorrhizal fungal spores)

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increased. Also the N concentration in leaves and litter increased, while the carbon-to-nitrogen (C/N) ratio of leaves and litter decreased.

Keywords C/N ration • Leaf litter • Leaves • Plant diversity • Soil microbial diversity

27.1 Introduction

Nitrogen (N) availability has increased globally during the 20th century due to industrialization and the use of N-containing fertilizers. As demands for food and energy continue to increase, the amount of N created and the magnitude of its consequences will also increase (Galloway et al. 2008), threatening semi-natural ecosystems since their stability depends upon low soil fertility (Bobbink et al. 1998; Phoenix et al. 2006).

Although most research on the effects of increased N availability has been conducted in temperate regions (northern Europe and America—Bobbink et al. 1998, 2010; Phoenix et al. 2006), the fate and the impact of N enrichment on ecosystems appears to be strongly dependent on climate (Galloway et al. 2008), ecosystem type and successional stage (Goodale et al. 2003). Mediterranean-type ecosystems occur worldwide and are especially sensitive to stress, as increased temperature and drought favour development of desert and grassland. Their distinctive seasonality of resource availability (water, nutrients and temperature) and very low levels of N availability (Gallardo et al. 2000; Cruz et al. 2008) reinforce the likelihood of N enrichment acting as a driving force for ecosystem structure and function. We are undertaking an integrated system-level study in a biodiversity and endemism hotspot for vascular plants (a Mediterranean ecosystem), where there is a need for a science based approach to management and policy (Phoenix et al. 2006). Our approach encompasses an examination of chemistry, microbiology, physiology and ecology in several compartments of the ecosystem.

27.2 Aims and Objectives

The aims of the work reported here were to:

- Determine the effects of increased N availability on the diversity (richness and evenness) and composition of above- and below-ground com-munities in a Mediterranean ecosystem.
- Understand the effect of N enrichment on the functionality of a Mediterranean ecosystem.
- Identify useful indicators of 'N saturation' for Mediterranean ecosystems.

27.3 Material and Methods

The study site is located in Arrábida (southern Portugal), a region with a typical Mediterranean climate: hot and dry summers, and mild and wet winters. The site belongs to the Natura 2000 network (PTCON0010 Arrábida/Espichel). Soil is skeletal (topsoil layer of approximately 15–20 cm) and true profiles cannot be discerned. Silt dominates in the soil (50%), while sand and clay contents are 30% and 20%, respectively (silt-sand-loam). The vegetation consists of a dense maquis, which developed after a fire event four years before the beginning of the N additions (summer 2003). The vegetation is dominated by a Mediterranean fire obligate seeder species (after a fire these species regenerate only by seed germination), *Cistus ladanifer* L. (Clemente 2002; Dias et al. 2011). Nitrogen availability (dose and form) at the site has been modified by the addition of NH_4NO_3, 40 (40AN) and 80 (80AN) kg N ha^{-1} year^{-1}, or NH_4^+, 40 kg N ha^{-1} year^{-1} (40A) (control plots are not fertilized) since January 2007. Nitrogen was added in three equal applications throughout the year, coinciding with distinct biological activities (spring, summer and middle autumn/winter). The experimental design consisted of 12 plots, each of 400 m^2. All measurements and analyses were performed within an internal 100 m^2 square.

Five soil-sampling locations were identified per plot, corresponding to the four corners and the centre. From each sample location, soil samples (2 cm diameter and 15 cm depth) were removed, sieved and stored at 4°C until analysed. Soil samples were analysed for soil microbial diversity (soil bacteria and arbuscular mycorrhizal fungal spores) and carbon-to-nitrogen (C/N) ratio. Sampling took place in spring.

Changes in plant community composition were sampled within one 5 m × 5 m square per experimental plot (within the internal 100 m^2). Percentage of vascular plant species cover (herbaceous included), and of bare soil were recorded. Each species' cover was calculated from the total projected crown area (calculated from two perpendicular diameters, assuming elliptical shape).

Changes in belowground community structure and diversity were analysed. Temperature Gradient Gel Electrophoresis (TGGE) fingerprinting was applied to monitor the impact of the N additions in the soil bacteria community structure. Arbuscular mycorrhizal fungi were further assessed through morphological identification of arbuscular mycorrhizal fungal spores (Dias et al. 2014, Chap. 28, this volume) and analysis of mycorrhizal morphotypes on root-tips.

27.4 Major Results and Discussion

The studied ecosystem was highly N-responsive: one year of N enrichment was sufficient to change plant (Dias et al. 2011) and soil microbial communities (bacteria—Fig. 27.1—and arbuscular mycorrhizal fungal communities—(Dias et al. 2014, Chap. 28, this volume). The N fertilization increased plant diversity (richness and evenness—Dias et al. 2011): plant richness appeared to respond to the N dose

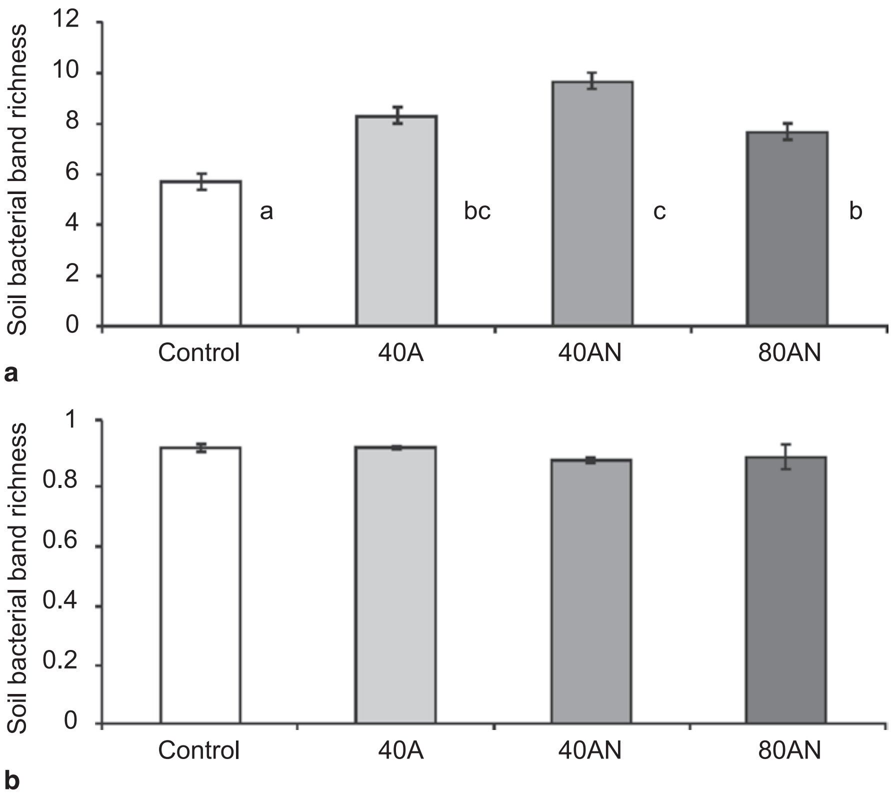

Fig. 27.1 Response of the soil bacterial community to distinct N availabilities (Control, 40A, 40AN, and 80AN) in terms of band richness (**a**), and evenness (**b**). Soils were collected in the second Spring of N fertilization. Band richness and evenness were calculated based on the numerical analysis of TGGE profiles. Different letters refer to statistically significant differences between treatments (ANOVA $p < 0.05$ followed by a Bonferroni test). Values represent the mean ($n=3$ experimental plots per treatment) ± se

while plant evenness appeared to respond to the form of N. This increase in diversity seems to contradict most of the worldwide studies published so far (see Bobbink et al. 2010 for review). However, current knowledge suggests that the effects of N enrichment depend on the initial N status of the system: on highly productive sites, there is a potential for biodiversity loss and vice versa (Emmett 2007; Chalcraft et al. 2008). Similar results have been reported for lichen community diversity in cork-oak woodland (Pinho et al. 2009) and other systems under similar circumstances (e.g. Calvo et al. 2005).

Increased N availability promoted the appearance of new herbaceous maquis species and maintained the ruderals. Changes in plant cover were analysed on a plant group basis highlighting the effects of increased N availability. Plant groups could be viewed as: (i) benefiting from N enrichment—ruderals and herbaceous maquis species; (ii) benefiting from N enrichment as long as there was no ammo-

Table 27.1 Responses of the C (top 3 rows), N (middle 3 rows) concentrations and the C/N ratio (bottom 3 rows) of the soil and *C. ladanifer's* leaves and leaf litter to N enrichment (Control, 40A, 40AN and 80AN). Soils and *C. ladanifer's* leaves were collected in Spring 2008, while the leaf litter was collected in Summer 2008 (the time of the year when these plants shed their leaves). Different letters (a and b) refer to statistically significant differences between treatments (ANOVA $p < 0.05$ followed by a Bonferroni test). Values represent the mean ($n=3$ experimental plots per treatment) ± se

		Control	40A	40AN	80AN
C (%)	Soil	1.7 ± 0.2	1.6 ± 0.2	1.9 ± 0.0	1.7 ± 0.3
	Leaf	48.9 ± 0.1	48.5 ± 0.3	48.5 ± 0.1	48.5 ± 0.1
	Litter	45.6 ± 0.5	44.2 ± 0.6	45.8 ± 1.7	45.4 ± 1.3
N (%)	Soil	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
	Leaf	1.4 ± 0.1[a]	1.6 ± 0.1[ab]	1.7 ± 0.1[ab]	1.8 ± 0.0[b]
	Litter	0.3 ± 0.1[a]	0.6 ± 0.1[ab]	0.6 ± 0.0[ab]	0.8 ± 0.0[b]
C/N ratio	Soil	16 ± 0	15 ± 1	15 ± 0	14 ± 1
	Leaf	36 ± 1[a]	31 ± 2[ab]	28 ± 2[b]	28 ± 0[b]
	Litter	166 ± 81	81 ± 16	83 ± 2	55 ± 2

nium toxicity—ericaceous, legume shrubs and grasses; and (iii) disadvantaged by N enrichment especially in the form of ammonium—summer semi-deciduous (Dias et al. 2011).

Nitrogen enrichment also increased the diversity of the soil microbial community: increased richness and evenness of arbuscular mycorrhizal fungal spores (Dias et al. 2014, Chap. 28, this volume) and increased bacteria band richness (Dias et al. 2011 and Fig. 27.1). Plots fertilized with 40AN displayed the highest bacterial band richness, while non-fertilized plots had the lowest. Increasing the N dose to 80AN did not increase richness further, rather it reduced richness compared with the 40A and especially the 40AN, suggesting adverse effects at higher N doses. The form of N did not affect soil bacterial band richness, since the ammonium treatment (40A) was not significantly different from the mixed N (40AN). Bacterial band evenness showed no differences between treatments.

Soil analyses in the second spring after the beginning of the N additions showed low concentrations of C and N and low C/N ratio (Table 27.1) which were within the range of other Mediterranean soils (Cruz et al. 2008; Gallardo et al. 2000; Rutigliano et al. 2009). Moreover, data show that the soil C and N concentrations and the C/N ratio did not respond to the N additions (40 or 80 kg N ha^{-1} $year^{-1}$). Considering that the soil C/N ratio has been used to predict the N retention capacity of the soil (Emmett 2007) and considering the low C/N ratios (soil C/N < 25, indicates the soil does not store N—Hyvönen et al. 2008), our data suggest that soils in Mediterranean ecosystems, with their very low C content, do not function as N reservoirs.

In contrast to the soil, *C. ladanifer* (the dominant plant species—Clemente 2002; Dias et al. 2011) responded to the N enrichment with increased N concentrations and decreased C/N ratios in both green leaves and leaf litter (Table 27.1). Carbon concentrations in green leaves and litter were not affected by N additions. In comparison to the control, fertilization with 80AN resulted in significantly higher

N concentrations in both leaves and litter while both treatments receiving 40 kg N ha^{-1} $year^{-1}$ showed intermediate N concentrations, suggesting that this parameter responded to the N dose. On the other hand, both treatments receiving ammonium nitrate (40AN and 80AN) displayed lower leaf C/N ratios compared with 40A and significantly lower than the control, suggesting that the C/N ratio responded to the form of N. In the litter, the addition of 40 kg N ha^{-1} $year^{-1}$ (40A and 40 AN) reduced the C/N ratio by similar amounts, and doubling the ammonium nitrate (80AN) reduced the C/N even more, indicating the C/N ratio was most affected by N dose (Table 27.1).

The rapid and significant response of *C. ladanifer* in terms of C/N ratio highlights the plants' role in N retention in carbon, nutrient poor soils, such as found in Mediterranean ecosystems. Data suggest that plants retain N through two distinct pathways: effective uptake via the roots and effective remobilisation and withdrawal of the N prior to leaf fall (litter C/N ratio—Craine 2009). Similar results were obtained in another Mediterranean-type ecosystem (Vourlitis et al. 2007), reinforcing the use of the C/N ratio in litter especially and leaves, as indicators of N enrichment for Mediterranean ecosystems. Finally, the data highlight the effectiveness of plants at competing with microorganisms for the added N (Schimel and Bennett 2004).

27.5 Concluding Remarks

For the richness and evenness of the bacterial community and N and C concentrations in the leaf, litter and soil no significant effects of N form, reduced compared with the combination of reduced and oxidised N, were found. However, the N dose was important for bacterial community richness: N additions significantly increased richness however, 80 kg N ha^{-1} $year^{-1}$ decreased richness compared with 40 kg N ha^{-1} $year^{-1}$. The highest N load significantly increased leaf and litter N concentrations (0 cf. 80 kg N ha^{-1} $year^{-1}$).

Nitrogen enrichment in the present Mediterranean ecosystem changed above- (Dias et al. 2011) and below-ground communities (Fig. 27.1 and Dias et al. 2014, Chap. 28, this volume), highlighting the important role of plants in N retention. The biodiversity increase in above and below-ground communities probably represents an alleviation of the N limitation. Given that community changes in species composition are likely to change the biota's functional traits, N-driven biodiversity changes are likely to alter ecosystem processes (Chapin et al. 1997).

The present study suggests the existence of potential N enrichment indicators, namely litter and to a lesser extent leaf C/N ratios (Table 27.1), arbuscular mycorrhizal fungal species (Dias et al. 2014, Chap. 28, this volume) and increased cover of ruderal plant species (Dias et al. 2011). However, given that this study has only evaluated responses over <2 years, it will be important to evaluate these indicators and the dose response over a longer time-frame. Finally and although establishing the linkage between biodiversity and ecosystem function is a substantial scientific challenge (Fitter et al. 2005), we are currently addressing the effects of N enrichment on decomposition, soil-atmosphere gaseous fluxes and key soil N processes (fixation, nitrification and denitrification).

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Chapter 28
Species of Arbuscular Mycorrhizal Fungal Spores can Indicate Increased Nitrogen Availability in Mediterranean-type Ecosystems

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Abstract Mycorrhizal fungi form ecologically important connections between plants and soils, and although nitrogen (N) enrichment has been implicated in the decline of ectomycorrhizal fungal diversity, they are rarely considered in studies

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investigating the effects of increased N availability on plant species diversity. This chapter describes the effects of N enrichment on the soil fungal community and in particular on arbuscular mycorrhizal fungal (AMF) spores, in a Mediterranean ecosystem in a Natura 2000 site in southern Portugal (PTCON0010 Arrábida/Espichel). Soil fungal community structure was affected by the addition of 80 kg N ha^{-1} year^{-1} as NH_4NO_3 within 2 years. The effects of N addition on AMF diversity (richness and evenness) appear to depend on the form of N, since the addition of 40 kg N ha^{-1} year $^{-1}$ as ammonium increased AMF spore richness and evenness proportionally more than the addition of 40 kg N ha^{-1} year^{-1} as ammonium plus nitrate. The composition of AMF species may serve as a sensitive indicator of N enrichment.

Keywords Arbuscular mycorrhizal fungi • Evenness • Mediterranean • Richness • Soil fungi

28.1 Introduction

Nitrogen (N) availability is increasing globally (Galloway et al. 2008), which may cause severe damage to environmental systems at local, regional and global scales, as availability of nutrients is a key factor in determining ecosystem function and stability (Bobbink et al. 1998). Sala et al. (2000) developed biodiversity change scenarios in terrestrial ecosystems, ranking increased N deposition as the third main driver. Subsequent works inferred that N deposition constitutes a threat to biodiversity (Phoenix et al. 2006; Clarisse et al. 2009). Although micro-organisms comprise much of the Earth's biodiversity and have important roles in ecosystem functioning (Fitter 2005), most studies have focused solely on the threat that increased N availability poses for plant diversity (see Bobbink et al. 2010). However, in recent years, there has been a growing awareness amongst plant and soil microbial ecologists of the need to understand the connectivity between plants and soil microbes. Given the importance of fungi in ecosystem processes, such as decomposition and the provision of plant nutrients (through the formation of mycorrhizal symbiosis), it is likely that N availability can potentially interfere with the soil fungal community directly or through effects on biomass/litter composition. Despite the fact that mycorrhizal fungi form ecologically important connections between plants and soils, they are rarely considered in studies investigating the effects of N enrichment on species diversity. Some studies conducted in northern Europe and America, where ectomycorrhizal associations with forest trees are common (see Wallenda and Kottke 1998 for review) have addressed this issue: Lilleskov et al. (2002) implicated N enrichment in the decline of ectomycorrhizal fungal diversity. The ecological and functional importance of other types of mycorrhizal fungi varies in accordance with the ecosystem type.

Although arbuscular mycorrhizal fungi (AMF) significantly increase plant access to nutrients, and their effects are more relevant under stress conditions (low nutrient and water availability, namely in Mediterranean ecosystems), few studies have focused on N-driven changes in AMF. Enhanced N availability has been shown to change Mediterranean plant communities (Allen et al. 1998; Bonanomi et al. 2006; Vourlitis et al. 2009; Dias et al. 2011), which may influence (or be influenced by) the efficiency of the mycorrhizal symbioses in the acquisition of nutrients (namely N and P) and therefore on the relative competitive capacity of co-existing plant species.

28.2 Aims and Objectives

The aims of the work reported here were to:

- Study the short-term effects of N enrichment on the soil fungal community (and in particular AMF community) in a Mediterranean ecosystem; and
- Understand the effect of N dose and form on soil fungi and AMF spores.

28.3 Material and Methods

The study site is located in Arrábida (Portugal, 38°29' N, 9°01' W), with a typical Mediterranean climate: hot and dry summers, and mild and wet winters. The site belongs to the Natura 2000 network (PTCON0010 Arrábida/Espichel). The soils have been classified as Calcic rhodo-chromic luvisoils and calcareous chromic cambiols, according to the FAO system (Cruz et al. 2008). The soil is approximately 15–20 cm deep and has a silt-sand-loam texture (Correia 1988). The vegetation consists of a dense maquis (Eunis habitat type F5.2), established through a secondary succession after a fire event in the summer 2003 (four years before the beginning of N additions). The applied treatments were: addition of NH_4NO_3, 40 (40AN) and 80 (80AN) kg N ha^{-1} $year^{-1}$, or 40 (40A) kg N-NH_4^+ ha^{-1} $year^{-1}$, control plots are not fertilized. Fertilization started in January 2007. Nitrogen is added in three equal applications throughout the year and each treatment has three replicates (400 m^2 experimental plots).

The effects of N enrichment on soil fungal community and AMF spores were assessed in December 2008. Temperature Gradient Gel Electrophoresis (TGGE) fingerprinting was applied to monitor the impact of the N additions on the soil fungal community structure: total DNA was extracted from the soil samples and universal primers defined for fungal 18S rRNA genes were used for PCR amplification. The resulting amplification products were separated by TGGE. AMF spores were extracted from soil samples by wet sieving following sucrose gradient centrifugation. AMF spores were identified to species from the subcellular structures forming the asexual spores. Differences in community parameters per treatment were analyzed by a one-way ANOVA, followed by a Bonferroni test ($p < 0.05$), or by a Games-Howell test whenever homogeneity of variances was not confirmed by the Levene's test.

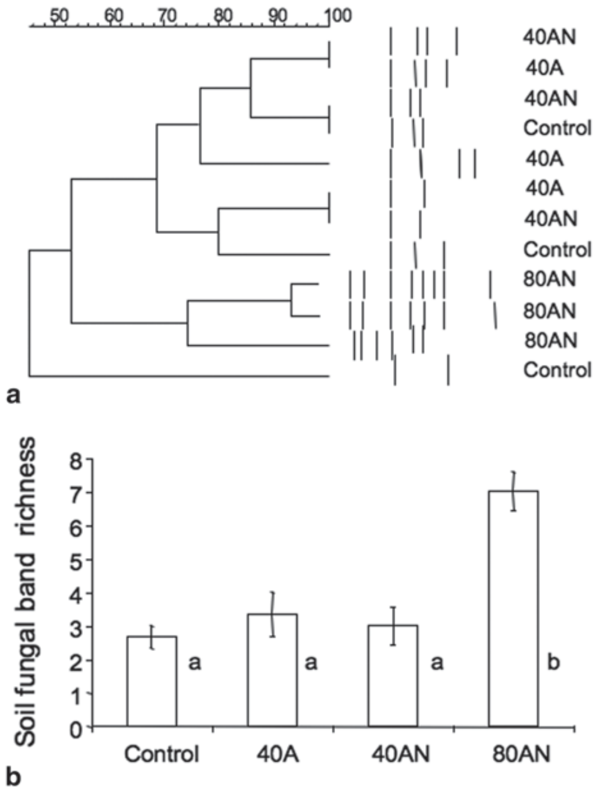

Fig. 28.1 Response of soil fungal community to N additions including ammonium (*A*) or ammonium with nitrate (*AN*), in terms of dendrogram (**a**) and band richness (**b**) according to treatments (see materials and methods). The soil was sampled in December 2008. Different letters refer to statistically significant differences between treatments (ANOVA $p<0.05$ followed by a Bonferroni test). Values represent the mean ($n=3$ soil samples per treatment) ± se

Differences between the two treatments receiving 40 kg N ha^{-1} $year^{-1}$ were analyzed by a t-test ($p<0.05$). When data violated normality, a Kruskal–Wallis test (non-parametric, $p<0.05$), was applied. SPSS software, version 17.0, was used for all tests.

28.4 Results and Discussion

Nitrogen enrichment changed the soil bacteria (Dias et al. 2014, Chap. 27, this volume) and fungal communities (Fig. 28.1). Based on similarity levels in the dendrogram for the soil fungal community (Fig. 28.1a), two main clusters could be observed, which included: 80AN plots (75 % similarity), and all the remaining treatments including the controls that were very heterogeneous and therefore scattered through the dendrogram. This clustering was corroborated by the soil fungal bands richness (Fig. 28.1b): 80AN plots showed a significantly higher number of bands than the remaining treatments. Thus, short-term N additions of 80AN to a N poor ecosystem increased the diversity of soil fungi.

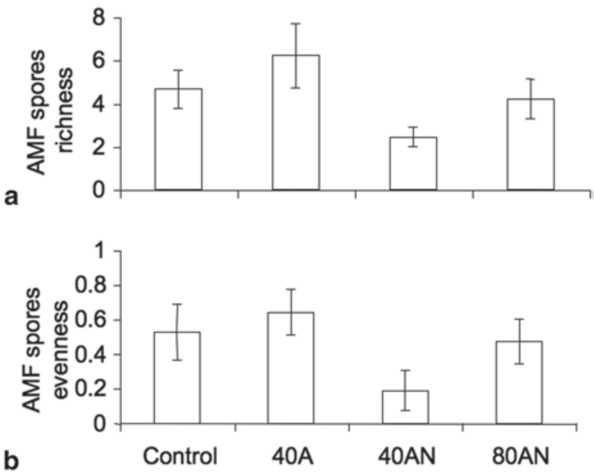

Fig. 28.2 Response of AMF spores richness (**a**) and evenness (**b**) to distinct N availabilities. Values represent the mean ($n=9$ soil samples per treatment) ± SE

In order to evaluate if the changes in the soil fungal community were accompanied by changes in its functionality, the community of AMF spores was also assessed. A total of 16 species of AMF was identified from the genus *Glomus* (12 species), *Acaulospora* (3 species) and *Paraglomus* (1 species). AMF spores were highly responsive to N enrichment. Two years of N addition was sufficient to induce changes in terms of richness, evenness (Fig. 28.2) and species composition (Table 28.1). Some species were exclusive to the 40A such as *Acaulospoa morrowiae* and *G. mosseae*, while others were detected in all treatments (e.g. *G. coremioides* and *G. fasciculatum*). The total number of AMF species was within the range of AMF species identified in a similar Californian Mediterranean-type ecosystem (Egerton-Warburton and Allen 2000).

The effects of the N fertilization treatments on AMF spore richness and evenness (Fig. 28.2) were more dependent on the N form than on the N dose. Since the biggest and significant differences in AMF spore richness and evenness were found between the 40A and 40AN treatments (t-test $p=0.046$ and 0.05 respectively). Taking into account data from the 80AN, these observations suggest that nitrate influences mycorrhizae more than ammonium, corroborating observations by Atkinson (2009).

Nitrogen enrichment did not reduce AMF spores richness contrary to other studies (e.g. Egerton-Warburton and Allen 2000; Lilleskov et al. 2002; Högberg et al. 2003). This opposite response could be due to the low initial N availability in the ecosystem, the short time scale of the N enrichment and/or be related to the observed changes in plant community (Dias et al. 2011). Indeed, Egerton-Warburton et al. (2007) found that the host-plant (C_3 or C_4) was an important determinant of AMF community structure (spores and hyphal community) in grasslands subject to distinct N availabilities.

Nitrogen enrichment changed the species composition of the AMF spores. Five groups of AMF were identified: those only observed in control plots; those only observed in N fertilized plots; those only observed in the plots receiving 40 kg

Table 28.1 List of the AMF spores species observed in soil samples ($n=3$ per experimental plot) collected in December 2008. The species of AMF spore were grouped according to their presence (*light grey*) or absence (*no fill*) in soils with distinct N availabilities. (Control, 40A, 40AN and 80AN; $n=3$ experimental plots per treatment)

AMF spore species	Control	40A	40AN	80AN
Glomus etunicatum				
Glomus sp1				
Acaulospora mellea				
Glomus geosporum-like				
Glomus sp4				
Acaulospora excavata				
Paraglomus occultum				
Glomus mosseae				
Glomus sp5				
Glomus sp6				
Acaulospora morrowiae				
Glomus coremioides				
Glomus glomerulatum				
Glomus fasciculatum				
Glomus sp2				
Glomus sp3				

N ha^{-1} $year^{-1}$ of ammonium—40A or 80AN; those observed in all treatments (Table 28.1). Based on the mutually exclusive nature of the first two groups of AMF spores we suggest that species included in these two groups could be used to indicate low and high N availability, respectively. Such shifts in the AMF community in response to N enrichment were also observed by Egerton-Warburton and Allen (2000) in their study of the effects of N enrichment on nine communities of coastal sage scrub, a Mediterranean-type ecosystem dominated by deciduous shrubs.

Changes in the species richness of AMF spores and composition may reflect changes in the AMF communities colonizing plant roots, which could have important consequences for the efficiency of the mycorrhizal symbiosis with respect to nutrient acquisition (namely N and P), the relative competitive capacity of coexisting plant species and stress tolerance.

28.5 Conclusions

- Numerical analysis of TGGE fingerprinting showed that soil fungal community responded to short-term 80AN in terms of richness and their structure;
- The effects of N addition on AMF diversity (richness and evenness) appear to depend on the form of the N addition, since 40A had greater AMF richness and evenness than 40AN.
- Changes in soil fungal community were not related to changes in AMF spores.
- The species composition of AMF spores may provide a sensitive indicator of N enrichment, at least in Mediterranean ecosystems.

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Chapter 29
Nitrogen Biogeochemistry Research at Fernow Experimental Forest, West Virginia, USA: Soils, Biodiversity and Climate Change

Frank S. Gilliam

Abstract Nitrogen (N) saturation arises when atmospheric inputs of N exceed biological N demand, resulting in loss of NO_3^- in streams, accompanied by the loss of nutrients (Ca and Mg) that are essential to forest health. Previous studies have shown that some watersheds the Fernow Experimental Forest (FEF), West Virginia, USA, are among the more N-saturated sites in North America. Research from the Gilliam laboratory at Marshall University (West Virginia, USA) began focusing specifically on N biogeochemistry in 1993 with establishment of plots at FEF to carry out long-term *in situ* ("buried bag") incubations in three watersheds: two control (WS4, WS7) and one treatment (WS3). This was done in conjunction with the Fernow Watershed Acidification Study, established by the USDA Forest Service in 1989 to treat an entire watershed (WS3) with aerial applications of 35 kg N ha^{-1} $year^{-1}$. The initial period (1993–1995) exhibited increases in rates for all watersheds, but especially in treated WS3. This period has been followed by declines in net nitrification, which is consistent with current declines in stream NO_3^- and has been especially pronounced in WS3 since 1998. Also during this time, sampling of the herbaceous layer (vascular plants ≤1 m in height) has revealed pronounced changes in response to N treatments on WS3, especially in the increase of the shade-intolerant *Rubus* spp. Future work will investigate the effects of freezing on soil N dynamics. Preliminary results indicate that freezing exacerbates the symptoms of N saturation already seen in soils at FEF, further increasing already high rates of net nitrification.

Keywords Forest biodiversity • Herbaceous layer • Nitrogen saturation • Temperate hardwood forest

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29.1 Introduction

Nitrogen (N) has been the focus of extensive basic and applied ecological research, more recently and more specifically by biogeochemists. This extends from the discovery of nitrogen (N) as an element in 1772, to its central place in von Liebig's Law of Minimum for plant growth articulated in 1827, to the discovery of symbiotic N fixation in 1888, to the development of the Haber-Bosch process in 1913 (initiating of its use as fertilizer in crop production), and finally to the present awareness that excess N in the environment can alter the structure and function of ecosystems (Vitousek et al. 1997; Aber et al. 1998; Fenn et al. 1998). As with any scientific discipline, N biogeochemistry has undergone numerous paradigm shifts over time (Vitousek and Howarth 1991; Schimel and Bennett 2004).

It is becoming increasingly apparent that excess N in the environment can cause notable declines in plant species diversity in a variety of terrestrial and aquatic ecosystems (Bobbink et al. 1998, 2010; Gilliam 2006; Lu et al. 2010; Rabalais 2002). Site-specific variability in plant and soil response to excess N precludes broad generalizations regarding the mechanisms behind these effects in terrestrial ecosystems. For example, in temperate hardwood forests, experimentally-added N has been shown to increase cover/biomass of a few nitrophilous herbaceous species, decreasing the usually much higher numbers of N-limited herb species (Gilliam 2006; Bobbink et al. 2010). By contrast, tropical evergreen broadleaf forests are typically less N-limited and more phosphorus-limited, and additions of N have been shown to decrease herb stratum diversity by eliminating ferns and seedlings of diverse tree species via aluminum mobility, calcium leaching, and enhanced fine root mortality (Lu et al. 2010).

Biogeochemical research at Fernow Experimental Forest (FEF), West Virginia, USA, has a rich history (Adams et al. 2006). Collection of hydrochemical data began for the long-term reference watershed (WS4) in 1980, with research on silvicultural practices pre-dating that. Research that focused more specifically on N biogeochemistry was initiated via the Fernow Watershed Acidification Study, which began as a now-terminated pilot study in 1987 on a watershed adjacent to Fernow. In 1989, it was established on FEF proper, and remains currently on-going. A distinctive feature of the Watershed Acidification Study is that it involves a whole-watershed application of simulated acidic deposition via three aerial additions of $(NH_4)_2SO_4$ per year, representing a total N addition of 35 kg N ha^{-1} $year^{-1}$. This is applied as solid powder, initially via helicopter and currently via airplane, and remains one of few studies utilizing N manipulations at the scale of an entire watershed (Adams et al. 2006).

In 1991, 15 permanent vegetation plots were established in each of four watersheds of contrasting stand age at FEF, with a particular focus on interactions between the forest canopy and the herbaceous stratum, as well as plant-soil interactions, with a focus on how these interactions might vary with forest succession (Gilliam and Roberts 2003). A sub-set of seven of these original plots in each of three watersheds—WS3, WS4, and WS7—were selected in 1993 for monthly *in* *situ* incubation of soil to examine spatial and temporal patterns of net N mineralization and nitrification. This represented the first work at FEF specifically to address a phenomenon that until that time had been described more in Europe and experimental studies in the northeastern United States—N saturation.

Nitrogen saturation arises when atmospheric inputs of N exceed biological N demand, resulting in loss of NO_3^- in streams (Aber et al. 1998). In addition to creating environmental problems for impacted aquatic systems, N saturation is also commonly accompanied by the loss of nutrients ($Ca^{2+}$and Mg^{2+}) (the mobile anion effect) that are essential to plant growth and forest health. Some of the earlier studies published on N saturation in the US (e.g., Stoddard 1994; Gilliam et al. 1996; Peterjohn et al. 1996, 1999) have identified some watersheds at FEF to be among the more N-saturated sites in North America. Increased mobility and leaching of $Ca^{2+}$and Mg^{2+}has been clearly being linked at FEF to increased N deposition, associated enhanced nitrification and movement of NO_3^-, along with evidence of decreases in growth rates of dominant tree species (Peterjohn et al. 1996; Christ et al. 2002; May et al. 2005; Gilliam et al. 2005; Adams et al. 2006). Other problems associated with N saturation include increased production of the greenhouse gas, N_2O (Peterjohn et al. 1998; Wallenstein et al. 2006a). Work at FEF has also suggested that N saturation has led to phosphorous limitation in several watersheds (Gress et al. 2007).

Here I summarize the research on N biogeochemistry that has been carried out at FEF by ecologists at Marshall University, Huntington, West Virginia, USA: (1) long-term monitoring of rates of net N mineralization and nitrification using *in situ* incubations, (2) herbaceous layer dynamics, and (3) effects of freezing on soil N dynamics.

29.2 Methods

29.2.1 Study Site

The Fernow Experimental Forest occupies approximately 1,900 ha of the Allegheny Mountain section of the unglaciated Allegheny Plateau near Parsons, West Virginia (39° 03′ N, 79° 49′ W). Precipitation at FEF averages approximately 1,430 mm $year^{-1}$, being higher during the growing season and increasing with elevation. Concentrations of acidic species in wet deposition (including snow) (H^+, SO_4^{2-}, and NO_3^-) are among the highest in North America (Gilliam and Adams 1996). Watershed soils are coarse-textured Inceptisols (loamy-skeletal, mixed mesic Typic Dystrochrept) of the Berks and Calvin series sandy loams derived from sandstone (Gilliam et al. 1994).

Dominant tree species on FEF watersheds vary with stand age. Early-successional species, such as black birch (*Betula lenta* L.), black cherry (*Prunus serotina* Ehrh.), and yellow-poplar (*Liriodendron tulipifera* L.) are dominant in young stands, whereas late-successional species, such as sugar maple (*Acer saccharum* Marshall) and northern red oak (*Q. rubra* L.), are dominant in mature stands. Dominant herbaceous layer species vary less with stand age and include stinging nettle (*Laportea canadensis* (L.) Wedd.), violets (*Viola* spp.) and several ferns (Gilliam et al. 2006).

Three watersheds have served as sites for various studies. WS4 supports a >100 year-old mixed-aged stand, serving as the long-time reference watershed at FEF. WS7 supports an approximately 40 year-old even-age stand, and whereas WS3 supports an approximately 40 year-old even-age stand and serves as the "treatment" watershed, whereas WS4 and WS7 were the controls. WS3 has received three aerial applications of $(NH_4)_2SO_4$ per year, beginning in 1989. March (or sometimes April) and November applications represent approximately 7.1 kg N ha^{-1}; July applications are approximately 21.2 kg N ha^{-1}. The total amount of N deposited on WS3 (application plus atmospheric deposition) is approximately 54 kg N ha^{-1} $year^{-1}$, or about three times ambient inputs (Adams et al. 2006).

29.2.2 Field Sampling

Mineral soil is collected on an on-going basis on WS3, WS4, and WS7 by hand trowel at five points within each of seven plots per watershed to a depth of 5 cm using methods following Gilliam et al. (1996). These five samples are bulked, thoroughly mixed, and then placed in two polyethylene bags—one brought back to the laboratory for immediate extraction and analysis (see *29.2.3 Laboratory and data analyses* below) and the other incubated *in situ* by burying it 5 cm beneath the mineral soil surface for ~30 d during all months of the growing season. This was initiated in 1993 and is reported here up to 2005.

The herbaceous layer is sampled on an on-going basis on WS3 and WS4 within seven circular 0.04-ha sample plots (adjacent to soil plots described previously). Each vascular plant species <1 m in height is identified and visually estimated for cover (%) within 5 1-m^2 circular sub-plots in each sample plot. Sub-plots were located within sample plots using a stratified-random polar coordinates method, which was employed to avoid over-sampling the center region of circular plots (Gilliam et al. 2006). This was initiated in 1991 and is reported here through 2003.

To determine the effects of soil freezing on soil N dynamics, mineral soil was taken at three sites shown by previous investigations to represent a gradient in rates of net nitrification: LN (low nitrification rates), MN (medium rates), and HN (high rates), using methods described in Gilliam et al. (2010). Sub-samples of soil from each plot were extracted for analysis of NH_4^+ and NO_3^- immediately upon return to the laboratory (see *29.2.3 Laboratory and data analyses* below). Approximately 50 g of each sample was placed into each of three 120-mL sterile polyethylene Whirl-Pac® bags for freezing treatment as follows: 0, −20, and −80 °C. The −80 °C treatment was chosen as an extreme temperature to determine whether −20 °C may represent a temperature threshold for freezing effects, i.e., if there are no differences between −20 and −80 °C. The remaining soil was kept in the original bag and refrigerated at 4 °C as Control. All treated samples were subjected to treatments for 7 d.

29.2.3 Laboratory and Data Analyses

All mineral soil, including that from *in situ* incubations and the soil freezing experiment, was extracted with 1N KCl (10:1 volume:weight) and analyzed for $NH_4^+$and NO_3^-. From 1993 to 1995 this was done with an Orion 720A pH/ISE meter and NH_4^+ and NO_3^- electrodes. For the 2005 field samples, NH_4^+ and NO_3^- were determined colorimetrically with a TrAACS 2000 continuous flow spectrophotometer. For the soil freezing experiment, $NH_4^+$and NO_3^- were determined colorimetrically with an AutoAnalyzer III continuous flow spectrophotometer.

Temporal patterns of *in situ* net N mineralization and nitrification were assessed with second-order polynomials. Species diversity of the herbaceous layer was calculated using the Shannon-Wiener index with natural log (ln) transformation (Gilliam et al. 2006). Means for herb layer diversity, species richness, and cover were compared between WS3 and WS4 and among years (1991 to 2003) using repeated measures analysis of variance (ANOVA). Mean net N mineralization and nitrification potentials were compared among freezing treatments within sites and among sites within treatments using ANOVA and least significant difference tests.

29.3 Results and Discussion

29.3.1 In Situ Incubations

As reported in Gilliam et al. (2001), annual net N mineralization and nitrification increased on all three watersheds during the period 1993–1995, with sharpest increases noted for N-treated WS3. It is thus quite notable that the 2002 and 2005 sampling revealed substantially declining rates for all watersheds since this time, with net nitrification on WS3 currently > 80 % less than the 1995 maximum (Fig. 29.1). Temporal patterns in net nitrification at FEF are consistent with observations of declining concentrations of NO_3^- in streams for WS3, WS4, and WS7, and in soil water in WS3 and WS4 (soil solution is not sampled in WS7) (Adams et al. 2006). Furthermore, these patterns of decline are consistent with those at the more synoptic scale of several watersheds throughout the northeastern United States (Goodale et al. 2005).

Although it is not clear what specific mechanisms are causing such a precipitous decline in net N mineralization and nitrification, several studies have shown that both microbial biomass and composition change drastically with experimental additions of N (Gilbert et al. 1998). Indeed, Schmidt et al. (2004) found that although

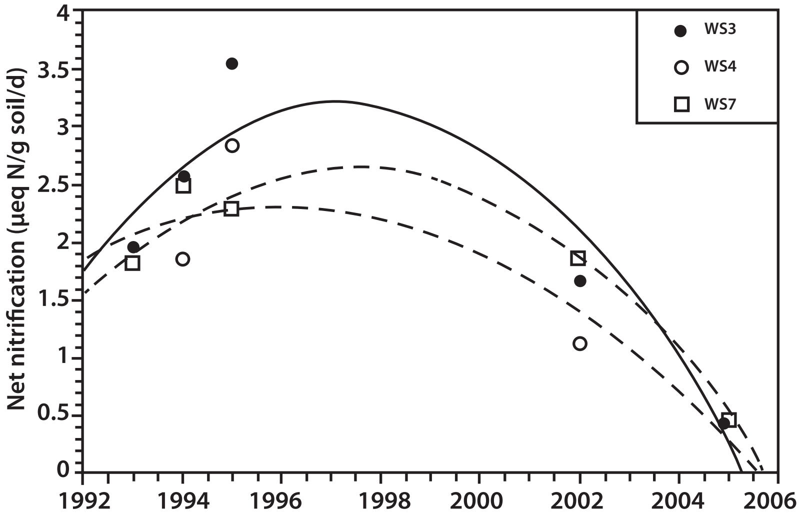

Fig. 29.1 Mean net nitrification for control (WS4 and WS7) and treatment (WS3) watersheds, 1993–2005

soil and microbial N pools were higher in N-fertilized plots, both microbial activity and biomass were lower following N fertilization, with negative effects being more profound in the growing season.

Demoling et al. (2008) observed 40 and 30% reductions in microbial biomass and activity, respectively, from N additions to Swedish coniferous forest soils. They also found profound changes in microbial composition in response to N treatments. More recently, Treseder (2008) performed a meta-analysis of 82 published field studies of the effects of N additions on microbial biomass, estimating that excess N reduced microbial biomass by 15% across all studies.

Although this is an area requiring further research, increases in N supply to forests clearly have the potential to alter the microbial communities of forest soils and do so at the watershed scale. Wallenstein et al. (2006b) provided clear evidence to indicate that microbial immobilization of N might not be a major mechanism to explain decreases in stream NO_3^- observed at FEF (Adams et al. 2006).

Thus, it is possible that excess N-mediated shifts in microbial communities are toward communities that simply process N at much lower rates (i.e., lower net N mineralization and nitrification) rather than those that affect immobilization.

29.3.2 Herbaceous Layer

The herbaceous layer, defined here as vascular plants ≤1 m in height, can represent >90% of plant species richness of forest ecosystems (Gilliam 2007). It is also the forest stratum of highest potential sensitivity to changes in resource availability, such as light and, especially, soil N (Gilliam and Roberts 2003). There was an initial period (1991–1994) representing up to a 6 year treatment period during which there were no detectable responses of the herb layer to the N treatment on WS3 (Fig. 29.2). This is in sharp contrast to other field-based N manipulation studies, wherein decreases in herb layer diversity have been observed within a one-year period (see Bobbink et al. 2010 for recent review).

Repeated sampling in 2003 indicated a substantial decline of species diversity of the herbaceous layer in response to aerial N additions, a decrease that appears to be related to loss of species (lower species richness) and increased herb layer cover (Fig. 29.2). Most of this decline appears to have arisen from unexpected increases in the shade-intolerant *Rubus* spp. (data not shown). Contemporaneously, spatial variability in *Rubus* spp. cover has decreased on WS3, consistent with declines in spatial variability of soil N (Gilliam et al. 2001), supporting the N homogeneity hypothesis suggested by Gilliam (2006).

29.3.3 Effects of Soil Freezing

Paradoxically, global warming is a predicted increase in the probability of soils in north-temperate regions of North America to freeze during the winter, the result of warming-related decreases in snow cover, thus minimizing the insulating effects of snow pack (Groffman et al. 2001). Because of previous observations that net nitrification can increase following soil freezing (see Groffman et al. 2001 for review) and because WS4 exhibits numerous symptoms of N saturation (including generally high net nitrification and NO_3^- leaching), an experiment was designed to examine the effects of freezing on net N mineralization and nitrification on soils along a gradient of weathering/nitrification in WS4. The gradient was as follows: LN (highly weathered soils with negligible net nitrification), HN (to less weathered soils with high nitrification), and MN (intermediate weathering and nitrification).

The results of this experiment are reported in full in Gilliam et al. (2010) and are summarized here. Freezing had profound effects on N dynamics in N-saturated soil, with responses varying between temperature treatments and along the gradient (Fig. 29.3).

Furthermore, lack of significant differences in net N mineralization and nitrification between −20 and −80 °C treatments (Fig. 29.3) suggests that −20 °C may represent a threshold temperature for response of these processes to freezing. In addition, freezing response of N mineralization differed greatly from that of nitrification, suggesting that soil freezing may de-couple two processes of the soil N cycle that are otherwise tightly linked at our site. Results also suggest that soil freezing at temperatures commonly experienced at this site can further increase net nitrification in soils already exhibiting high nitrification from N saturation.

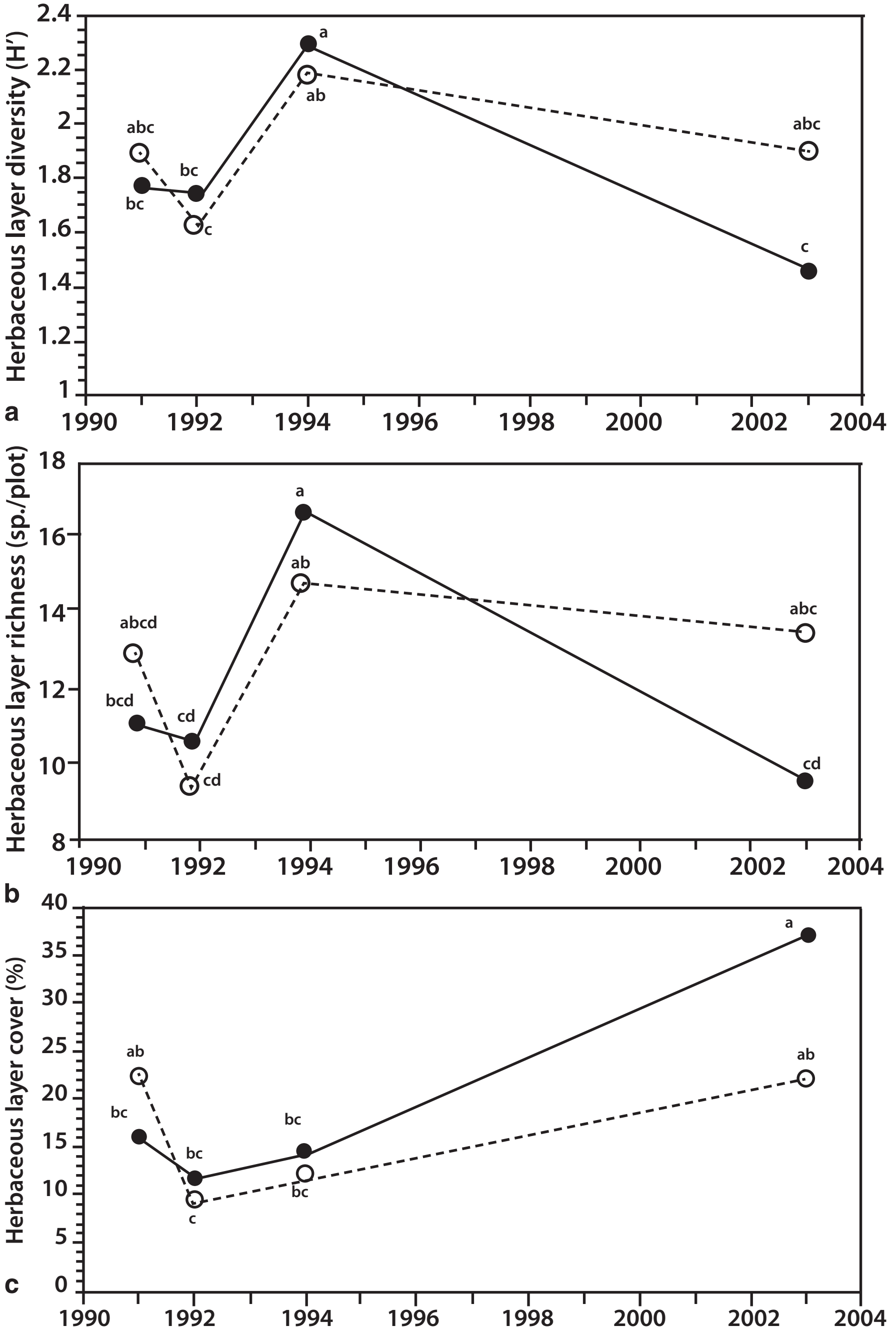

Fig. 29.2 Species diversity (**a**), species richness (**b**), and cover (**c**) for control (WS4—*open circles*, *dashed line*) and treatment (WS3—*solid circles* and *lines*) watersheds, 1991—2003. Means with the same superscript are not different between years and watershed at $P < 0.05$.

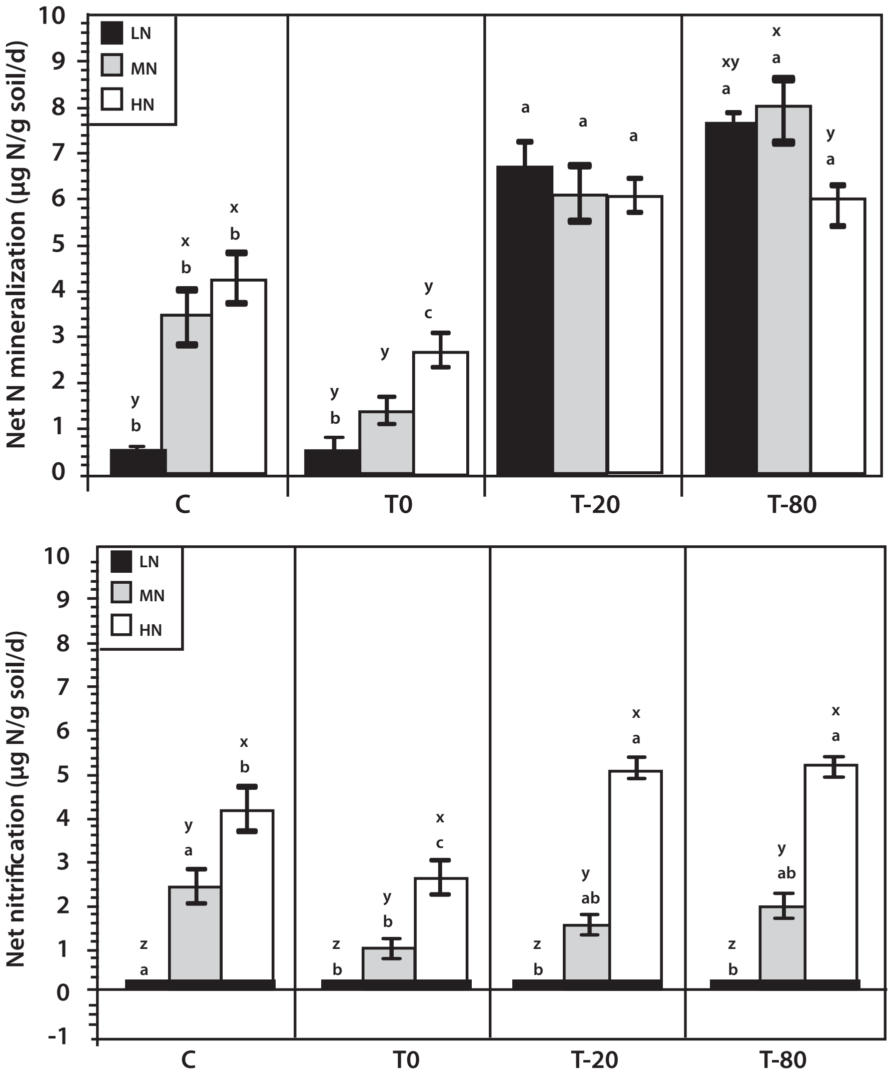

Fig. 29.3 Effects of freezing on net mineralization and nitrification at three sample sites in WS4, FEF, WV. Means (±1 SE) with the same superscript (*x*, *y*, *z*) are not significantly different ($P < 0.05$) between sites for a given treatment. Means with the same superscript (*a, b, c*) are not significantly different ($P < 0.05$) between treatments for a given site. See text for site abbreviations. C, T0, T-20, T-80 = control, 0°C, -20°C, and -80°C treatments, respectively. Modified from data taken from Gilliam et al. (2010)

29.3.4 Future Work

Future research at FEF out of the Gilliam lab at Marshall University includes continuation of all work summarized herein. Through cooperation with the Peterjohn lab at West Virginia University (with funding from the National Science Foundation's Long Term Research in Environmental Biology program), we are continuing full growing-season *in situ* incubations to measure net N mineralization and nitrification and mid-growing season sampling of the herbaceous layer. In addition, we will carry out soil freezing experiments to include analyses of microbial communities of soils along the weathering gradient of WS4.

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Part III
Critical Loads and Levels Approaches and Regional Upscaling

Chapter 30
Development of the Critical Loads Concept and Current and Potential Applications to Different Regions of the World

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Abstract The chapter addresses whether the critical load of nutrient nitrogen (N) is a relevant, necessary and sufficient indicator to address adverse effects of reactive nitrogen (N_r) on biodiversity in different regions of the world. Based on a description of the critical loads concept for nutrient N, and the relationship to biodiversity endpoints, applications of the critical load for nutrient N are summarized in the context of policies under the Long-range Transboundary Air Pollution (LRTAP)

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Convention. Potential applications of critical loads are addressed with respect to the relevance of adverse effects of N under the Convention on Biological Diversity (CBD). The chapter considers the prospects for effect-based applications in different regions of the world and poses some questions that need to be addressed. Finally, the potential for a broader indicator for N (a ‘threshold’ rather than a ‘load’) that could apply to all forms and impacts of N is considered, as it could potentially increase the coherence between CLRTAP and CBD.

Keywords CBD • Critical loads • Dynamic models • LRTAP • Nitrogen deposition • Steady-state mass balance

30.1 Introduction

Excess atmospheric deposition of reactive nitrogen (N_r) compounds can cause adverse effects to biodiversity and thereby affect ecosystem structure and functions (see Bobbink and Hicks 2014, Chap. 14, this volume and de Vries et al. 2014, Chap. 41, this volume). These impacts are triggered by both acidification and eutrophication. However, acidification is not only caused by nitrogen (N) deposition, but also by sulphur (S) deposition as an important cause of the acidification risk to the health of ecosystems in many regions of the world. In the context of this workshop, the focus of this chapter is on the impacts of nutrient N.

When atmospheric deposition of N_r is at or below critical loads, it is assumed not to cause adverse effects to plant species diversity. Deposition that exceeds a critical load can affect biodiversity to the extent where provisioning, regulating, supporting and cultural services of nature (see de Vries et al. 2014, Chap. 41, this volume and Erisman et al. 2014, Chap. 51, this volume) are jeopardized. However, these endpoints may differ between regions of the world. Therefore, the global usefulness of the critical loads concept needs to be carefully addressed with respect to regionally specific importance of ecosystem services.

The main question addressed in this chapter is whether the critical load of nutrient N is a relevant, necessary and sufficient indicator to address adverse effects of N_r on biodiversity in different regions of the world. First a short description is provided of the concept of critical loads of nutrient N, and the relationship to biodiversity endpoints. Current applications of the critical load for nutrient N are then summarized in the context of policies in the field of air pollution under the Long-range Transboundary Air Pollution (LRTAP) Convention. Next, potential applications of critical loads are addressed, with respect to the relevance of adverse effects of N under the Convention on Biological Diversity (CBD). Finally, the chapter considers the prospects for effect-based applications in different regions of the world and poses some questions that need to be addressed. This synthesis is framed with reference to the Conventions addressed in this workshop, names the LRTAP Convention and the CBD.

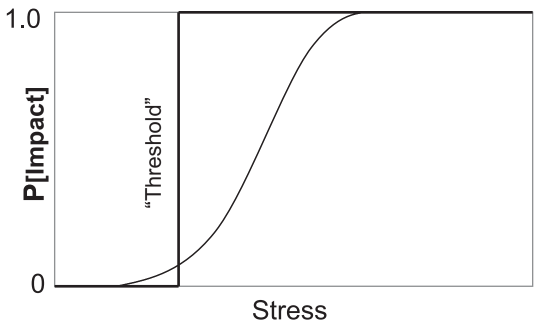

Fig. 30.1 The critical load as "threshold" in the context of damage functions

30.2 The Nutrient Nitrogen Critical Loads Concept and Biodiversity: A Summary

A critical load is defined as 'a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge' (Nilsson and Grennfelt 1988). To understand the concept, one can think of a damage function, in which a threshold can be identified above which stress leads to a high probability of impact (Fig. 30.1).

There are two established ways to determine critical loads, i.e. empirical and modelled[1] (Fig. 30.2). Empirical critical loads are established through N addition experiments on sites at which bio-geochemical conditions and the effects of the N addition on species diversity can be compared to a control. The empirical approach is limited to situations where N inputs dominate the effects on biodiversity. Regional applications of empirical critical loads require the extrapolation of site-specific findings. Empirical critical load ranges have been assigned in relation to vegetation changes in European natural areas (Achermann and Bobbink 2003) classified following the European Nature Information System (EUNIS, Davies et al. 2004). European empirical critical loads have been adopted under the LRTAP Convention and included in the Mapping Manual (UBA 2004). In the USA, work is ongoing to derive empirical critical loads to ecoregions (Pardo et al. 2011). Furthermore, a first assessment of impacts of N deposition on ecosystems worldwide with related empirical critical N loads is described in Bobbink et al. (2010).

Modelled critical loads can be applied to all situations in which an environmental quality criterion exists. Concentrations of N in the soil solution have been used as environmental quality criterion to compute critical loads for nutrient N in relation to vegetation changes (Table 30.1). Apart from vegetation changes, N deposition can affect a number of ecosystem services of which a preliminary overview can be found in Hettelingh et al. (2008) and which are further addressed in part IV of this volume.

[1] Integrated bio-geochemical models can also be used to derive critical loads (see e.g. de Vries et al. 2007, 2010).

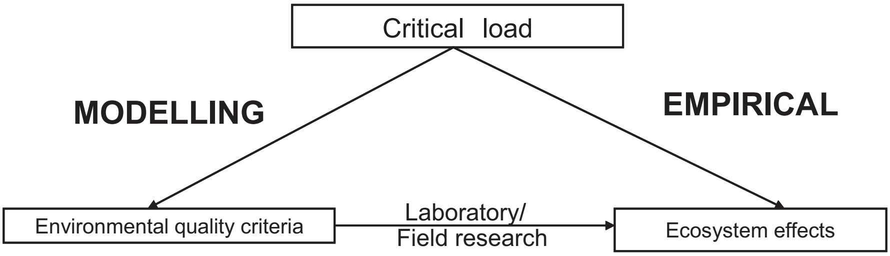

Fig. 30.2 Empirical and modelled approaches to derive critical loads (adapted from de Vries and Posch 2003)

Table 30.1 Critical N concentrations, $(N)_{crit}$, in soil solution. (Source: de Vries et al. 2007) to avoid specified changes of biological diversity

Impact	Critical N concentration (mg $N.l^{-1}$)	
	UBA (2004)	de Vries et al. (2007)
Vegetation changes in Northern Europe		
Lichens to cranberry (lingonberries)	0.2–0.4	0.2–0.4
Cranberry to blueberry	0.4–0.6	0.4–0.6
Blueberry to grass	1–2	1–2
Grass to herbs	3–5	3–5
Vegetation changes in Western Europe		
Coniferous forest		2.5–4
Deciduous forest	–	3.5–6.5
Grass lands		3
Heath lands	–	3–6
Other impacts on forests		
Nutrient imbalances	0.2–0.4	–
Elevated nitrogen leaching/N saturation	–	1
Fine root biomass/root length	–	1–3
Sensitivity to frost and fungal diseases	–	3–5

The critical N concentration is used in the N mass balance to derive a critical load of nutrient N as follows:

$$CL_{nut}(N) = N_i + N_u + N_{de} + Q \cdot [N]_{crit} \tag{30.1}$$

Nitrogen immobilization, N_i, is approximated by the long-term immobilization of 0.5–1 kg N ha^{-1} $year^{-1}$. Nitrogen uptake, N_u, is the long-term average removal by harvesting (accompanied by a proportional removal of base cations), and denitrification, N_{de}, depends on the soil moisture. The runoff (Q) is assessed from the difference between precipitation and actual evapotranspiration and the acceptable N concentration is related to the natural leaching from a N-limited stand. For more details, we refer to Posch et al. (1993) and reviews and revisions thereof, as adopted in the Mapping Manual (UBA 2004).

The disadvantage of a simple steady-state soil model is that there is not a direct linkage between a critical N concentration in solution and plant species diversity. Furthermore, steady state models do not allow prediction of the temporal response of ecosystems to deposition scenarios, for example, in terms of impacts on plant species diversity. This requires the use of the dynamic integrated soil-vegetation models. Such models can also be used to assess critical loads, while accounting for differences in sensitivity to perturbation depending on their current state and recent history. In an overview report and paper, de Vries et al. (2007, 2010) describe the possibilities of multi-species models in combination with dynamic soil-vegetation models to (i) predict plant species composition or diversity as a function of atmospheric N deposition and (ii) calculate critical N loads in relation to an acceptable plant species diversity change. They also discuss the potential of linked biogeochemistry-biodiversity models to support pollution abatement policy, amongst others in view of the validation status of the models and the potential of the models to assess critical loads. In general, one can say that a combination of empirical critical N loads and integrated soil-vegetation models (as e.g. done by Van Dobben et al. 2006) is the most promising approach to assess reliable critical N loads in view of biodiversity impacts at a regional scale.

As mentioned before, N is one of the components that also causes acidification. Critical loads for acidification are computed using critical limits for indicators such as the ratio between base cations and aluminium or pH, with a strong emphasis on soil chemical requirements for environmental health. The relationship between soil chemical indicators and biodiversity is currently receiving increasing attention, but not addressed further in the context of this chapter. Critical loads for acidification have been computed and mapped in Asia (Hettelingh et al. 1995a). Critical loads for S, N and acidity in China were computed and mapped by Duan et al. (2001), and for Europe and northern Asia by Reinds et al. (2008). On a global scale, the Stockholm Environment Institute (SEI) has assessed the sensitivity of soils to acid deposition (Kuylenstierna et al. 2001), and Bouwman et al. (2002) derived and mapped critical loads of acidity and nutrient N for terrestrial ecosystems.

Critical loads of nutrient N have been mostly used in semi-natural areas in Europe to protect biodiversity, but may need more attention elsewhere. Agricultural areas are not addressed through the critical load approach. On the other hand, agricultural practices including the use of fertilizer are an important source of N inputs to nature in the form of ammonia. In Europe, ammonia deposition on natural receptors is the prevailing cause of critical load exceedance, although the deposition of oxidized N alone causes exceedance in many receptors as well.

In other parts of the world, the importance of oxidized N may be more important than in Europe, because of other energy mixes and emission abatement technologies. On the other hand, the substitution of nature by agricultural land, thereby affecting the geographical distribution of N receptors, may be more important in other regions of the world than in Europe. The relative importance of receptors, biodiversity-endpoints and N deposition in relation to one another varies among regions in the world. This has implications for the use of critical loads to support policies in the field of air pollution and biodiversity.

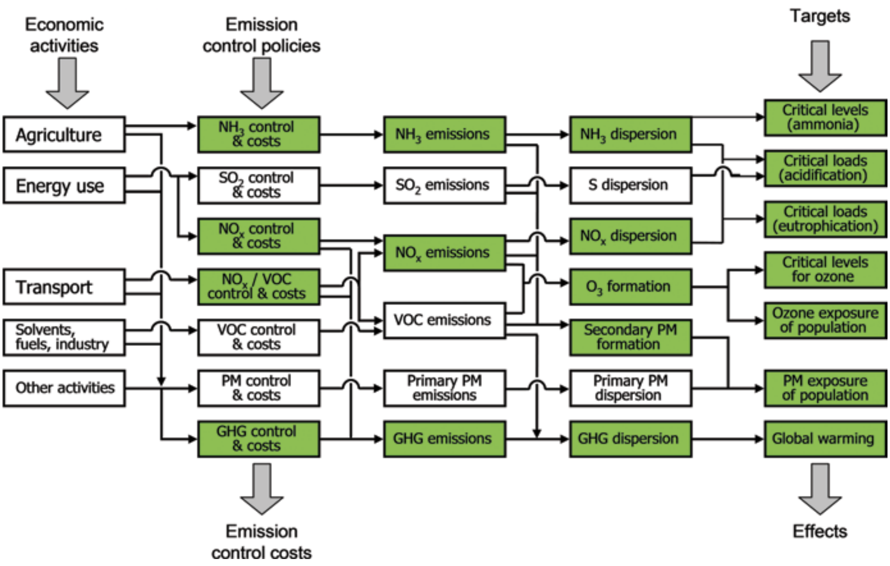

Fig. 30.3 Integration of nitrogen pressure-impacts in the GAINS model (adapted from Winiwarter et al. 2011)

30.3 Current and Potential Applications Under the LRTAP Convention

Critical load exceedances are used under the LRTAP Convention to assess impacts of emission abatements on the environment (Hettelingh et al. 1995b, 2001, 2007). In addition to critical loads for N in relation to eutrophication, use is made of critical acid loads (N and S) in view of acidification. Furthermore, critical levels (see UBA 2004) and health guidelines are important threshold indicators to protect human health and the environment.

The multiple relationships (green shading) by which N_r emissions and control-policies contribute to the risk of adverse effects, is illustrated in Fig. 30.3.

It can be seen from Fig. 30.3 (last column) that N relevant policy targets can be set based on critical levels for ammonia, critical loads for acidification, critical loads for eutrophication, critical levels of ozone for vegetation and WHO health guidelines for ozone and particulate matter. The link to global warming is reflected incompletely, as this would increase the complexity of the figure. Then, interactions would need to be addressed with carbon compounds from emissions that are currently not addressed under the LRTAP Convention.

Reductions of the exceedance of critical loads and levels has been an explicit policy target in establishing two effect-based LRTAP Convention protocols including the protocol to abate acidification, eutrophication and ground level ozone (Gothenburg Protocol 1999), as well as the National Emission Ceilings (NEC) Directive for European Union countries in 2001 (see: http://ec.europa.eu/environment/

air/pollutants/ceilings.htm). In short, in Europe the effect-based approach, involving both the use of critical loads and levels, has been applied successfully, although more still needs to be done to reduce current exceedance levels.

Note that biodiversity is adversely affected when any of the critical loads or levels are exceeded. In Europe the need to reduce emissions of reduced and oxidized N may be driven by regional (local) requirements to meet critical loads and levels. This might be even more so in other regions of the world, especially where urban air quality standards and WHO health guidelines drive air pollution abatement policies. The reason is that the improvement of urban air quality will, as a co-benefit, also reduce the exceedance of critical loads or levels in rural parts of these regions, and thus diminish the risk to biological diversity. But, what can be the role of critical loads when biodiversity is the prime policy target, such as under the Convention on Biological Diversity?

30.4 Current and Potential Applications Under the UN Convention on Biological Diversity

Biological diversity is defined by the 1992 United Nations Convention on Biological Diversity (CBD) as "the variability among living organisms from all sources including, *inter alia*, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are part; this includes diversity within species and ecosystems". The change of biodiversity comes in many forms including changes of species abundance, species richness and homogenization and is caused by a large variety of drivers, of which human activities have become of significance in approximately the last 100 years (see also Millennium Ecosystem Assessment 2005; EEA 2007). The importance of biological diversity for human well being is well established by its underpinning of ecosystem services which the Millennium Ecosystem Assessment has classified as provisioning, regulating, supporting and cultural services (see part IV of this volume). The CBD formulated a target to be reached in 2010 "to achieve a significant reduction of the current rate of biodiversity loss at the global, regional and the national level as a contribution to poverty alleviation and to benefit of all life on earth". In support of meeting its target in 2010, the CBD developed a number of indicators including the 'change of abundance of selected species'. The indicators are listed in Table 30.2. Nitrogen deposition is among the indicators, however without reference to a critical load for N. The scenario analysis in a modelling study of Ten Brink et al. (2007) has addressed main drivers of loss in biodiversity in 2050 relative to the Mean Species Abundance (MSA) in various regions in the world. Using a Business-as-usual scenario from the FAO, which focuses on land use changes, the study concludes that world MSA decreases from 70 % in 2000 to 63 % in 2050. The role of N turns out to be insignificant in comparison to the influence of the change to agricultural area. Nitrogen is mentioned to play a (minor) role only in Europe and South and East Asia. The question is to what

Table 30.2 Set of headline indicators agreed on the conference of the parties to the CBD through decision VII/30 and VIII/15. (Source: Ten Brink et al. 2007, pp. 23)[a]

Focal area	Indicator
Status and trends of the components of biological diversity	**Trends in extent of selected biomes, ecosystems, and habitats**
	Trends in abundance and distribution of selected species
	Coverage of protected areas
	Change in status of threatened species
	Trends in genetic diversity of domesticated animals, cultivated plants, and fish species of major socioeconomic importance
Sustainable use	Area of forest, agricultural and aquaculture ecosystems under sustainable management
	Proportion of products derived from sustainable sources
	Ecological footprint and related concepts
Threats to biodiversity	**Nitrogen deposition**
	Trends in invasive alien species
Ecosystem integrity and ecosystem goods and services	Marine Trophic Index
	Water quality of freshwater ecosystems
	Trophic integrity of other ecosystems
	Connectivity/fragmentation of ecosystems
	Incidence of human-induced ecosystem failure
	Health and well-being of communities who depend directly on local ecosystem goods and services
	Biodiversity for food and medicine
Status of traditional knowledge, innovations and Practices	Status and trends of linguistic diversity and numbers of speakers of indigenous languages
	Other indicator of the status of indigenous knowledge
Status of access and benefit-sharing	*Indictor of access and benefit-sharing*
Status of resource transfers	**Official development assistance provided in support of the Convention**
	Indicator of technology transfer

[a]Indicators shown in bold typeface have been assessed in Ten Brink et al. (2007). Indicators in italics are still under development

extent this result would change if the scenario had focused on drivers other than those where the substitution of nature for agricultural area is predominant.

In addition to the 2010 target of CBD the European Commission developed its Biodiversity Conservation Strategy (ECBS), which was adopted in 1998. In support of the ECBS, the European Environment Agency (EEA 2007) developed indicators to monitor the progress towards the CBD 2010 target in a project entitled "Streamlining European 2010 Biodiversity Indicators" (SEBI 2010). For this 26 indicators were proposed as summarized in Table 30.3. The exceedance of the critical load of N features as indicator 9.

From Tables 30.2 and 30.3 it is obvious that the critical load indicator is currently of moderate importance to the support of CBD policies.

A way to improve the use of critical loads in both Conventions is to address relationships between critical load exceedance and ecosystem services. A first attempt

Table 30.3 The 26 indicators proposed by the SEBI 2010 process. (Source: EEA 2007, p. 6)

The 26 indicators proposed by the SEBI 2010 process	
1	Abundance and distribution of selected species
2	Red List Index for European species
3	Species of European interest
4	Ecosystem coverage
5	Habitats of European interest
6	Livestock genetic diversity
7	Nationally designated protected areas
8	Sites designated under the EU Habitats and Birds Directives
9	Critical load exceedance for nitrogen
10	Invasive alien species in Europe
11	Occurrence of temperature-sensitive species
12	Marine Trophic Index of European Seas
13	Fragmentation of natural and semi-natural areas
14	Fragmentation of river systems
15	Nutrients in transitional, coastal and marine waters
16	Freshwater quality
17	Forest: growing stock, increment and fellings
18	Forest: deadwood
19	Agriculture: nitrogen balance
20	Agriculture: area under management practices potentially supporting biodiversity
21	Fisheries: European commercial fish stocks
22	Aquaculture: effluent water quality from finfish farms
23	Ecological Footprint of European countries
24	Patent applications based on genetic resources
25	Financing biodiversity management
26	Public awareness

was made in Hettelingh et al. (2008) and will be addressed further in de Vries et al. 2013, Chap. 41, this volume and Erisman et al. 2014, Chap. 51, this volume).

30.5 Prospects for Effect-Based Applications in Different Regions of the World

In support of the revision of air pollution agreements in Europe, both empirical and modelled critical loads are used, as schematically shown in Fig. 30.4.

Figure 30.4 illustrates the use of exceedances of computed (top route) and empirical critical loads (bottom route) in the effect-based support of N emission reduction alternatives. The relation to biodiversity and ecosystem functions depends on how effects of critical load exceedances propagate through ecosystems. For this both dynamic models and dose-response functions are used. Thus the use of both computed and empirical critical loads increases the robustness of scenario findings. An extension of Fig. 30.4 to include critical levels would further enhance the robustness of effect-based assessments under the LRTAP Convention.

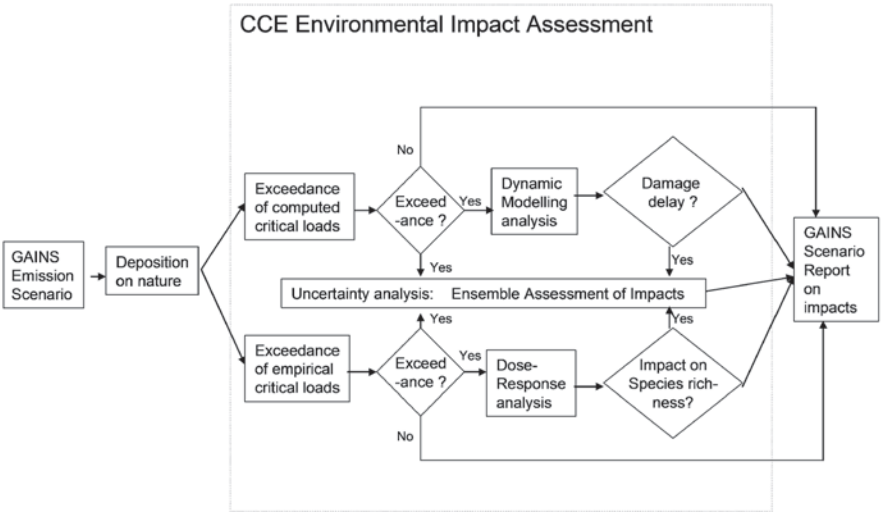

Fig. 30.4 The use of the exceedance of computed and empirical critical loads as part of an effect-based assessment of emission abatement scenario alternatives under the LRTAP Convention. (Source Hettelingh et al. 2008)

Further work is needed to extend Fig. 30.4 to include drivers and impacts that are relevant to other regions of the world.

30.6 Issues for Further Discussion

While biodiversity is an endpoint common to both the LRTAP Convention and the CBD, the development and use of critical loads is operational only under the LRTAP Convention. Convention on Biological Diversity indicators addressing N deposition do not include critical loads or exceedances. However, in Europe the implementation of CBD targets included exceedance of critical loads in its "Streamlining European 2010 Biodiversity Indicators" (SEBI 2010).

Other indicators related to excess ambient concentrations of N_r, i.e. critical levels of ammonia and ozone, relating to biodiversity and human health endpoints are included under the LRTAP Convention, but not used under either CBD or SEBI 2010. Conversely, other indicators that are relevant to express the risk to biodiversity have been included in the set of indicators of both CBD and SEBI 2010, but do not (yet) feature in the effect-based work of the LRTAP Convention. Moreover, the appropriateness of biodiversity endpoints and critical thresholds of N_r is not only delimited by these (and other) policy frameworks, but is also driven by regional and socio-economic differences.

To make the critical load concept more useful in the context of CBD, the following questions need to be addressed:

- Is it possible to assess empirical and (integrated) model based critical loads in different regions of the world?
- If yes, are changes in the critical load formulation needed to make them more relevant (e.g. sufficient to address N impacts to biodiversity) in other regions of the world?
- Should different critical thresholds (e.g. concentration levels, deposition levels) of ammonia, NO_x and ozone be accounted for in view of interacting impacts on growth and biodiversity?
- What is the possibility to make use of the most recent insights in soil-vegetation modelling?
- What could be the institutional framework for large scale regional applications of critical loads?

Further to this discussion, there is interest in the international community in developing a much broader indicator for N (a 'threshold' rather than a 'load') that could apply to N_r (reduced and oxidized forms, as well as the ozone formation potential of (oxidized) N). A move towards a threshold approach for N_r, with biodiversity and human health endpoints could potentially increase the coherence between CLRTAP and CBD approaches in an effect oriented policy context. For example, as stated above in Sect. 30.3, the improvement of urban air quality will, as a co-benefit, also reduce the exceedance of critical loads or levels in rural areas, and thus diminish the risk to biological diversity. Such a development may help the international community move towards a more integrated and holistic treatment of N impacts on human well-being and the environment.

See Clair et al. 2014, Chap. 50, this volume and Erisman et al. 2014, Chap. 51, this volume for the results of the working group discussions on these topics.

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Chapter 31
Nitrogen Deposition as a Threat to the World's Protected Areas Under the Convention on Biological Diversity (CBD)

Albert Bleeker, W. Kevin Hicks, Frank Dentener, James N. Galloway and Jan Willem Erisman

Abstract This chapter combines information on the world's protected areas (PAs) under the Convention on Biological Diversity (CBD), common classification systems of ecosystem conservation status, and current knowledge on ecosystem responses to nitrogen (N) deposition, to determine areas most at risk. The results show that 2,600 PAs located in both the G200 Ecoregions and Biodiversity Hotspots are exposed to a deposition > 10 kg N ha^{-1} year^{-1} with projections for 2030 indicating that this situation is expected to continue. Furthermore, 62 PAs are projected to receive > 30 kg N ha^{-1} year^{-1} by 2030; with forest and grassland ecosystems in Asia particularly at risk. Many of these sites are known to be sensitive to N deposition

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effects, both in terms of biodiversity changes and ecosystem services they provide. Urgent assessment of high-risk areas identified in this study is recommended to inform the conservation efforts of the CBD.

Keywords Biodiversity • Ecoregions • Hotspots • Nitrogen deposition • Protected areas

31.1 Introduction

As part of the United Nations (UN) Convention on Biological Diversity (CBD), the Programme of Work on Protected Areas (POWPA) was established in 2004 to reduce significantly the current rate of biodiversity loss at the global, regional, national and sub-national levels by 2010. Despite the fact that atmospheric nitrogen deposition has been recognized on several occasions as a threat to biodiversity (e.g. Bobbink et al. 1998; Phoenix et al. 2006; Bobbink et al. 2010), the POWPA has so far not addressed this issue. Here we overlay the protected areas (PAs) with global estimates of nitrogen (N) deposition to allow a preliminary assessment of the extent to which these areas may be under threat by N. The areas of the PAs that coincide with either the World Wildlife Fund (WWF) G200 Ecoregions (after Olson and Dinerstein 2002) or Biodiversity Hotspots (Myers et al. 2000) are considered to give an indication of the potential importance of N deposition impacts on the conservation value of the PAs.

31.2 Protected Areas and Nitrogen Deposition

The POWPA was established to *'support the establishment and maintenance of comprehensive, effectively managed, and ecologically representative national and regional systems of protected areas'*. This global network of PAs differ widely in their purpose and the way in which they are managed and are categorized within the IUCN (International Union for Conservation of Nature) classification system, which classifies PAs according to their management objectives. The IUCN categories (Table 31.1) do not provide information on how protected areas are managed, but give indirect information about the level of protection for individual PAs (I = highest and VI = lowest level of protection).

The N deposition data used here are NO_y plus NH_x mean model values of the 26 models participating in the ACCENT IPCC-AR4 multimodel evaluation exercise (Dentener et al. 2006), where deposition entails removal from the atmosphere by wet scavenging and dry deposition on terrestrial and aquatic ecosystems. The study compared modelled results with available wet deposition measurements and concluded that modelled results were within 30 % of European and North American wet deposition measurements and 50 % in other regions. This study uses N

Table 31.1 IUCN Classification of protected areas. Reprinted from Bleeker et al. (2011) with permission from Elsevier

Category	Title	Managed for
Ia	Strict Nature Reserve	Science
Ib	Wilderness Area	Wilderness protection
II	National Park	Ecosystem protection and recreation
III	Natural Monument	Conservation of specific natural features
IV	Habitat/Species Management Area	Conservation through management intervention
V	Protected Landscape/Seascape	Landscape/seascape conservation and recreation
VI	Managed Resource Protected Area	Sustainable use of natural ecosystems

deposition estimates for the year 2000 and for 2030 based on a 'current legislation' (CLE) scenario (Fig. 31.1).

The result of linking the N deposition for 2030 with the PAs is shown in Table 31.2, where the distribution of the PAs over different deposition and IUCN classes is presented. In total about 126,000 PAs are used in this study, with a total surface of about 34,000,000 km^2.

31.3 Protected Areas Under Threat

Fig. 31.2 and Table 31.2 show that a large number of PAs are exposed to N deposition higher than 10 kg N ha^{-1} year^{-1}. This level represents a threshold above which changes in ecosystem structure and functioning have occurred in Europe (see Phoenix et al. 2006; Bobbink et al. 1998 and 2010). Some ecosystems in the Arctic and sub-arctic regions are sensitive to lower rates of N input (i.e. 5–10 kg N ha^{-}1 year^{-}1). Deposition higher than 10 kg N ha^{-1} year^{-1} is shown in red (increasing between 2000 and 2030) and orange (decreasing between 2000 and 2030). About 40 % of the number of PAs and 11 % of the total area are above 10 kg N ha^{-1} year^{-1} deposition. Yellow areas in Fig. 31.2 signify areas that might be under threat in the near future, with N deposition of 5–10 kg N ha^{-1} year^{-1} and showing an increasing deposition trend between 2000 and 2030. These yellow areas correspond to about 23 % of the number of PAs and 30 % of the area.

31.4 Overlays of Protected Areas with WWF Ecoregions and Biodiversity Hotspots

The WWF G200 Ecoregions are defined as areas containing a distinct assemblage of natural communities and species that constitute priority conservation areas, which if conserved would protect a broad diversity of the earth's ecosystems

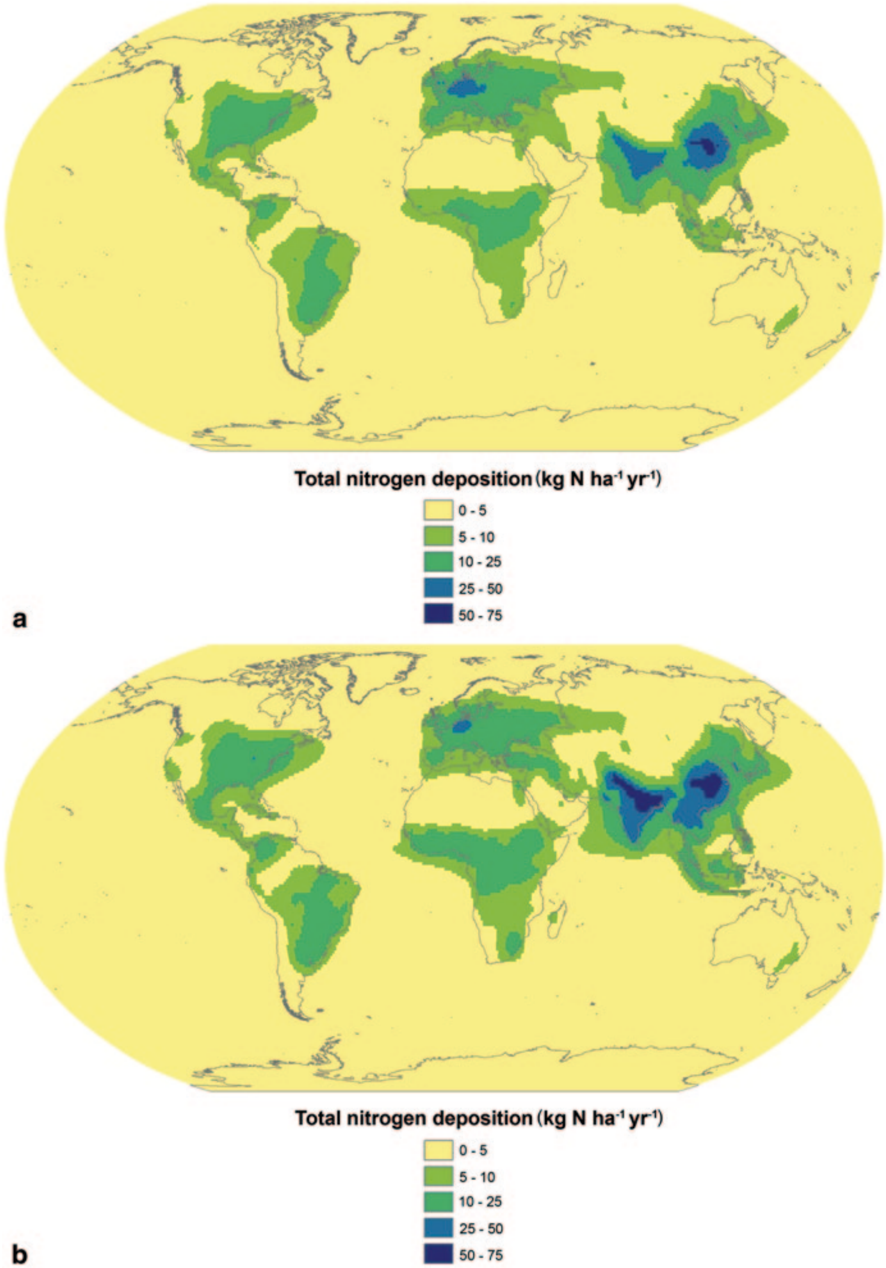

Fig. 31.1 Spatial distribution of nitrogen deposition (in kg N ha^{-1} $year^{-1}$) for 2000 (*top*) and 2030 (*bottom*). Reprinted from Bleeker et al. (2011) with permission from Elsevier

Table 31.2 Number of protected areas distributed over IUCN and deposition classes (in kg N ha^{-1} $year^{-1}$)

Category	Deposition class (in kg N ha^{-1} $year^{-1}$)				
	>10	>15	>20	>25	>30
Ia	1,165	182	1	0	0
Ib	126	16	1	1	0
II	597	239	155	67	40
III	4,747	564	58	2	0
IV	21,727	12,901	4,538	267	193
V	10,286	8,019	4,347	846	581
VI	595	118	33	14	7
Not Applicable	632	258	115	57	38
Not Known	10,930	3,307	724	129	68
Total	*50,805*	*25,604*	*9,972*	*1,383*	*927*

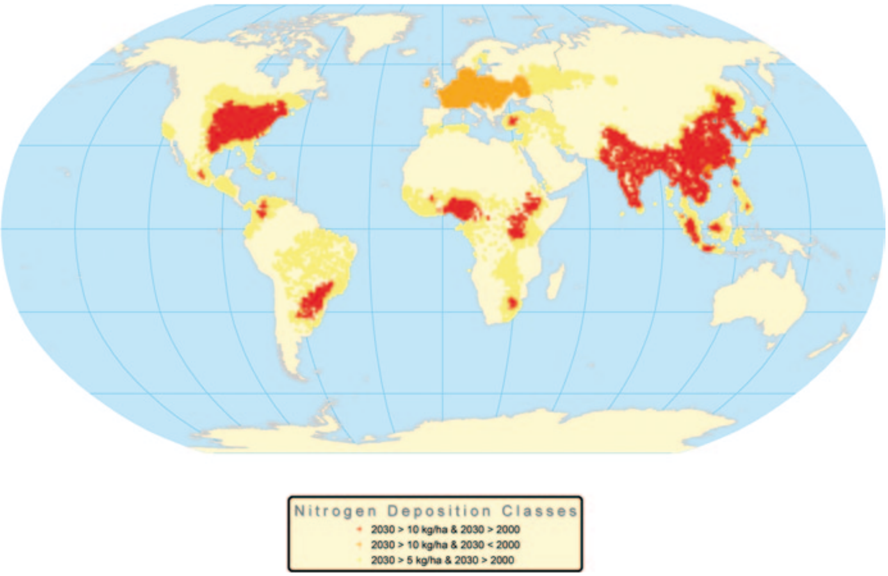

Fig. 31.2 Distribution of deposition classes (see text for details). Reprinted from Bleeker et al. (2011) with permission from Elsevier

(see Fig. 31.3). Many PAs are located in the Temperate Broadleaf & Mixed Forest ecoregion type (52 %), while in terms of area most of the PAs are located in Tropical & Subtropical Moist Broadleaf Forest (20 %). Table 31.3 shows that some of these areas are receiving rates of N deposition in excess of 30 kg N ha^{-1} $year^{-1}$ (ranging up to 47 kg N ha^{-1} $year^{-1}$) which for temperate forests in Europe has caused significant impacts on structure and function, whilst research into responses of tropical ecosystems to such high rates of nitrogen deposition is still in its infancy.

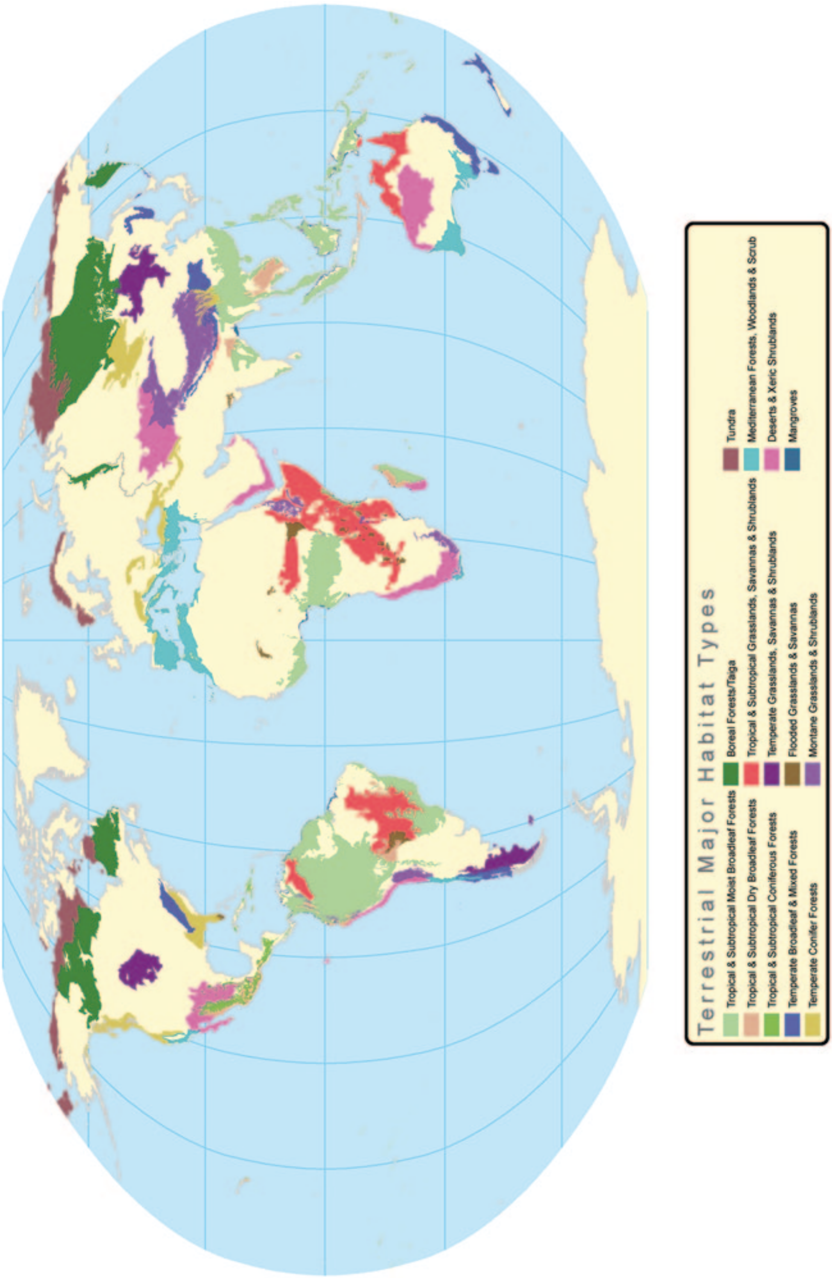

Fig. 31.3 Spatial distribution of the WWF G200 Ecoregions. Reprinted from Bleeker et al. (2011) with permission from Elsevier

Table 31.3 Area (in ha) of protected areas for the G200 Regions and Hotspots (number of protected areas between brackets) where N deposition >30 kg N ha^{-1} $year^{-1}$. Adapted from Bleeker et al. (2011) with permission from Elsevier

G200 Regions	Himalaya	Indo-Burma	Mountains of Southwest China	Total
Eastern Himalayan broadleaf and conifer forests	132,644 (4)			132,644 (4)
Hengduan Shan conifer forests			3,919 (2)	3,919 (2)
Naga-Manapuri-Chin Hills moist forests		105,373 (10)		105,373 (10)
Southeast China-Hainan moist forests		495,286 (20)		495,286 (20)
Terai-Duar savannas and grasslands	280,763 (16)			280,763 (16)
Western Himalayan temperate forests	113,386 (10)			113,386 (10)
Total	*526,793 (30)*	*600,659 (30)*	*3,919 (2)*	*1,131,371 (62)*

Biodiversity Hotpots (Myers et al. 2000) are firstly defined by level of endemism (uniqueness to an area) and secondly by degree of threat (>70 % primary habitat for endemics lost). Figure 31.4 shows the spatial distribution of these Biodiversity Hotspots.

In total about 2,600 sites that are located in both the G200 Ecoregions and Biodiversity Hotspots are exposed to a deposition higher than 10 kg N ha^{-1} year⁻1, 62 of them are exposed to levels higher than 30 kg N ha^{-1} $year^{-1}$ (respectively 1,700,000 and 25,000 km^2). These high levels (up to 41 kg N ha^{-1} $year^{-1}$) occur in Asia; more specifically the Himalaya, Indo-Burma and Southwest China region (see Table 31.3).

31.5 Conclusions and Recommendations

From this study the following conclusions can be drawn:

- It is clear that significant areas of the UNEP Protected Areas Programme are receiving elevated deposition that is set to increase in the future, especially in Asia.
- Some of these PAs are known to be sensitive to N deposition impacts, are of high conservation value and have high numbers of endemic species.

It is recommended that some PAs, such as those in the tropics, should be studied closely to determine if they are being impacted or are at risk. The potential for using the critical load approach in some of the temperate areas outside of Europe and North America should be investigated (see also Bobbink et al. 2010).

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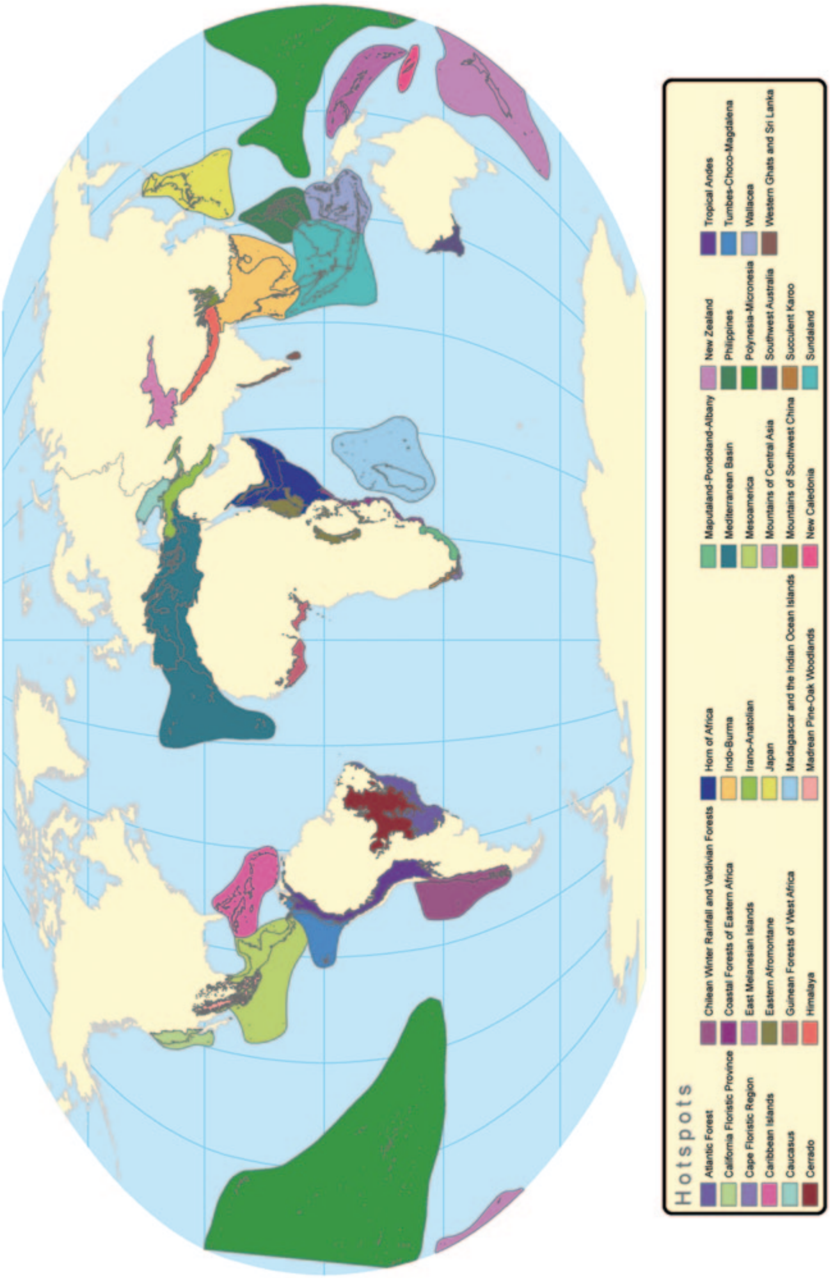

Fig. 31.4 Spatial distribution of the Biodiversity Hotspots. Reprinted from Bleeker et al. (2011) with permission from Elsevier

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Chapter 32
How Much is too Much? Nitrogen Critical Loads and Eutrophication and Acidification in Oligotrophic Ecosystems

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Abstract Ecosystem impacts from nitrogen (N) deposition are related to (1) the degree to which plant growth responds to increases in N supply and (2) soil buffering capacity. Herbaceous communities dominated by plants adapted to low nutrient supply typically have low capacity to take up inputs of N. As a result they are more highly susceptible to loss of base cations, acidification, and increased production of toxic aluminium, manganese, and iron. Here we show that alpine ecosystems with acidic parent material display loss of biotic uptake together with soil acidification at relatively low inputs of N deposition, and can possibly reach extreme levels of acidification as indicated by a shift from an aluminium to an iron dominated soil buffering system.

Keywords Acidification • Alpine ecosystems • Aluminium toxicity • Base cations • Eutrophication

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32.1 Introduction

Exposure to elevated inputs of anthropogenic nitrogen (N) deposition elicits a series of changes in terrestrial ecosystems associated with both enhancement and inhibition of biogeochemical processes (Aber et al. 1998; Galloway et al. 2003). Initially, growth of plants may increase as the constraint of N supply on Net Primary Productivity (NPP) is relaxed, sometimes associated with altered dominance of species and gains or losses in diversity. This stage is usually referred to as a **eutrophication** stage. Eventually higher rates of nitrification, elevated NO_3^- concentrations, and leaching of base cations lead to acidification of soils, increases in soluble aluminium, and potentially to decreases in rates of NPP. This **acidification** stage exposes organisms to toxic levels of aluminium (Al) and iron (Fe). The degree to which eutrophication delays acidification may vary substantially among ecosystems. Forest ecosystems, which have been studied to a greater degree than most other systems, may experience significant biological buffering of N deposition effects. In contrast, nutrient poor ecosystems may experience relatively little eutrophication, and therefore have greater sensitivity to detrimental ecosystem impacts due to N deposition. Here we report that alpine ecosystems of several mountain ranges, characterized by low rates of N cycling, a flora adapted to low N supply, and acidic parent material, experience modest or nil increases, or in some cases, decreases in NPP, in response to N deposition (Bowman et al. 2006, 2008, 2012). In these systems the potential for soil acidification is high. We describe an extreme case of acidification in a system subjected to decades of elevated N and sulphur deposition, where soluble iron appears to be joining aluminium as the dominant soil cation.

32.2 Experimental Approach

At each research site, N fertilization treatments were applied to 5 replicate plots. The N levels varied among the sites (2–15 g N/m^2/yr, all added as NH_4NO_3 in solution), but the graded input allowed comparison of general response functions at each site. Response variables included aboveground NPP (biomass), species composition (data not shown), soil pH, soil inorganic N (lysimeter and resin bag (data not shown)), and extractable cations. The sites included two in the Rocky Mountains (USA), characterized by low to modest current rates of N deposition that show trends of increasing with time, and one site in the Western Tatra Mountains (Slovakia), with modest current rates of deposition, but a long legacy of high acid deposition during the latter part of the 20th century (Table 32.1).

Table 32.1 Sites of alpine nitrogen deposition experiments

Site	Ambient deposition (kg/ha/yr)	Soil C:N	Soil pH
Chapin Pass, Mummy Range, Rocky Mountain National Park	4	13.4±0.13	5.84±0.04
Niwot Ridge, Front Range Rocky Mountains	7	16.9±0.2	5.60±0.06
Mount Salatin, Western Tatra Mountains	12 (historically much higher)	17.1±0.25	3.50±0.05

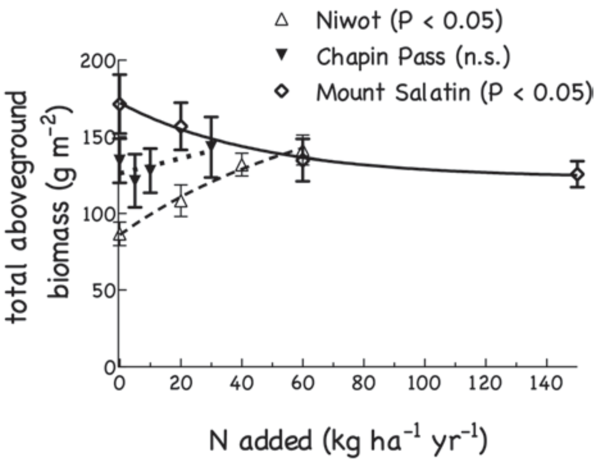

Fig. 32.1 Response of aboveground biomass to N addition in 3 sites differing in ambient N deposition rates: Chapin Pass < Niwot < Mount Salatin. Data were analyzed using least-squares regression, with block as a categorical variable. Biomass was collected 3 years after initiation of the experiment at the Chapin Pass and Salatin sites, and 5 years after initiation at the Niwot site (no significant NPP response at the Niwot site 2 and 7 years after initiation of the experiment)

32.3 Results

Vascular plant diversity (Shannon-Wiener index) was affected by N addition only at the Niwot site, and was due to changes in evenness, and not species richness. Richness did not change at any site due to N addition. Plant growth was enhanced by N additions only at the Niwot site, although interannual variation in NPP was greater than the increase due to N fertilization, and no significant increase in two of the three years measured (data from those years not shown, Bowman et al. 2006). In contrast, biomass was not affected at the Chapin Pass site, and decreased significantly at the Salatin site with N addition (Fig. 32.1).

Soil pH decreased at the Niwot and Salatin sites, but not at the Chapin Pass site (Fig. 32.2). Extractable Ca^{2+} decreased significantly in the already apparently depleted pool in the Salatin soils, and did not change significantly in the Niwot and Chapin Pass soils (Fig. 32.3a). Soil extractable Mg^{2+} decreased with N additions at the Niwot and Salatin sites, but not at the Chapin Pass site (Fig. 32.3b).

The acidic cations Al^{3+} and Fe^{3+} changed significantly in response to N addition at the Salatin site, but in opposite directions, with a decrease in Al^{3+} and an increase in Fe^{3+} (Fig. 32.4). Extractable Al^{3+} increased at the Niwot site.

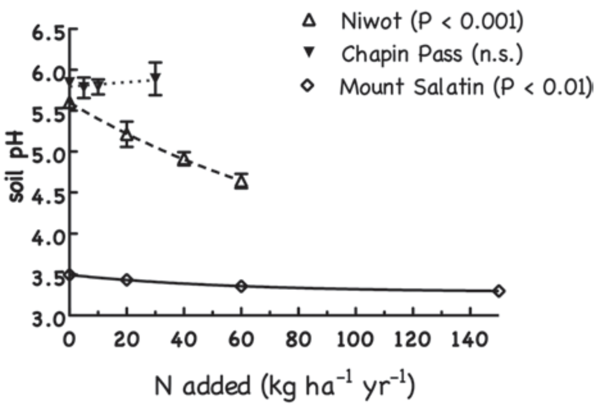

Fig. 32.2 Response of soil pH (H_2O paste) to N addition in 3 sites differing in ambient N deposition rates: Chapin Pass < Niwot < Mount Salatin. Data were analyzed using least-squares regression, with block as a categorical variable. Data were collected 4 years after initiation of the experiments at the Salatin and Chapin Pass sites, and 8 years after initiation of the experiment at the Niwot site

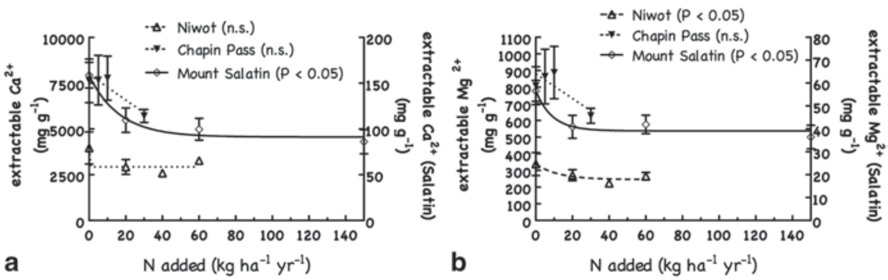

Fig. 32.3 Response of soil extractable ($BaCl_2$) Ca (**a**) and Mg (**b**) to N addition in 3 sites differing in ambient N deposition rates: Chapin Pass < Niwot < Mount Salatin. Data were analyzed using least-squares regression, with block as a categorical variable. Data were collected 4 years after initiation of the experiments at the Salatin and Chapin Pass sites, and 8 years after initiation of the experiment at the Niwot site

32.4 How Much is too Much?

Responses of these three alpine sites, representing a gradient in ambient N deposition, indicate that increases in plant growth will not buffer soil acidification substantially (Fig. 32.5), and that acidification due to N deposition is a significant risk in nutrient-poor ecosystems with acidic parent material. The extreme conditions of acidity at the Salatin site (Bowman et al. 2008) should be avoided. Early warning signs, such as changes in the abundance of N-sensitive plant species, should be used as “critical loads” for managing sensitive systems, rather than symptoms of acidification (e.g. Ca/Al ratios).

Acknowledgments Funding for this research was provided by the U.S. National Science Foundation, the National Park Service, and the Slovak Academy of Sciences.

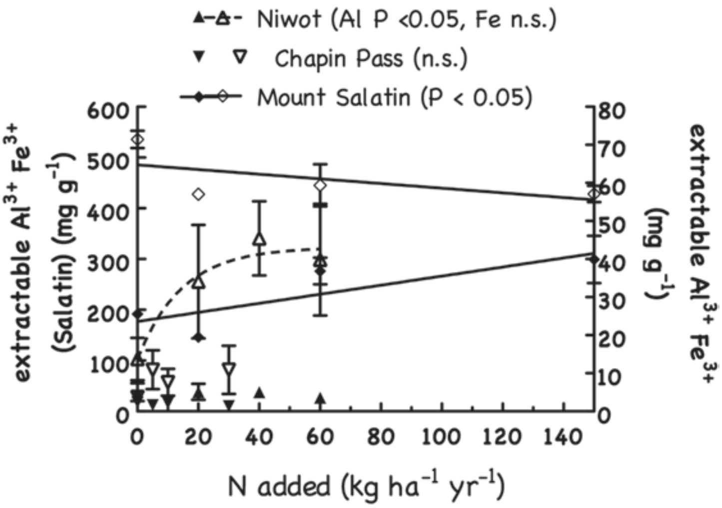

Fig. 32.4 Response of soil extractable ($BaCl_2$) Al (open symbols) and Fe (closed symbols) to N addition in 3 sites differing in ambient N deposition rates: Chapin Pass < Niwot < Mount Salatin. Data were analyzed using least-squares regression, with block as a categorical variable. Data were collected 4 years after initiation of the experiments at the Salatin and Chapin Pass sites, and 8 years after initiation of the experiment at the Niwot site

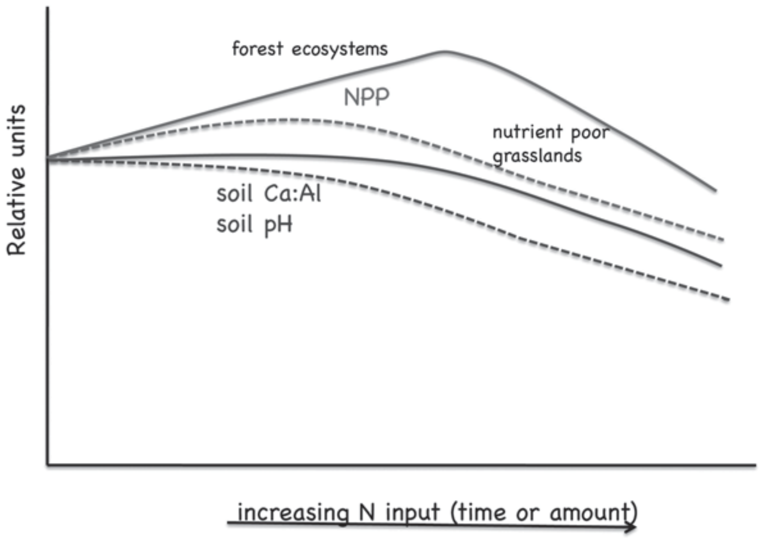

Fig. 32.5 Theoretical response of NPP, soil Ca/Al ratios, and pH of forest ecosystems and oligotrophic grasslands to increases in amounts of and/or exposure time to N deposition, demonstrating different magnitudes of eutrophication and thresholds of acidification. (after Aber et al. 1998)

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Chapter 33
Predicting Lichen-based Critical Loads for Nitrogen Deposition in Temperate Forests

Linda H. Geiser, Sarah E. Jovan, Douglas A. Glavich and Mark E. Fenn

Abstract Critical loads (CLs) define the quantitative exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur, according to present knowledge. Management according to CLs generated for epiphytic lichens, a highly nitrogen (N)-sensitive indicator, should protect forested ecosystems from N deposition effects. We tested the hypothesis that epiphytic lichen community composition, specifically the relative contribution of oligotrophs vs. eutrophs to species richness, can be predicted from mean annual precipitation and N deposition. We applied a multiple linear regression model developed for the North American Marine West Coast Forests to dry, mesic, and wet deciduous forests in California and Scotland. Replication of previously published CLs using this model validated our hypothesis, implying that lichen-based CLs for N can be estimated for other temperate forests where natural lichen community composition and mean annual precipitation are known.

Keywords Air pollution • Critical load • Lichen community composition • Nitrogen deposition • Temperate forest

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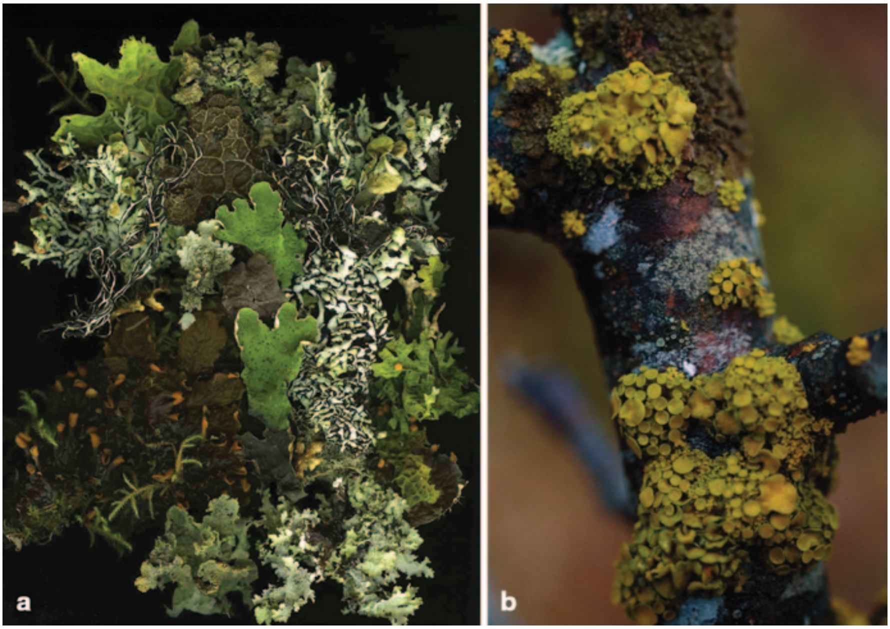

Fig. 33.1 **a**, **b** Typical oligotrophic (*left*) and eutrophic (*right*) lichens of North American Marine West Coast Forests. Oligotrophs play important ecological roles; eutrophs are smaller species with fewer apparent ecological roles

33.1 Introduction

A 'critical load' (CL) is 'the quantitative exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur, according to present knowledge' (UBA 2005). Because epiphytic lichens are highly nitrogen (N)-sensitive forest ecosystem components, lichen-based CLs can help identify deposition targets that convey forest-wide protection. Lichens are valuable ecosystem components in their own right; they contribute to biodiversity and they play integral ecological roles as nesting material, essential winter forage for rodents and ungulates, invertebrate habitat, and in nutrient cycling (McCune and Geiser 2009; Fig. 33.1, this chapter). Working with epiphyte community data for the North American Marine West Coast Forests (MWCF) ecological region, Geiser et al. (2010) developed a regression model of lichen community response to N deposition and precipitation.

Here, we hypothesize that N deposition, precipitation, and lichen community composition relationships are consistent across temperate forests. To test this hypothesis, we used the Marine West Coast Forests model to re-calculate CLs for a dry, Mediterranean forest in California, a mesic coniferous forest in California and a wet coastal hardwood forest in Scotland and compare them with existing published values. If the model can replicate published results, then the model can potentially provide first estimates of lichen CLs in other temperate forests.

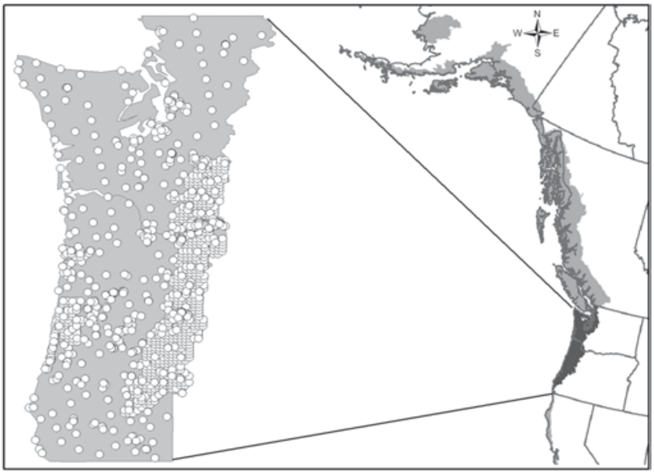

Fig. 33.2 Distribution of Oregon and Washington lichen survey plots (*left*) within North America's Marine West Coast Forests ecological region (*shaded area, right*)

33.2 Methods

The MWCF model was developed for wet coniferous forests of Oregon and Washington using lichen community survey data from ~1500 sites (Fig. 33.2).

Survey sites were ordinated using Non-metric Multi-dimensional Scaling Analysis based on community composition. Overlays of vectors indicating direction and strength of correlations with other environmental variables allowed interpretation of the resulting ordination (Fig. 33.3).

Each survey site was assigned an 'air score' equivalent to its distance along Axis 1, the air pollution vector indicated by nitrogen and sulphur accumulation in the epiphytic lichen, *Platismatia glauca* (Geiser and Neitlich 2007). A regression model was built to relate 'air score' response to N deposition and mean annual precipitation (Geiser et al. 2010). It predicted CLs at a response threshold selected by the authors of air score 0.21, equivalent to 41–30% oligotrophs and < 34% eutrophs (Table 33.1). Critical loads varied across the landscape, increasing with precipitation, and were 3–9 kg N ha^{-1} $year^{-1}$ between 40 and 450 cm (Fig. 33.4). We used the term oligotroph and eutroph in lieu of the more traditional lichenological terms, 'acidophyte' and 'nitrophyte', because our data is based solely on total N deposition independent of pH.

We tested the hypothesis that the West Coast Marine Forests model captures the general relationship between N deposition (kg ha^{-1} $year^{-1}$), community composition, and precipitation (cm); Eq. 33.1;

$$\text{Critical load} = 6.6979 \text{ threshold air score} + 0.0161 \text{ mean annual precipitation} + 0.6148 \quad \text{(Eq. 33.1)}$$

by using the model to calculate N CLs (Eq. 33.1) for three temperate forests (Table 33.2) where they can be compared to previously published lichen-community based N CLs.

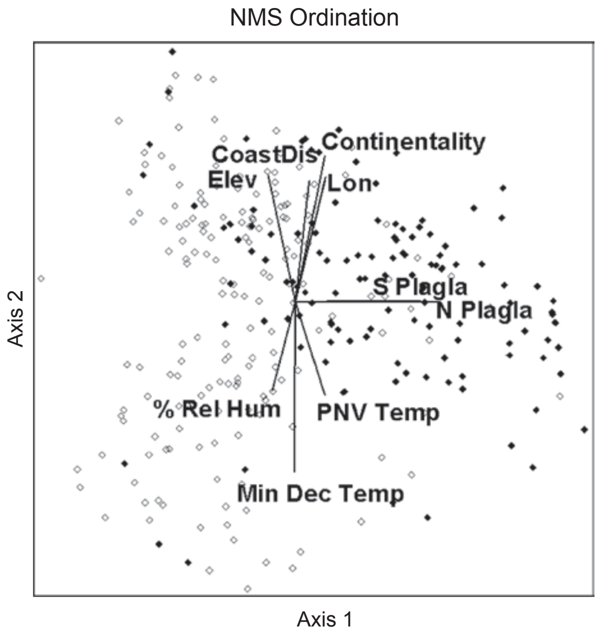

Fig. 33.3 NMS ordination of lichen survey sites. Sites close together in space have similar community composition. Air scores are the survey site position along Axis 1, which was correlated with increasing nitrogen and sulphur concentrations in the lichen, *Platismatia glauca* (Nplagla; Splagla). Climate was scored along Axis 2, the gradient from coastal to continental climates. Abbreviations: Coast Dis = distance from the ocean, Continentality = mean maximum August—mean minimum December temperature, Lon = longitude, Min Dec Temp = mean minimum December temperatures, PNVTemp = mean annual temperature, Rel Hum = relative humidity. Open diamonds (◊) indicate clean sites, closed diamonds (♦) indicate urban and semi-rural sites. Reprinted from Geiser and Neitlich (2007) with permission from Elsevier

Table 33.1 The MWCF model of lichen response to N deposition (estimated by the Community Multi-scale Air Quality model) accounts for the influence of mean annual precipitation. Precipitation presumably has a diluting or leaching effect on lichen N accumulation

Linear Regression Model	r^2 adj	Term	Estimate	S.e.	t Ratio	Prob > |t|
Air Score = $\beta_0 + \beta_1 * P + \beta_2 N$	0.35	β_0	−0.0918	0.0323	−2.84	0.0046
P = precipitation in cm		β_1	−0.0024	0.0001	−18.26	<0.0001
N = N deposition = kg ha^{-1} yr^{-1}		β_2	0.1493	0.0068	21.86	<0.0001

33.3 Results

The MWCF model produced CL estimates that were remarkably close to published values in all three comparison areas (Table 33.3). For the California Sierras, the model predicted CLs that were within 0.8 kg N ha^{-1} $year^{-1}$ of those predicted by Fenn et al. (2008) for the two strictest community response thresholds and framed

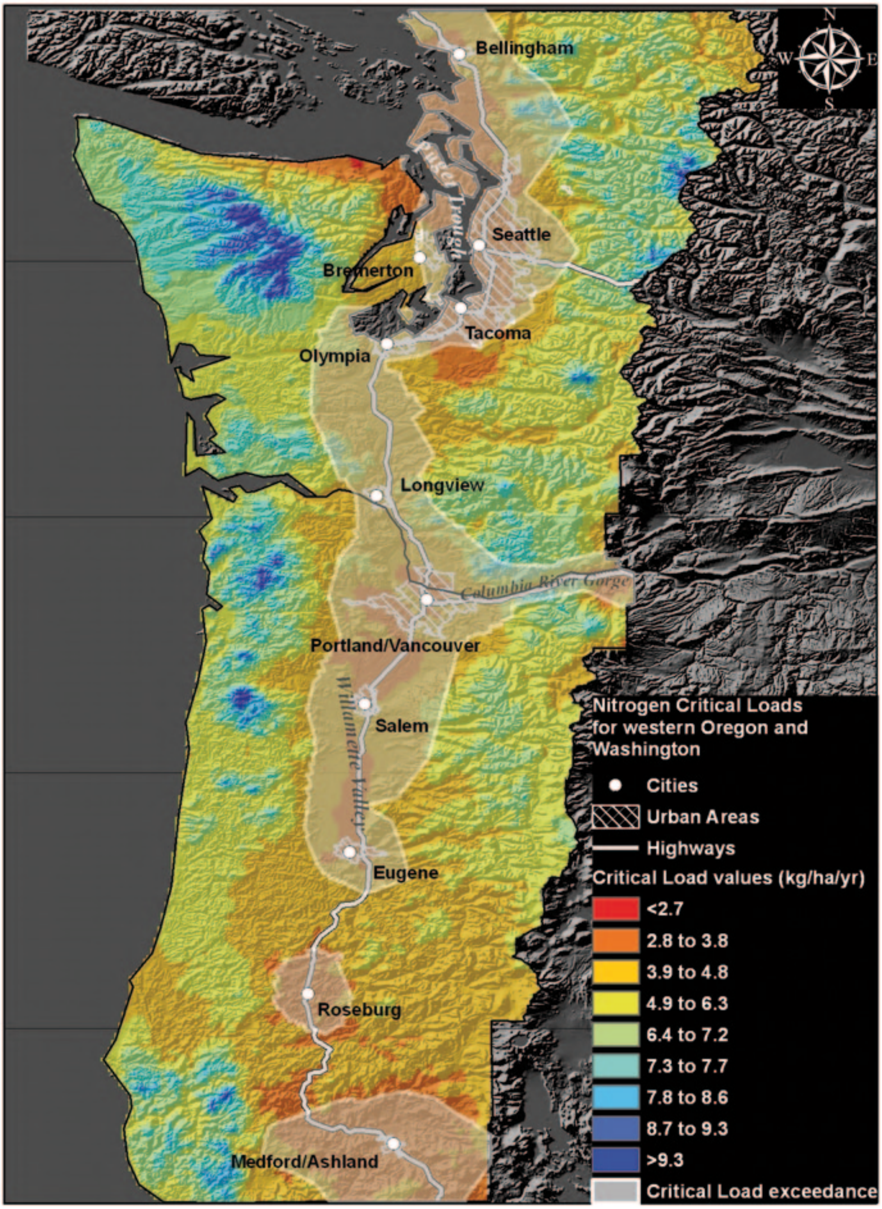

Fig. 33.4 Map of N critical loads for western Oregon and Washington, US. Critical loads are the amount of N deposition necessary to shift epiphytic macrolichen communities to an air score of 0.21, the point where oligotrophic species comprise 41–30 % and eutrophs comprise 27–34 % of the community. Critical loads vary over the landscape because precipitation moderates lichen response. White shading, associated with largest urban and agricultural areas and low elevations, indicates likely CL exceedances from 1994–2002 (air score ≥ 0.21). Reprinted from Geiser et al. (2010) with permission from Elsevier

Table 33.2 New nitrogen CLs were calculated using the MWCF model for three forests with previously published lichen CLs

Parameter	California's Greater Central Valley	California's Sierra Nevada	Scotland's Atlantic Oakwoods
Publication	Fenn et al. (2011)	Fenn et al. (2008)	Mitchell et al. (2005)
Forest type	Dry, deciduous	Mesic, coniferous	Wet, deciduous
Ecological region	Mediterranean California	Northwest Forested Mountains	Temperate Oceanic Forest
Published CL	5.5	3.1, 5.2, 10.2	11–18
Response threshold	50% eutrophs	40%, 25%, and 0% oligotrophs	~0% oligotrophs (inferred from authors' species lists)
Mean Annual precipitation (cm)	17–120	111	150

the third. For the Greater Central Valley, the MWCF CLs for minimum and maximum precipitation differed from the CL suggested by Fenn et al. (2011) by no more than 2.4 ha^{-1} $year^{-1}$. MWCF model CLs for the Mitchell et al. (2005) study in Scotland were nearly identical to published values (10.8–17.5 kg ha^{-1} $year^{-1}$ vs. 11–18 kg ha^{-1} $year^{-1}$). It is interesting to note that substituting the MWCF response threshold (i.e. presuming at least 30% oligotrophs under natural background conditions instead of 0% currently observed at cleanest sites), generated a CL of 5.5 kg N ha^{-1} $year^{-1}$ for the Scotland study, similar to other western North American lichen-based N CLs.

33.4 Discussion

The MWCF regression model, generated from CMAQ-modelled N deposition data, can predict N CLs at any desired lichen community composition (response threshold) and precipitation level. Close replication by this model of previously published CLs for dry to mesic forests of California and wet forests of Scotland suggests a consistent relationship between N deposition, precipitation and lichen-community composition across temperate (including Mediterranean) forests. This relationship may be used to predict N CLs in other temperate forests where clean-site (or historical) lichen community composition and precipitation ranges are known. Lichen-based CLs for western North America range from 3–10 kg N ha^{-1} $year^{-1}$ which, together with a CL of 5.6 predicted by our model for wet Atlantic oak woods of Scotland using North American marine forest lichen response thresholds, supports efforts to lower the UNECE CL for European forests. Ground-truthing of CMAQ-modelled estimates would increase confidence in CL estimates generated by regression models.

Table 33.3 Application of the MWCF model to datasets from California and Scotland, substituting relevant precipitation ranges and lichen community thresholds, yielded CLs comparable to published CLs. Applying the more protective response threshold (air score 0.21) to the Scotland dataset yielded CLs comparable to North American studies

Study Area	Threshold Lichen community composition	Air score equiv	Ann precip. (cm)	CL using MWCF model kg $ha^{-1}yr^{-1}$	Publ. CL	Reference
Marine W. Coast Forests, Oregon-Washington	30–41 % oligotrophs	0.21	44	2.7		Geiser et al. (2010)
	30–41 % oligotrophs	0.21	186	5		Geiser et al. (2010)
	30–41 % oligotrophs	0.21	451	9.2		Geiser et al. (2010)
California Sierra Nevada, USA	40 % oligotrophs	0.02–0.21	111	2.5–3.8	3.1	Fenn et al. (2008)
	25 % oligotrophs	0.33–0.49	111	4.6–5.7	5.2	Fenn et al. (2008)
	0 % oligotrophs	1.0–2.0	111	9.1–15.8	10.2	Fenn et al. (2008)
California Greater Central Valley, USA	50 % eutrophs	0.33–0.49	17	3.1–4.2	5.5	Fenn et al. (2011)
	50 % eutrophs	0.33–0.49	156	5.3–6.4	5.5	Fenn et al. (2011)
Atlantic Oak Woods, Scotland	0 % oligotrophs	1.0–2.0	221	10.8–17.5	11–18	Mitchell et al. (2005)
	30–41 % oligotrophs	0.21	221	5.6		Geiser et al. (2010)
Boreal Sweden	β-diversity & cover	n.a.	n.a.		5–10	Nordin et al. (2005)
Netherlands	β-diversity & cover	n.a.	n.a.		8–9	Van Dobben et al. (2006)

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Chapter 34
Using Fire Risk and Species Loss to set Critical Loads for Nitrogen Deposition in Southern California Shrublands

Edith B. Allen, Leela E. Rao, Gail Tonnesen, Robert F. Johnson, Mark E. Fenn and Andrzej Bytnerowicz

Abstract Southern California deserts and coastal sage scrub (CSS) are undergoing vegetation-type conversion to exotic annual grassland, especially in regions downwind of urban areas that receive high nitrogen (N), primarily as dry deposition. To determine critical loads (CLs) of N that cause negative impacts, we measured plant and soil responses along N deposition gradients, fertilized vegetation at different N levels, and used biomass production output from the DayCent model. Nitrogen deposition gradients were identified from the CMAQ model and compared with measured N deposition values. Coastal sage scrub receives N deposition as high as 30 kg ha^{-1} year^{-1}, while the desert has levels up to 16 kg ha^{-1} year^{-1}. These ecosystems are subject to increases in exotic species production, loss of native species diversity, and increased fire risk at relatively low CLs. For instance, a gradient survey in CSS showed that exotic grass cover increased and native plant species richness declined by almost 50% above 10 kg N ha^{-1} year^{-1}. Fertiliza-

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tion studies in desert creosote bush scrub showed a significant increase in exotic species biomass with 5 kg N ha^{-1} $year^{-1}$ in a wet year, and biomass output from DayCent modelling indicated an increased fire risk from exotic grasses with 1 t per ha production during years with moderate to high precipitation at 2.2–8.8 kg N ha^{-1} $year^{-1}$. The difference in CL between desert and CSS is related to the different criteria used (diversity loss in CSS, productivity and fire risk in desert), as well as responsiveness of native vs. exotic plant species to N and the degree to which precipitation and soil N limits plant growth in the two vegetation types.

Keywords Coastal sage scrub • Desert • Fire risk • Invasive plant species • Plant species richness

34.1 Introduction

There is growing interest in the United States for implementing nitrogen (N) critical loads (CLs) to manage anthropogenic atmospheric N deposition (Porter et al. 2005). Critical loads are defined as the amount of pollutants below which there are no adverse ecological effects (Burns et al. 2008). The criteria for setting CLs may range from species-level impacts of N eutrophication on diversity and species shifts (Bobbink et al. 2010), to ecosystem-level impacts on processes such as nutrient leaching (Fenn et al. 2010). In arid regions with high buffering capacity of the soil, infrequent run-off, and low productivity, the immediate effect of N deposition is often on vegetation productivity, species shifts, and diversity changes from fertilization (Fenn et al. 2003; Allen et al. 2009). The arid and semi-arid regions of the western United States have experienced exotic annual grass invasions that have caused increased fuel for fire, which may be coupled with reduced diversity of native species. We report two different criteria for setting CLs in California deserts and coastal sage scrub (CSS). The CL for desert creosote bush scrub (CB) and pinyon-juniper woodland (PJ) was determined using a biogeochemical process model to calculate exotic annual plant productivity and increased fire risk. The CL for CSS was determined by diversity losses over a N deposition gradient.

34.2 Nitrogen Critical Load Based on Plant Diversity Losses

Coastal sage scrub is a high diversity, Mediterranean-climate vegetation type primarily in southern California, with some 200 sensitive plant species (legally protected by the Endangered Species Act, or under consideration for protection, Skinner and Pavlik 1994). It is highly invaded by exotic Mediterranean annual grasses and forbs and is experiencing vegetation-type conversion and losses in diversity (Allen et al. 2000), and is subject to high levels of N deposition and increased fire frequency (Fenn et al. 2003; Talluto and Suding 2008). The modelling approach used in the desert has not been applied to setting a N CL in CSS. However, assessing diversity losses (Bobbink et al. 2010) has proved useful to setting CLs, as we discovered during a survey along a N deposition gradient.

Table 34.1 Percentage (%) cover and richness of plant groups and extractable soil N (ammonium plus nitrate) along a N deposition gradient in western Riverside County, California. Sites are arranged from north to south along an urban to rural gradient. Nitrogen deposition is total wet plus dry deposition based on the CMAQ model (Tonnesen et al. 2007 and unpublished) and calculated using the inferential method (Fenn et al. 2011)

Site	Exotic grass % cover	Native forb % cover	Shrub % cover	Native forbs species per 3 ha	Soil N µg/g	N deposition kg N ha^{-1} year^{-1}	
						CMAQ	Inferential
Jurupa Hills	63.5	4	2.2	16	37.7	19.6	
Box Springs	69.2	18.5	2.4	31	32.6	14.7	20.2
Botanic Garden	36.0	25.4	0.2	20	28.9	13.4	
Lake Perris	0.5	26.1	2.8	30	20.3	11.1	
Mott Reserve	6.7	14.3	11.2	37	30.6	11.1	8.9
Lopez Canyon	11.1	19.6	19.3	67	9.6	9.0	6.6
Tucalota Hills	1.5	35.7	35	50	10.5	8.7	

Seven sites were selected in CSS vegetation on north-facing slopes along a north to south, urban to rural N deposition gradient. The sites lie in the physiographic region known as the Riverside-Perris Plain along a 70 km stretch with an average 34 cm precipitation annually, and with similar soils on granitic parent material (Padgett et al. 1999). Modelled N deposition using the Multiscale Community Air Quality (CMAQ) model (Tonnesen et al. 2007 and unpublished 4 km^2 grid data) ranged from 9–20 kg ha^{-1} year^{-1}. We compared modelled with N deposition values calculated from passive sampler atmospheric concentration data (Fenn et al. 2009), reported here as inferential values (Fenn et al. 2011). At each site percent cover and species richness was assessed in three, 1-ha plots at peak biomass of the growing season (May, 2003). Soil samples were collected during the dry season (October), as extractable soil N concentration is highest in dry soil just prior to the rainy season (Padgett et al. 1999).

Nitrogen deposition (wet plus dry) decreased along an urban to rural gradient from 19.6 to 8.7 kg ha^{-1} year^{-1} using the CMAQ model (Table 34.1). Of the three sites where inferential calculations were made, the one at the high end of the gradient had higher N deposition, and two at the lower end had lower deposition than modelled by CMAQ. Soil extractable N was highest at the northern, more polluted end of the gradient, conforming to the deposited N values. Exotic grass cover was highest at the polluted end of the gradient, and native forb and shrub cover were lowest. Forb species richness shown in bold in Table 34.1 shows a rapid drop in richness, suggesting a critical load of 10 kg N ha^{-1} year^{-1} using the CMAQ model, and 7.8 kg N ha^{-1} year^{-1} by the inferential method.

34.3 Nitrogen Critical Load Based on Fire Risk

Fires have increased in frequency in arid southern California because of increased invasive annual grasses (Brooks and Matchett 2006) coupled with N deposition and wet years that increase productivity above the threshold for carrying fire, which is about 1 t ha^{-1} of fine fuel (Rao et al. 2010). Because deserts have discontinuous woody fuel, the invasive species now carry fire between shrubs, a function that native annual forb vegetation seldom performed historically except following the wettest periods, which resulted in infrequent fire events. Nitrogen fertilization can elevate this productivity even further, interacting with precipitation to increase biomass to values above the productivity threshold for fire (Allen et al. 2009; Rao and Allen 2010; Rao et al. 2010). Areas of the Mojave and Sonoran Desert have burned once, or in some instances, multiple times in the last two decades, even in areas with relatively low precipitation (Brooks and Matchett 2006). The impacts of elevated N on fire risk was determined for two vegetation types, arid creosote bush scrub (CB) and semiarid pinyon-juniper woodland (PJ). Native shrub and woodland recovery is slow, so multiple or even single fires in invaded vegetation can result in vegetation-type conversion to exotic annual grassland (Brooks et al. 2004).

We used the daily version of the Century model (DayCent) to determine CLs of N deposition for its effects on increasing annual vegetation productivity and fire risk in CB and PJ. This model takes into account changes in soil nutrients, moisture, and texture, thus allowing it to be used to estimate vegetation productivity across landscapes with varying soil and environmental characteristics (Parton et al. 1988). Input parameters were N deposition rates, soil N, C, and P, precipitation using local records, and soil texture (Rao et al. 2010). Biomass was parameterized using annual species productivity measured yearly since 2003 in plots fertilized with N at 0, 5, and 30 kg N ha^{-1} $year^{-1}$ (Allen et al. 2009; Rao et al. 2010). These plots had increased productivity of invasive grasses with 5 kg N ha^{-1} $year^{-1}$ only in the wettest years, and for 30 kg in average to wet years, and no consistent decreases in native species richness (Allen et al. 2009).

To determine the CL for a site, the model was run for 100 years at incrementally increasing N deposition loads from background (0.5 kg ha^{-1}) up to a maximum N deposition load (14 kg ha^{-1}). The proportion of years in which biomass exceeded the fire threshold, or fire risk, was calculated for each deposition loading. Simulations that produced greater than 1 t ha^{-1} of biomass were assumed to exceed the fire-carrying threshold, as this amount of grass biomass is the minimum to carry fires (Anderson 1982). The CL was defined as the amount of N deposition when the fire risk began to increase exponentially above background levels. We also calculated the N-deposition load at which the fire risk began to level off, or the fire risk stabilization load. For example, fire risk increased from deposition at both CB and PJ calibration sites at CLs of 2.2 and 3.6 kg $ha^{-1}year^{-1}$ for CB and PJ respectively, stabilizing at a fire risk of 5.5 and 8.8 kg N ha^{-1} $year^{-1}$ (Fig. 34.1).

The values of the CLs and fire stabilization loads in Fig. 34.1 are specific to the model calibration sites. To extrapolate across the landscape, average CLs and fire risk stabilization loads were calculated for multiple precipitation regimes × soil textures × N-deposition levels (Rao et al. 2010). In general, CL values decreased with increasing precipitation due to primary limitation by water in this arid system. Averaging across the soil textures evaluated and the range of precipitation common for CB vegetation in this region (mean annual precipitation < 21 cm) the average CL for CB was 3.2 kg ha^{-1} and fire risk stabilization occurred with 9.3 kg ha^{-1} N

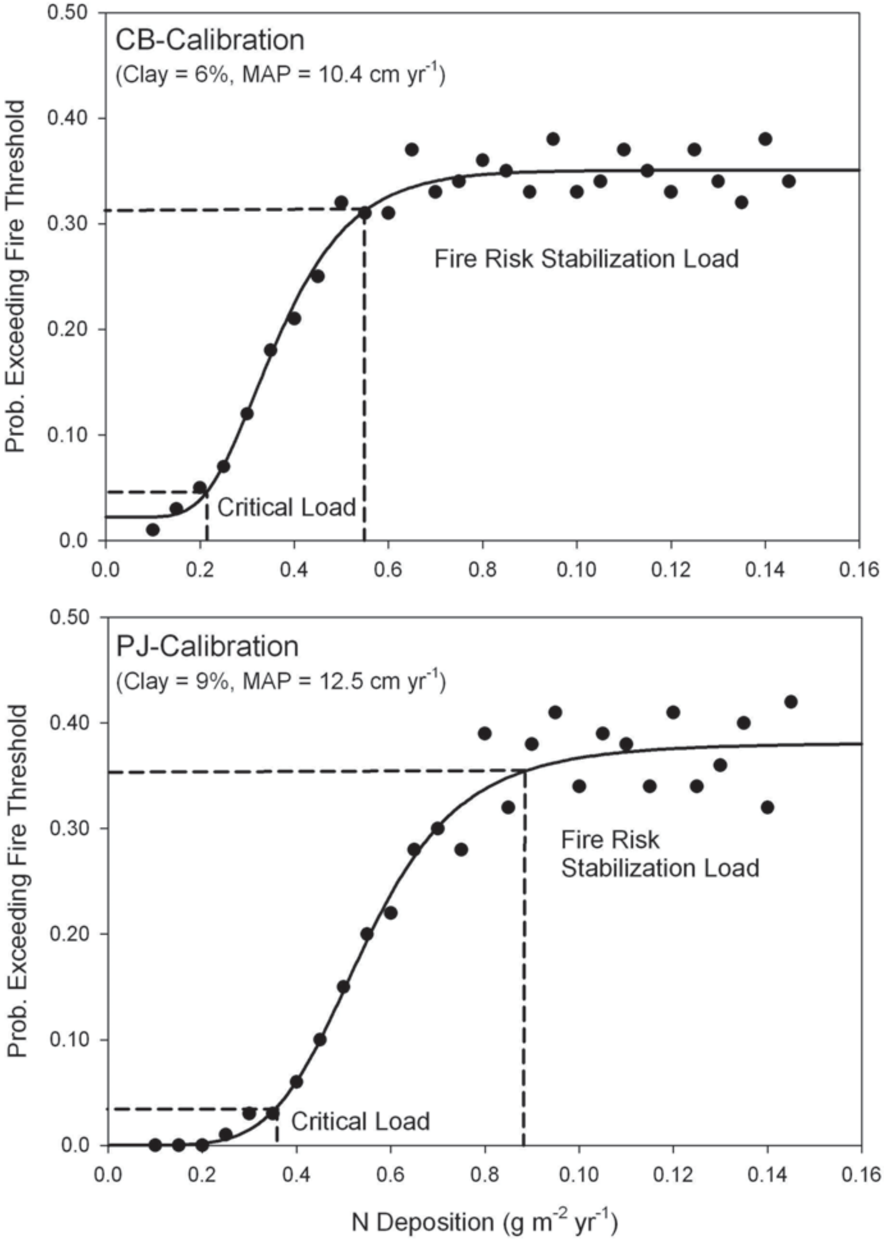

Fig. 34.1 Fire risk for creosote bush scrub (CB) calibration and pinyon-juniper woodland (PJ) calibration sites calculated as the probability that annual biomass will exceed the fire threshold (1 t ha^{-1}) under a given N deposition load. The critical load, the point at which fire risk begins to increase exponentially, is 2.2 and 3.6 kg N ha^{-1} of N deposition for CB and PJ respectively. The fire risk begins to level out at the fire risk stabilization load, which is 5.5 and 8.8 kg ha^{-1}. Between the critical load and fire risk stabilization load the fire risk changes very rapidly with N deposition (from Rao et al. 2010)

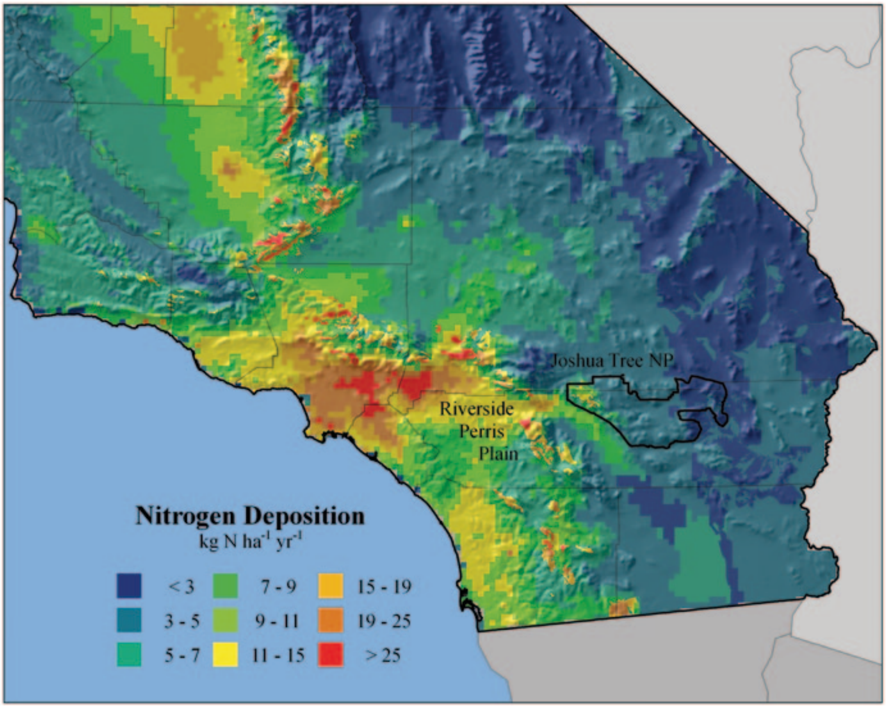

Fig. 34.2 Model of N deposition in southern California (From Tonnesen et al. 2007). Measurements of air quality, soil N, and species composition were taken from N deposition gradients in the Mojave/Colorado deserts (Joshua Tree National Park) and coastal sage scrub (Riverside-Perris Plain)

deposition. Similarly, the average CL for PJ was 3.9 and fire risk stabilization occurred at 8.7 kg ha^{-1} N deposition.

34.4 Nitrogen Deposition and Critical Load Exceedence in Southern California

Simulated N deposition data from the U.S. Environmental Protection Agency CMAQ (Community Multiscale Air Quality) model were developed for California (Tonnesen et al. 2007). The original model was processed on a 36 km^2 grid, and was updated on a 4 km^2 grid to improve local scale accuracy (Fig. 34.2). This model was used as the base map to determine CL exceedence using the CL values for desert and CSS vegetation.

Both modelled and measured values of N deposition are used to estimate CL exceedences for diversity loss in CSS (Fig. 34.3). The rapid loss in native richness between N deposition values of 9–11 (modelled) and 6.6 to 8.9 kg ha^{-1} year^{-1} (inferential method) suggests a more stringent 7.8 to a more conservative CL value

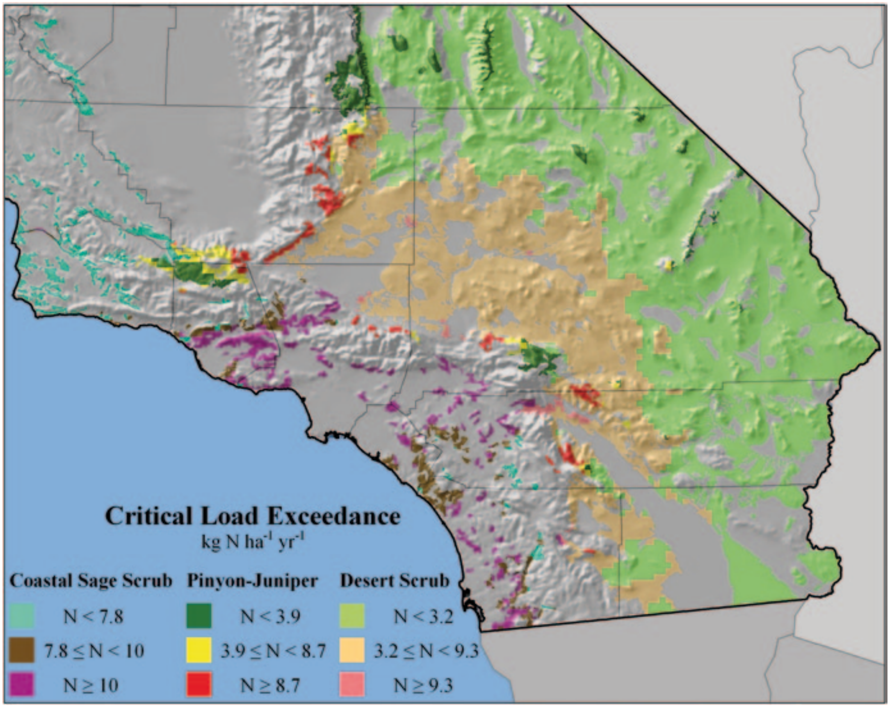

Fig. 34.3 Critical N loads for coastal sage scrub for loss of native forb diversity is 7.8 to 10 kg ha^{-1} $year^{-1}$. 33 to 53 % of CSS area exceeds CL using the higher and lower estimates of CL. Critical N loads for CB and PJ for moderate to high fire risk (fine fuel production = 1 t ha^{-1}) is 3.2 to 9.3 kg ha^{-1} $year^{-1}$ for increased fire hazard (fine fuel = 1 t ha^{-1}). 15 to 28 % of PJ, and 0.6 to 31 % of CB land area, exceeds CL using the higher and lower estimates of N deposition

of 10 kg ha^{-1} $year^{-1}$ for N deposition. More frequent species richness surveys at a greater number of sites, and more widespread N deposition measurements would confirm which value is more realistic. Of the total 632 km^2 of CSS in California, 33 % is in exceedance of the higher CL level and 53 % exceeds the lower CL level. CSS is a highly fragmented vegetation type, as shown in Fig. 34.3, that occurs in low elevation sites interspersed by higher elevation chaparral and oak woodlands, and often surrounded by urban and agricultural development. Furthermore, as Table 34.1 shows, many sites designated as CSS are actually dominated by exotic Mediterranean annual grasses with sparse shrubs.

Surrounding chaparral vegetation is more resilient to invasion and recovers more readily from fire, and also has a higher CL for N deposition of 14 kg ha^{-1} $year^{-1}$ (Fenn et al. 2010). Chaparral has sclerophylous evergreen leaves, while CSS is summer drought-deciduous, and therefore more susceptible to invasion. The CL for chaparral is based on nutrient loading of runoff water, while our CL for CSS is based on rapid responses by plants that include many native understory annual species and a seasonally fluctuating canopy. The N CLs for the two desert vegetation types are based on values averaged over multiple soil texture types, and based on 21 cm precipitation (Fig. 34.3). A more precise map would incorporate variations in mean precipitation and in soil texture classes in different regions. Creosote bush scrub covers some 75,000 km^2, with CL exceedence on 0.6 to 31 % of the land area using the higher and lower estimates of N deposition. This indicates that under a modest precipitation regime of 21 cm, that is higher than much of the drier western CB area, the vegetation may have increased productivity of invasive annual interspace vegetation and be subject to increased fire because of increased N deposition. Similarly, PJ covers 6,600 km^2, and CL exceedence occurs in 15 to 28 % of the land area using the higher and lower estimates of N deposition.

The differences in CL between desert and CSS may be related to the different criteria used, plant species richness loss in CSS and exotic species productivity and fire risk in desert, but also to the degree to which precipitation and soil N limits plant growth in the two vegetation types. The more mesic (compared to deserts) CSS soils are deeper and richer in nutrients and organic matter, and native CSS plants are adapted to higher levels of resources than desert plants. Thus they would likely be impacted at higher levels of N deposition than desert plants. While we have observed that native desert plants respond to N with increased productivity, they only do so if invasive plants are inabundant (Allen et al. 2009). Additional studies to refine these CL values are underway. It is hoped that efforts such as this will guide regulatory agencies to control N pollution in these sensitive ecosystem types, and reduce the frequent fires and allow recovery of native species diversity.

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Chapter 35
Empirical Critical Loads of Nitrogen in China

Lei Duan, Jia Xing, Yu Zhao and Jiming Hao

Abstract For supplying the scientific basis of future nitrogen (N) emission control, the empirical critical loads of some forests and grasslands in China were determined by using reported field observations of N effects. Results showed that the critical loads of forest varied from 10~30 kg N ha^{-1} $year^{-1}$ for temperate deciduous forest to 170~300 kg N ha^{-1} $year^{-1}$ for subtropical coniferous plantation, and those of grassland varied from < 50 kg N ha^{-1} $year^{-1}$ for typical temperate steppe and alpine steppe to 150~250 kg N ha^{-1} $year^{-1}$ for subtropical grassland. These critical loads were much higher than 10–15 kg N ha^{-1} $year^{-1}$ and 10–30 kg N ha^{-1} $year^{-1}$, the common values of natural forest and grassland respectively in Europe. The critical load map, based on the median of critical load range of each vegetation type, indicated that the empirical critical loads were lower in the northwest part of China, and higher in the southeast. Although the critical loads of N in the southeast part of China, where high nitrogen deposition existed, were relatively high to very high, critical loads occurred in some areas in north China and the south of northeast China, and sporadically in southwest China and east China. Nitrogen emission abatement is required in these areas to avoid exceedance of the estimated critical loads.

Keywords Emission control • Empirical critical loads • Nitrogen saturation

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35.1 Introduction

Sulphur dioxide (SO_2) and nitrogen oxides (NO_x) emissions are the main cause of acid deposition and secondary air pollutions of fine particles ($PM_{2.5}$) and ozone (O_3) in China. The national SO_2 and NO_x emission in 2005 was estimated to be 30.7 and 19.6 Mt respectively, much larger than (SO_2), or close to (NO_x) that of Europe or the United States in the same year (Zhao et al. 2009a). Under strong environmental pressure, the Chinese government set compulsory targets to reduce national energy intensity (i.e., energy consumption per unit GDP output) and SO_2 emissions of 20% and 10% respectively, during the period 2005–2010. In recent years, great efforts have been taken and have led to a reduction of SO_2 emissions. However, fast increasing NO_x emissions, together with NH_3 emissions mainly from agriculture, are counteracting the efforts of SO_2 abatement (Zhao et al. 2009a). Both modelling and monitoring results show that nitrogen (N) deposition in east China and southwest China is relatively high and could even reach 40 kg N ha^{-1} $year^{-1}$ and above (Chen and Mulder 2007; Fan et al. 2007a; Zhao et al. 2009a). That level was considerably higher than those observed in Europe and North America (Holland et al. 2005). Although elevated N deposition has been shown to cause adverse effects on ecosystems (e.g., Aber et al. 1998), it is still unclear how serious the impacts are in China. The objective of this study was to synthesize current research relating nitrogen deposition to effects on terrestrial ecosystems in China and to identify empirical critical loads of N where possible. Although empirical critical loads have been summarized for many ecosystems in Europe (Achermann and Bobbink 2003) and the United States (Pardo et al. 2011), very few results have been reported for different ecosystems in other parts of the world, such as China.

35.2 Materials and Methods

Empirical critical loads were determined by using reported field observations of detrimental ecological effects and noting the deposition level at which the effect occurred (Achermann and Bobbink 2003). In recent years, fertilization experiments have been carried out in China for some forests and grasslands, most of which had not been studied much before. A range of critical load was assigned to each studied ecosystem, with the higher limit equal to the lowest input level at which a response occurs, and the lower equal to the highest input level where significant effects were not observed. It should be noted that the total N input includes not only the fertilizer treatment added, but also the atmospheric deposition received by the experimental treatments. In this study, a combination of methods was used to determine N deposition for a given vegetation type. Throughfall deposition data were used, if available (see Table 35.1), to determine the N deposition in forest ecosystems. Otherwise, simulated total deposition data (both wet and dry deposition) from the USEPA CMAQ model (V4.4) (Byun and Ching 1999) were used. The model calculated N

Table 35.1 Summary of critical loads of N for some forests and grasslands in China**.** Reprinted from Liu et al. 2011, with permission from Elsevier

Vegetation	Site	Dominant species	N dep kg ha^{-1} $year^{-1}$	N input kg ha^{-1} $year^{-1}$	CL[a] kg ha^{-1} $year^{-1}$	Main response	Study
Subtropical coniferous plantation	Shaxian, Sanming, Fujian, 11,743′ E, 2,631′ N	*Cunninghamia lanceolata*	53	120~240	170~300 (70~140)	Decrease in litter decomposition and needle K, Ca, and Mg content	Fan et al. 2007a, b, 2008; Liu et al. 2008
Subtropical monsoon evergreen broad-leaved forest	Dinghushan Biosphere Reserve, Zhaoqing, Guangdong, 11,233′ E, 2,310′ N	*Schima superba*	38	50~100	90~140 (30~70)	Change in photosynthetic and physiologic characteristics of dominant understory species	Fang et al. 2005; Lu et al. 2006, 2007; Xu et al. 2005
Subtropical coniferous forest	Tieshanping Forest Park, Chongqing, 10,641′ E, 2,937′ N	*Pinus massoniana*	42	<40	40~80 (15~30)	N leaching, biomass decrease in ground vegetation	Lin et al. 2007
Subtropical evergreen broad-leaved forest	Liangfengao Forest Park, Muchuan, Sichuan, 10,347′ E, 2,829′ N	*Neolitsea aurata*	18	<50	20~70 (30~70)	Decrease in nutrient release from the litter and the decomposition of lignin and cellulose	Song et al. 2007a, b, 2009
Temperate coniferous forest	Changbaishan Forest Research Station, Jilin, 12,742′ E, 4,141′ N	*Pinus koraiensis*	12	25~50	40~60 (15~30)	Decrease in soil microorganism	Zhao et al. 2008, 2009b
Temperate deciduous forest	Fusong, Jilin, 12,729′ E, 4,220′ N	*Populus alba, Betula platyphyl*	7	0~25	10~30 (15~30)	Decrease in soil microorganism	Zhao et al. 2008, 2009b

Table 35.1 (continued)

Vegetation	Site	Dominant species	N dep kg ha^{-1} year^{-1}	N input kg ha^{-1} year^{-1}	CL[a] kg ha^{-1} year^{-1}	Main response	Study
Typical temperate steppe	Inner Mongolia Grassland Ecosystem Research Station (IMGERS), Xilin River Basin, Inner Mengonia, 11,640′ E, 4,332′ N	*Leymus chinensis*	4	105~175	110~180 for degraded; <50 for natural (15~30)	Peak value reached for specific leaf area, leaf N content, and total chlorophyll content	Wan et al. 2008; Bai et al. 2010; Pan et al. 2004, 2005
Temperate dry grassland	Yunwushan Grassland Natural Reserve, Ningxia	*Thymus mongolicus*	3	50~100	50~100 (15~30)	Thymus mongolicus community replaced by Stipahungeana	Cheng et al. 1996
Subtropical grassland	Dongchuan Mudflow Monitoring Station, Xiaojiang River Basin, Yunan	*Heteropogon contortus*	4	150~250	150~250 (30~70)	Gramineae dominant	Zhang et al. 2004
Alpine meadow	Maqu Grassland Research Station, Gansu, 10,210′ E, 3,401′ N Haibei Research Station for Alpine Meadow, Qinghai, 3,737′ N, 10,119′ E	*Kobresia humilis*	2	<150	<150 (15~30)	Decrease in biodiversity	Yao et al. 2009; Shen et al. 2002
Desert steppe	Siziwangqi, Wulanchabu, Inner Mengonia, 11,154′ E, 4,147′ N	*Stipa breviflora*	4	<100	<100 (<15)	Increase in N_2O emission	Shan 2008
Alpine steppe	North to Qinghai Lake, Qinghai	*Stipapur purea*	2	<50	<50 (15~30)	Decrease in biodiversity	Zhou et al. 2004

[a] Values in brackets are critical loads of nutrient N calculated by the steady state mass balance (SSMB) method (Duan et al. 2001; Zhao et al. 2009a)

concentration and deposition in each 36×36 km^2 grid in a domain covering most of East Asia (Zhao et al. 2009a). Total deposition of nitrogen (NO_3^- and NH_4^+) of each studied site is shown in Table 35.1.

35.3 Results and Discussion

The empirical critical loads of some forests and grasslands are shown in Table 35.1. As can be seen from the table, the critical loads of forest varied greatly from 10~30 kg N ha^{-1} year^{-1} for temperate deciduous forest to 170~300 kg N ha^{-1} year^{-1} for subtropical coniferous plantation. The critical loads are also low (<100 kg N ha^{-1} year^{-1}) for temperate coniferous forest and subtropical forest (both coniferous and broad-leaved). The critical loads of grassland varied from <50 kg N ha^{-1} year^{-1} for typical temperate steppe and alpine steppe to 150~250 kg N ha^{-1} year^{-1} for subtropical grassland. Other grassland types with low critical loads (<100 kg N ha^{-1} year^{-1}) include desert steppe and temperate dry grassland.

The values of the critical loads above were based on the different responses of biological or chemical variables to the varying level of N inputs such as physiological variation, reduced biodiversity, elevated nitrate leaching, and changes in soil micro-organism. The critical loads of forest and grassland obtained in China were much higher than the common values of natural forest and grassland in Europe, i.e., 10–15 and 10–30 kg N ha^{-1} year^{-1} respectively (Achermann and Bobbink 2003). It is easy to understand that the gap was bigger for subtropical ecosystems than for temperate ecosystems, because the European data were mostly for the latter. The reasons for the difference include both special ecosystems (e.g., warm-humid subtropical forests have more capacity cycling nitrogen input), and the high uncertainty caused by very limited studies, as well as short-term observations under high nitrogen dose in China. Some studies (e.g. the first three in Table 35.1) were carried out where current nitrogen deposition had already been very high, and maybe even higher than the actual critical load. The researchers might therefore have lost the chance to see the changes of the ecosystem that had already occurred. In addition, the effects of nitrogen deposition might not be distinguished from other anthropogenic impacts such as soil acidification by higher sulphur deposition and soil degradation by over-grazing.

In a previous study, critical loads of nutrient N in China were calculated and mapped through the steady state mass balance (SSMB) method (Duan et al. 2001). The range of values extracted from the previous map for each vegetation type is also shown in Table 35.1. The two sets of values showed positive correlation, and could be comparable for temperate deciduous forest, subtropical evergreen broad-leaved forest, typical temperate steppe, and alpine steppe. However, the empirical critical loads were much higher than the calculated ones for other vegetation types. Based on the median of critical load range of each vegetation type, a critical load map was drawn, as shown in Fig. 35.1. The distribution of agricultural field, which was insensitive to atmospheric nitrogen deposition and assigned a very high critical load of >200 kg N ha^{-1} year^{-1}, is also shown in the map.

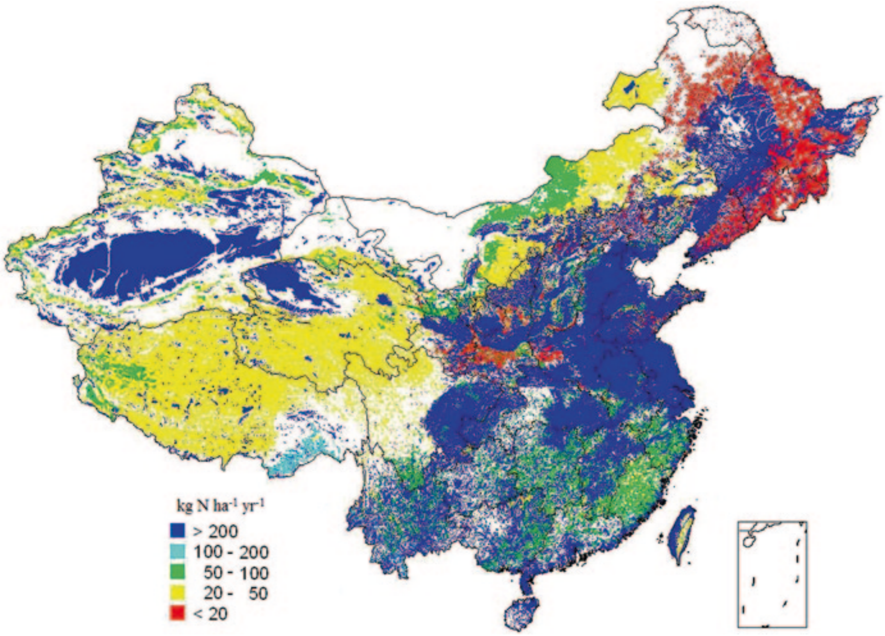

Fig. 35.1 Empirical critical loads of nitrogen in China. Blank means no data. (Reprinted from Liu et al. 2011, with permission from Elsevier)

As can be seen, the empirical critical loads were lower in the northwest of China, and higher in the southeast. The lowest critical load of N occurred mainly in northeast China and sporadically in north China, followed by northwest China, especially on the Qinghai-Tibetan Plateau and the east of Inner Mongolia. The N deposition in northeast China and northwest China was very low (<5 kg N ha^{-1} year^{-1}). In contrast, the critical loads of N in the southeast China, where high N deposition existed, were relatively high (subtropical in south China) to very high (agricultural in north China).

35.4 Conclusion

Empirical critical loads obtained from the reported results of N fertilization experiments has provided very important information on the current status of N problems in China, although more research on the effects of nitrogen deposition on ecosystems should be carried out. Since various weaknesses including extremely high dose, relatively short period, single response to observe, and the lack of deposition monitoring existed in the previous studies, future experiments should be well designed, and follow some uniform standards for empirical critical load estimation.

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Chapter 36
Challenges in Defining Critical Loads for Nitrogen in UK Lakes

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Abstract It is now widely recognised that the deposition of nitrogen (N) compounds can lead to both acidification and eutrophication impacts in upland lakes. While major reductions in sulphur (S) emissions and deposition in the UK have been largely matched by chemical recovery from acidification in surface waters, reductions in emissions of N compounds have not been matched by corresponding reductions in deposition. Here we explore two related issues in the use of critical loads for N in upland waters:

1. Identifying potential impacts of nutrient N in naturally nutrient poor systems of conservation importance and links to biodiversity, and
2. Problems in defining critical chemical limits with respect to reference conditions in upland lakes.

Empirical critical loads for nutrient N have been recommended to protect macrophyte communities of shallow softwater lakes in Europe. The recommended range of 5–10 kg N ha^{-1} year^{-1} is exceeded across most of the UK, but most oligotrophic lakes are of a different habitat type to those for which empirical critical loads have been recommended. Furthermore, while there is widespread evidence from nutrient bioassay work for N limitation of phytoplankton production in oligotrophic lakes there is little direct evidence to date of impacts on other biological groups

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in the UK, including macrophytes. A major problem is the lack of data on reference communities in unimpacted lakes and lack of identified "harmful ecological effects" required by the definition of critical loads. There are also fundamental differences in approach between the critical loads employed under the UNECE Gothenburg Protocol and the EU Water Framework Directive. We show that there are major challenges in application of critical loads for nutrient N which must be overcome if we are to protect designated sites of conservation interest and maintain, or allow recovery to, the good ecological status required by the EU Water Framework Directive.

Keywords Acidification • Eutrophication • Nitrogen deposition • Nitrogen limitation • Phytoplankton

36.1 Introduction

The definition of a critical load for nitrogen (N) deposition requires the specification of both a harmful effect and a sensitive indicator organism with the most widely used definition being: "*a quantitative estimate of the loading of one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge*" (Nilsson and Grennfelt 1988). For surface water acidification this is readily accomplished, but for potential nutrient nitrogen effects in lakes (i.e. N deposition as an agent of eutrophication) the nature of the harmful effect and the requisite dose-response function are more difficult to identify.

36.2 Acidification by Nitrogen Deposition

The role of NO_3^- in surface water acidification is well established (e.g. Curtis et al. 2005) and both steady-state and dynamic models are available to calculate critical loads and target loads for acid deposition (S+N) e.g. the First-order Acidity Balance Model (Posch et al. 1997). Leaching of NO_3^- leads to acid neutralising capacity (ANC) decline and hence can be linked to harmful effects because dose-response functions are known, e.g. for ANC & brown trout (Fig. 36.1). In this example, empirical studies of historical brown trout status (unchanged, reduced, extinct) from fishery records was linked to contemporary water chemistry data for a large number of Norwegian lakes to produce a relationship between ANC and probability of finding a healthy, reduced or extinct trout population. The UK currently submits critical loads for total acidity data for surface waters to the international mapping and modelling programmes co-ordinated under the Gothenburg Protocol of the UNECE Convention on Long-Range Transboundary Air Pollution and is one of only five countries to do so. A critical ANC value of 20 μeq l^{-1} is widely used, corresponding

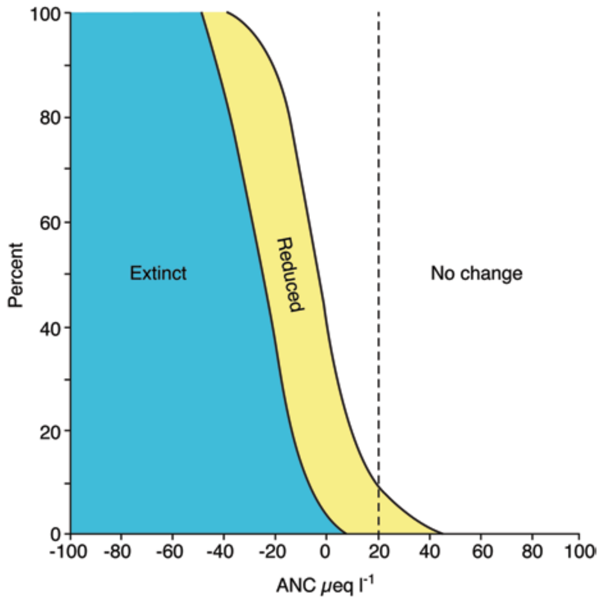

Fig. 36.1 Relationship between status of brown trout populations and ANC in Norwegian lakes (redrawn from Lien et al. 1996). *Dotted line* represents critical ANC used in the UK

to a 10 % probability of reduced brown trout populations and a 90 % probability of healthy populations (all other factors being equal).

36.3 Deposited Nitrogen as a Nutrient in Upland Lakes

Nutrient N deposition, rather than acidification, has been cited as the cause of ecological change in several studies of diatoms and phytoplankton in alpine and Arctic lakes (e.g. Baron et al. 2000; Wolfe et al. 2001; Fenn et al. 2003; Sickman et al. 2003) as well as humic lakes (e.g. Jansson et al. 1996). Phytoplankton bioassays have been used to demonstrate that N limitation of phytoplankton production is almost as common as phosphorus (P) limitation in oligotrophic UK lakes (Maberly et al. 2002; Curtis and Simpson 2007, Table 36.1). The widespread incidence of current N limitation of phytoplankton production in oligotrophic lakes is now well established in Europe and North America (Bergström and Jansson 2006). It has been speculated that some lakes where phytoplankton production is currently P-limited may have been N-limited prior to the onset of NO_3^- leaching due to N deposition, but this is difficult to prove. Paleolimnological techniques may be useful here but a major problem is that possible nutrient N effects are often masked by acidification and/or climate change which have occurred over similar timescales as increased N deposition; diatoms in particular are very sensitive to both drivers. Some authors have attributed increases in planktonic diatom taxa like *Cyclotella*, *Tabellaria* and *Asterionella spp.* to climate change (e.g. Smol et al. 2005), but the potential role of N deposition is still being debated.

Table 36.1 Summary of nutrient bioassay results in summer 2005, assessed as significant increases in chlorophyll-a following treatments with N, P or N+P relative to controls. *P* phosphorus-limitation, *N* nitrogen-limitation, *Co* co-limitation. From Curtis and Simpson (2007)

Site	OS Grid Ref.	June	July	September
Lake District, NW England				
Scoat Tarn	3159, 5104	P	P	P
Small Water	3455, 5100	Co	Co	Co
Burnmoor Tarn	3184, 5043	Co	N	Co
North Wales				
Llyn Edno	2663, 3497	Co	P	P
Llyn Gamallt Fawr	2745, 3439	Co	Co	N
Llyn Hiraethlyn	2743, 3370	N	N	Co
Llyn Mair	2653, 3413	Co	P	Co
Southern England				
Hammer Pond	5397, 1287	N	Co	N
Grampian Mountains, NE Scotland				
Loch Beanie	3160, 7686	Co	P	P
Lochnagar	3252, 7859	Co	P	P
NW Scotland				
Loch Coire nan Eion	1925, 8508	Co	Co	P
Loch Coire Fhionnaraich	1945, 8498	Co	N	Co
Loch Coire Mhic Fhearchair	1943, 8606	Co	P	P

36.4 Critical Loads for Nutrient Nitrogen for Lake Macrophytes

Empirical critical loads for nutrient N deposition to lakes were initially only proposed for shallow softwater lakes on sandy soils (Bobbink et al. 1998) based on studies of Dutch lakes where high inputs of ammonium led to the replacement of isoetid macrophyte communities with dense stands of *Juncus bulbosus* and/or aquatic mosses like *Sphagnum cuspidatum* and *Drepanocladus fluitans*. However, following the Expert Workshop on Empirical Critical Loads for Nutrient N held in Berne in November 2002, the habitat definition for inland surface waters for which empirical critical loads should be applied was broadened to include all softwater lakes (Achermann and Bobbink 2003).

The proposed range of empirical critical loads was set at 5–10 kg N ha^{-1} $year^{-1}$ with the highest level of confidence used under this system ("reliable"). This broader habitat definition, corresponding to EUNIS class C1.1 (permanent oligotrophic lakes, ponds and pools) is now appropriate for many UK upland waters. However, total N deposition levels exceed 5 kg N ha^{-1} $year^{-1}$ across almost all of the UK and 10 kg N ha^{-1} $year^{-1}$ across much of the country. In NW Scotland where the majority of these lakes occur, deposition varies from 5–10 kg N ha^{-1} $year^{-1}$ so exceedance would depend on which empirical value was selected. However, given the lack of evidence for N-induced changes in softwater macrophyte communities in the UK, empirical critical loads for nutrient N deposition to lakes are not currently included in official datasets submitted under the Gothenburg Protocol.

36.5 Reference Conditions, Water Framework Directive and Defining Impacts

A key problem for defining nutrient N critical loads for UK lakes is the lack of defined "harmful effects". Palaeolimnological work has demonstrated major changes in diatom communities but acidification has been a major driver, while bioassay studies demonstrate than N limitation of phytoplankton production is currently common. However, increased production *per se* due to N deposition is not necessarily a "harmful effect" unless there are demonstrable impacts like algal blooms or loss of biodiversity, and information on reference communities for organisms other than diatoms is generally lacking. Under the EU Water Framework Directive (WFD), there is a requirement to meet "good ecological status" by 2015 defined relative to a departure from reference conditions.

Recent analysis of chemical and biological trends in the UK Acid Waters Monitoring Network has shown major chemical and biological recovery from the effects of acidification, due mainly to 90% reductions in sulphur (S) deposition relative to maximum levels in the 1970s (Kernan et al. 2010). However, N deposition has declined relatively little over the last 20 years. Furthermore, some biological trends show "recovery" towards a new state not previously recorded, potentially due to the dual impacts of climate change and N deposition. For example, epilithic diatoms sampled annually over 20 years show the appearance of species not previously recorded (Fig. 36.2) even in lake sediment cores spanning the period of acidification and chemical recovery (>150 years). Furthermore, some changes in macrophyte communities are becoming apparent which are not linked to recovery from acidification, with expansion of coverage or depth ranges for some species and the appearance of species not previously recorded in some sites. Hence there is evidence of ecological changes in some lakes, but these cannot yet be linked causatively, let alone quantitatively, with nutrient N deposition, even where recovery from acidification can be ruled out. Climate change is a likely contributing factor.

36.6 Where Next for Nutrient Nitrogen Critical Loads?

There are two key issues in defining nutrient N critical loads for UK lakes:

1. A lack of "pristine" or reference lakes to provide information on refer- ence biological communities beyond diatoms, and
2. A lack of defined target organisms and harmful effects.

These problems are compounded by a shifting climatic baseline against the backdrop of recovery from acidification and ongoing high levels of N deposition.

It is clear that N limitation of phytoplankton production is relatively common in softwater lakes in the UK and therefore that changes to lake ecosystem structure and function may be caused by elevated N deposition. Future work must therefore address the following challenges:

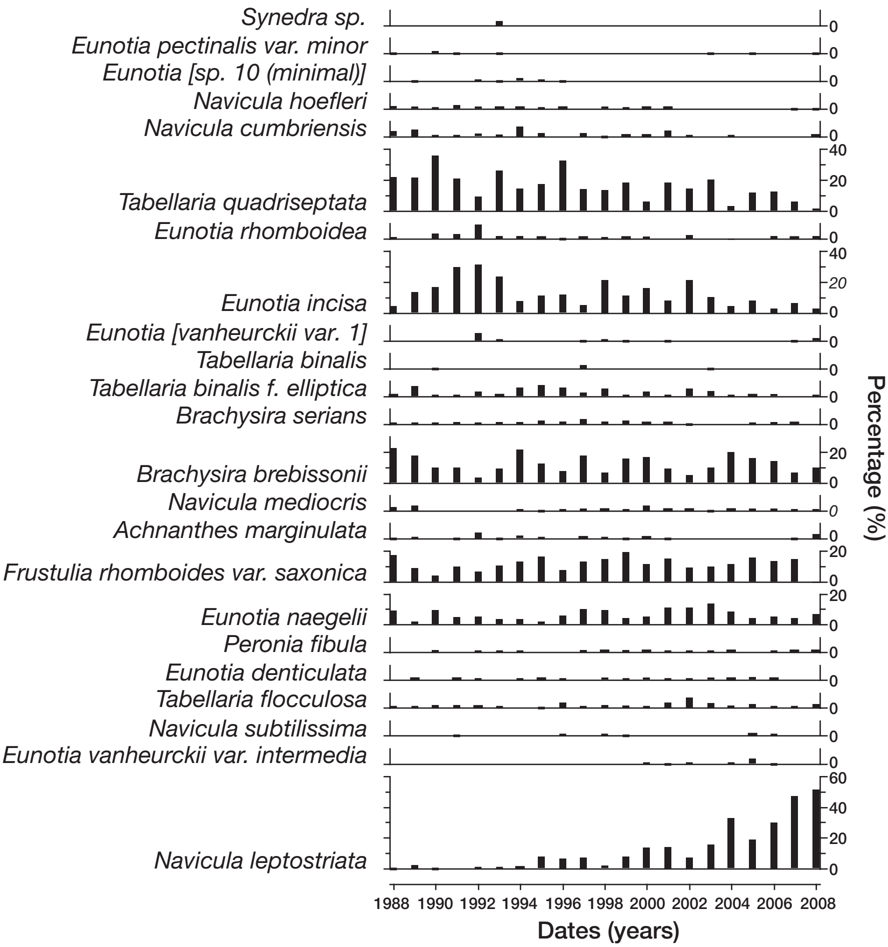

Fig. 36.2 Trends in epilithic diatoms in Round Loch of Glenhead (from Kernan et al. 2010). The species *Navicula leptostriata* was never common in the loch but has become the dominant species in the last 10 years

- development of approaches to determine reference biological communities e.g. other palaeolimnological proxies, analogue matching approach—so far these are only well established for diatoms;
- identification of appropriate sites, i.e. lakes where drivers of change other than N deposition may be ruled out (e.g. circumneutral lakes without direct catchment disturbance or nutrient sources, where acidification cannot be the driver of change)—requires consideration of climatic drivers;
- identification of harmful effects and quantification of critical loads—this is likely to require experimental work in addition to collection of relevant chemical

and biological data, to ascertain wider ecological effects of bottom-up changes in primary producers.

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Chapter 37
Proposing a Strict Epidemiological Methodology for Setting Empirical Critical Loads for Nitrogen Deposition

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Abstract Currently empirical critical loads are derived from manipulation experiments and field survey data and more recently these data have come under scrutiny as our understanding of how ecosystems respond to reactive nitrogen (N_r) deposition evolves. The importance of background nitrogen (N) deposition and the significance of the starting N capital, cumulative N, are now recognized. This has led to a credibility rating against which experimental data can be evaluated. However, there is still no robust and transparent system in place for setting empirical critical loads for nitrogen deposition. This chapter discusses some of the issues involved in the evaluation of the available data and proposes a testable approach to carry the system forward.

Keywords Critical loads • Cumulative deposition • Empirical model • Epidemiology • Nitrogen

37.1 Introduction

Empirical critical loads have been assembled based on manipulation experiments and field observation data (Grennfelt and Thörnelöf 1992; Achermann and Bobbink 2003; UBA 2004). The limits have been compared with model estimates and some

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differences are apparent. There are several problems associated with interpreting the observed data:

1. The relatively short term perspective of the available experiments (2–5 years) as compared to the long perspective of critical loads (50–300 years) and inherent ecosystem delays (5–150 years) remain as a significant problem for empirical critical loads, but for lack of better alternatives, we have so far worked with what is available. However, model simulations (Belyazid et al. 2006; Sverdrup et al. 2005, 2007) suggest that this may be a major problem and lead to overestimation of the critical load.
2. Separation of confounding factors (effects of acidity, nitrogen, climate change, animal browsing, droughts). In particular, acidity has a strong effect on many plants, and comparing nitrogen (N) experiments at say pH 4 and pH 6 for N effects will simply not do. Different N doses in experiments may alter pH between experiments.
3. The effect of background N deposition (Sutton et al. 2003) and long term effects of soil storage buildup. (The experiment may have been conducted in a N deposition regime beyond the effects region).
4. Lack of incorporation of effects of inter-plant competition in the ecosystem. The plant may have to put up with a sub-optimal niche, because a naturally occurring competitor has taken the best space.
5. Earlier there was an omission of the background deposition, based on the naïve assumption that any responses were to the addition alone (Sutton et al. 2003). Such omissions have mostly been recognized and compensated for in the database, however there is still work to be done to ensure all these numbers have been removed.
6. Several experiments are in the database even though the sites where they were undertaken had already been affected by N deposition loads way beyond the critical load. These experiments and their results need to be removed from the database as the results are inappropriate for critical loads assessment.
7. We lack proper epidemiological evaluation of the available results.

Many of the derived limits do not make sense in remote areas and in the Nordic countries. In several important cases for the Scandinavian mountains and Lappland, the proposed critical loads and derived limits have limited credibility. Early in the critical loads process, when deposition was high, small inaccuracies were less important, this is no longer the case. It is therefore timely to reassess the available data.

37.2 Objective

Despite these deficiencies in present methods of determining empirical critical loads, we acknowledge that up to now they have provided a very useful legislative tool. Our objective in this chapter is to outline suggested improvements or develop alternatives.

37.3 Methods Applied so Far

The presently applied method involves looking at experiments, and identifying the dose with the first statistically significant effect, as the critical load. No compensation is made for differences in soil pH in any systematic way. This methodology has a significant problem built in, as it sets the critical load automatically, when there is an effect, even though the effect level may be somewhat arbitrary. More importantly the effect and its level are not consistent between the experiments used. There is no predefined indicator impact effects level used to set the cutoff for reading off the critical load. This inevitably leads to too high critical load estimates and built-in inconsistencies which greatly expand uncertainty ranges. This all adds to the conclusion that the present empirical critical loads are provisional estimates, and probably, to an unknown degree, represent an overestimate of the real value. From the viewpoint of an ongoing environmental policy development perspective, this is not a problem, as long as it is realized and that the process is iterative towards improved estimates. From the point of view of the precautionary principle, present estimates are unsatisfactory in the long run.

The N doses in the available experiments should be described as the ambient deposition at the site plus any additions (treatments). Thus we have:

$$\text{Dose} = \text{Ambient Deposition} + \text{Additions} + \text{Fixation} \qquad \text{(Eq. 37.1)}$$

This must be applied throughout the database.

Parts of central Europe and the British Isles currently have N deposition >40–50 kg ha^{-1} $year^{-1}$, and have had this level or higher for many decades. Assessing biodiversity responses, from field N addition experiments at such sites, are arguably worthless for critical loads and limits assessments for the reasons already highlighted. Any such experiments will need to be removed from the database.

37.4 State-of-the-Art Methods

Any new methodology should follow that which can be derived from the experience made in the LRTAP effort to define critical loads, first for acidity, later for nitrogen, extended to critical levels for ozone and VOC, and finally into the field of heavy metals. The issue has also been raised for the treatment of persistent organic pollutants (POPs), but even if the concept is excellently fitted for the purpose, the timing is not yet right. For each ecosystem one or more of the following deliverables can be foreseen:

1. Identified parameters
2. Capacities
3. Critical rates of change

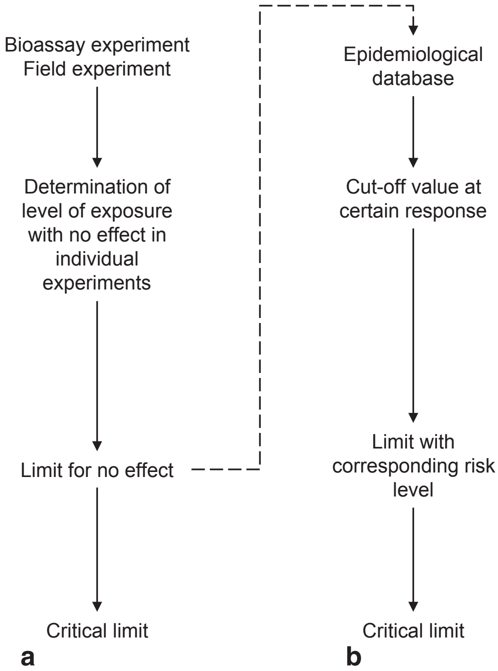

Fig. 37.1 Formal procedure for setting critical limits according to epidemiological principles

4. Critical time windows
5. Time-dependent guard-rails
6. Critical system structures

A state-of-the-art methodology needs to be described and then applied over the whole range of experiments, considering points 1–7 made above concerning confounding factors. For the setting of limits for heavy metals, a proper systematic method was drawn up, (see Fig. 37.1). For acidification this was systematically done with respect to aluminium and its counter ions calcium, magnesium and to some degree potassium. For acidity this methodology was also applied as shown in Fig. 37.2 for Norway spruce. The *Effects Cutoff* was set at 20 % effect and the critical limit read off as indicated in Fig. 37.2.

This was repeated for different tree species. Species specific limits, such as BC/Al = 1.2 for Norway spruce, BC/Al = 1 for pine, BC/Al = 0.8 for oak and beech BC/Al = 0.7 for birch were identified. This has been repeated, maintaining consistency, for a wide range of plants, almost 200 different species, originating from North America, Europe and China, where data was available (Sverdrup and Warfvinge 1993).

Some plants do not have a naturally decreasing pattern of response to increasing N availability, and the more N they get within the possible range, the stronger the growth response. For many plants, the downturn is not inherent to the plant, but an emergent effect of the competition: Plant A disappears, not because A cannot tolerate N, but because plant B outcompetes it for the space at the particular N levels.

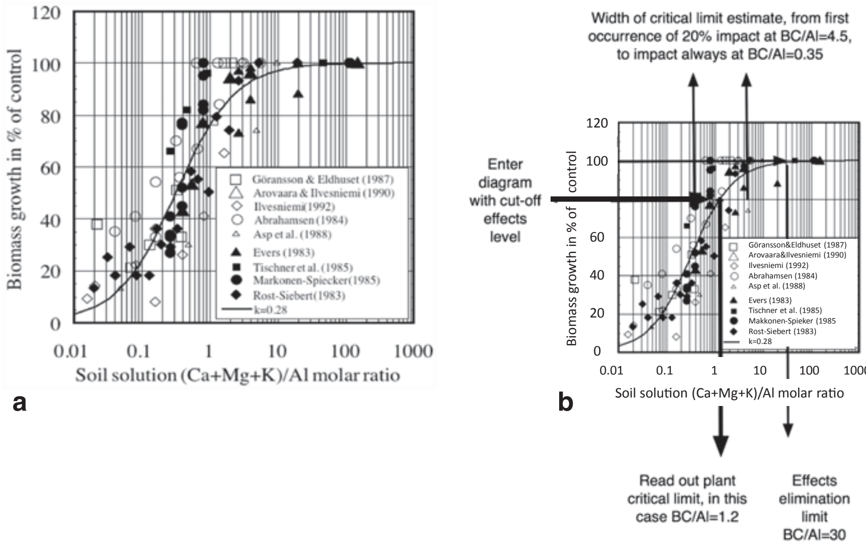

Fig. 37.2 **a** Dose response data collected for Norway spruce and used for estimation of critical limits used for estimation of critical loads for acidity (from Sverdrup and Warfvinge 1993). **b** Illustrates the systematic evaluation, to identify a critical limit for Norway spruce (BC/Al = 1.2) and an effects range (20 % effect in all experiments: BC/Al = 0.35, first incidence of 20 % impact begins at BC/Al = 4.5) Figures 37.2a and 37.2b incorporate values from: Göransson & Eldhuset (1987); Arovaara & Ilvesniemi (1990); Ilvesniemi (1992); Abrahamsen (1984); Asp et al. (1988); Evers (1983); Tischner et al. (1985); Makkonen-Spiecker (1985); Rost-Siebert (1983)

The N effect is made up of two parts, a promoting part and a retarding part. The promoting part is described in Sverdrup et al. (2007):

$$f(N+) = \frac{a_0 * [N]^{w+}}{\left(k_+ + [N]^{w+}\right)} \tag{Eq. 37.2}$$

where [N] is the concentration of N in solution (mg l^{-1}). The larger initial value (a_0), the greater the promotion. k+ describes when, i.e. how late, the effect occurs. W sets the steepness of the curve. The retarding effect is given by Sverdrup et al. (2007; Figs. 37.3 and 37.4):

$$f(N\_) = \frac{k\_}{(k\_ + [N]^{w-})} \tag{Eq. 37.3}$$

A large k_ gives very little retarding effect, while a small k_ has a substantial regarding effect. The exponent w sets the steepness of the curve. All plants need N, thus, there is always a point with zero growth at zero input of N. The apparent exception to this are those plants in symbiosis with N fixers, however this still amounts to an N input, moving them up the curve. The challenge is to estimate the size of

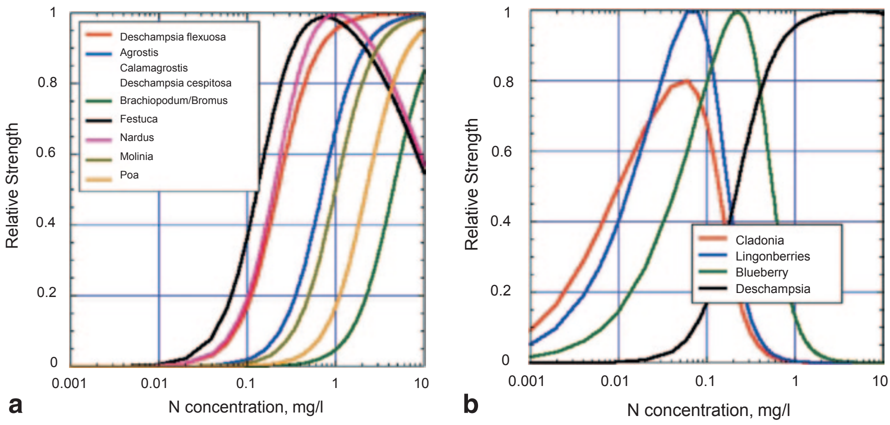

Fig. 37.3 **a**, **b** Examples of nitrogen response curves estimated from available single plant experiments and used for ForSAFE-VEG. The curves are partially based on unpublished experiments found in the archives of the former department of Plant Ecology at Lund University. Such curves can be used as the BC/Al-response diagram was used for Norway spruce in Fig. 37.2

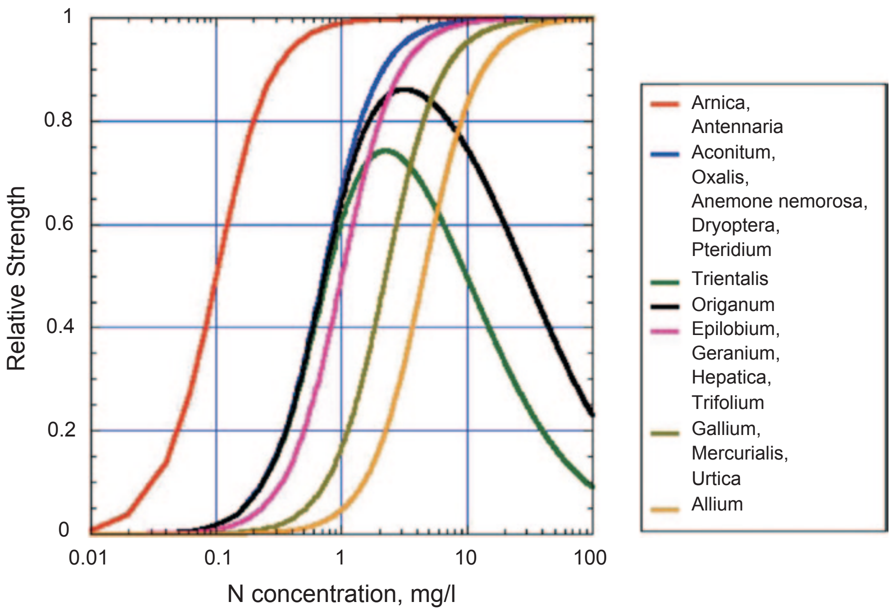

Fig. 37.4 Example of nitrogen response curves estimated from available single plant experiments and used for ForSAFE-VEG

the fixation. Thus, there is normally one free point on the graph, the 0.0 point. The N response curve for most plants (growth strength, height, weight, root length etc) and ecosystems (biomass, diversity indices, species composition aspects) must have a maximum.

37.5 A Methodology

The proposed methodology follows the scheme outlined in Fig. 37.1. An example of the treatment of observed data and critical load setting, in accordance with species decline is given as follows: The observed response (G) represents in reality the combined effect of many factors. We need for each case to estimate these, or have good reason for eliminating them from the analysis (see Sverdrup et al. 2007):

$$G = k_0 * g(pH) * f(N) * p(T) * k(water) \qquad \text{(Eq. 37.4)}$$

For most experiments, the temperature and soil moisture may be assumed to be the same between treatments, at least when they are located in the same place. Thus we may set p(T) to = 1 and k(water) to = 1, removing them. However, different N additions may affect soil pH, a factor that cannot be ignored and should be factored in to G (see above), especially when the N dose is large.

In order to establish an epidemiological database, the relative response is generated by taking the ratio between the estimated maximum value, and those observed at any dose of N. Thus we get: Effect = G/G_0; where G is the growth or length or the quantitative measure measured, G_0 the maximum point on the response curve, the internal normalization standard. When we use data from different sites, the differences between them with respect to pH, water, temperature must be considered, as well as, possibly access to light, if it is significantly different between the experiments or if it changes over time. The effect between the two experiments (treatments) will be approximated by:

$$\text{Effect} = g(pH) * f(N) * p(T) * k(water) / g(pH_0) * f(N_0) * p(T) * k(water) \qquad \text{(Eq. 37.5)}$$

If they are at the same site, the effects of temperature p(T) and water, k(water) can be set to 1:

The normalized N effect = $G/G_0 * g(pH_0)/g(pH)$, which can be used to eliminate most pH differences. pH functions are described for most naturally occurring European plants in Sverdrup and Warfvinge (1993). This empirical methodology can capture all the responses, however, the distinction illustrated in Fig. 37.5a, b may prove difficult. Plants only register the total occurrence of nitrogen, they cannot distinguish the source of N i.e. which comes from pollution, background fallout or addition. Plants can only respond to the form, concentration and dose of N and the temporal nature of the supply.

It is important to remind ourselves that "data" does not represent the truth; rather it has to be interpreted. Without a guiding principle for how it should be interpreted, "data" may be of little value or even misleading. Data represented in Fig. 37.6a are often interpreted, as drawn, with linear regressions. However, we now understand that with respect to N responses a curve such as illustrated in Fig. 37.6b is more appropriate. This captures what we know about ecosystem dynamics and Liebig's

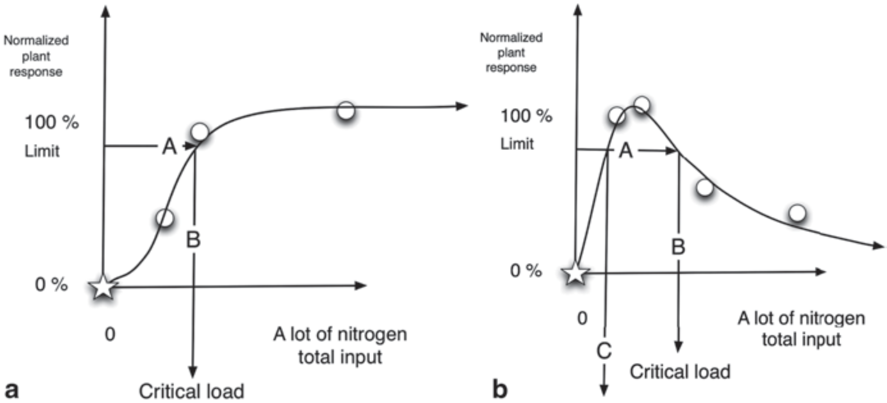

Fig. 37.5 Examples of two frequently observed response patterns in nitrogen addition experiments, for two basically different types of plants growing alone. Whole ecosystem assessments may respond in a similar fashion. **a** The figure shows a plant that only responds positively to added nitrogen. No retardation occurs within reasonable N doses for such plants, e.g. many grasses and legumes. **b** The diagram shows another typical response pattern, where initially added nitrogen promotes growth, later toxic effects or secondary retarders set in to reduce growth at higher dosages. In semi-natural ecosystems this is probably the most common response pattern. In the diagrams, the *star* depicts the free data point. We know that with no nitrogen, there can be no growth and no biodiversity

law of limiting nutrients: there is a promoting part from nothing to some nitrogen, a maximum and a declining part from optimal nitrogen towards too much nitrogen. The challenge is to construct a coherent method for setting critical loads that captures this dynamic i.e. the shape of the response curve.

37.6 We Do Know the Shape of the Response Curves

One of the challenges to adopting a robust, non-subjective approach that has been voiced is that, “we do not know the shape of the response curves”. We dispute this, believing we have a good working knowledge of what the response curves look like. When we have data, they show systematically similar shapes depicted in Figs. 37.5a and 37.6b based on laboratory and field data. We conclude that the time is right to adopt a proper methodology bearing in mind that:

1. With no N, there can be no plant or no biodiversity. (This is the star point in Figs. 37.5b and 37.6b).
2. If the site has N fixers, these organisms contribute a N input.
3. For some plants, experimental evidence shows that they can tolerate extremely high N inputs (Fig. 37.5a, some grasses like Poa are good examples).
4. For all plants and for biodiversity, an upper limit will be reached where everything is retarded, or poisoned or somehow retarded by more nitrogen. For some

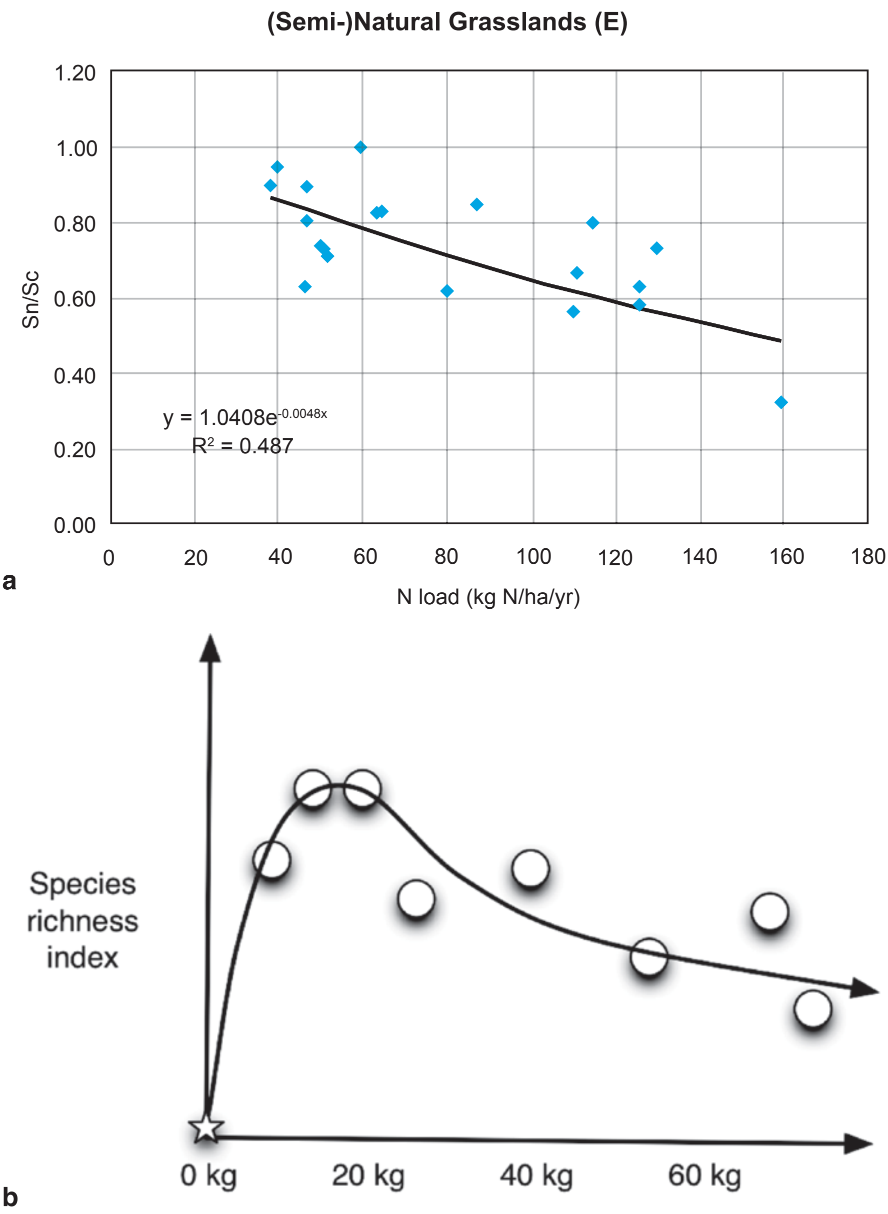

Fig. 37.6 **a** Data shown at the *top* are often interpreted with linear regressions, mostly because of lack of data extending to the lower end of the nitrogen load range (probably because such N sensitive species have already been lost from many of our ecosystems). **b** The diagram at the *bottom* describes the appropriate interpretation. The curve is not linear, but has a promoting part, from nothing to some nitrogen, and a declining part, from optimal towards too much N. From this, the challenge is to construct a coherent method for setting critical loads. Considering the effect of competition and feedback effects is probably beyond the approach of empirical critical loads, and a task for integrated models

plants, this occurs at relatively low N doses, for others at much higher N doses as compared to the pollution levels discussed. This effect is always present (Figs. 37.5b and 37.6a, b).

These rules also apply to biodiversity effects, where the whole interplay of plants acts out in an ecosystem. Here the whole ecosystem responds in a similar way to that depicted for single plants. Just like the single plant, the ecosystem has its own compensating mechanisms with limited capacity. In addition to having actual single plant data, we also have Ellenberg classifications, and much expert knowledge. With curves like those shown in Figs. 37.5a and 37.6b, experts are able to assign plants to or in-between existing curves or compose new curves from old, using this knowledge. Experts with this knowledge can be found in most countries with good scientific and ecological research traditions.

37.7 Conclusions

- The empirical response curve must have an early "promotion" part at very low N inputs, a maximum depending on indicator plant or ecosystem, and normally a "retardation" part for high N inputs (Figs. 37.5b and 37.6b).
- Such a response curve should provide the foundation for a strict epidemological methodology for setting empirical critical loads for N deposition.
- The empirical critical loads database for N is in urgent need of a complete revision: sufficient data exists, but the evaluation has so far been only approximate and somewhat unsystematic, now we have the means to fix this.

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Chapter 38
A Comparison of Empirical and Modelled Nitrogen Critical Loads for Mediterranean Forests and Shrublands in California

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Abstract Nitrogen (N) deposition is impacting a number of ecosystem types in California. Critical loads (CLs) for N deposition determined for mixed conifer forests and chaparral/oak woodlands in the Sierra Nevada Mountains of California and the San Bernardino Mountains in southern California using empirical and various modelling approaches were compared. Models used included the Simple Mass Balance (SMB) model for nutrient N and acidification (both site-specific and regional approaches) and the Daycent process-based biogeochemical simulation model. Empirical CLs reported herein were based on responses across N deposition gradients of lichen community functional groups and streamwater nitrate (NO_3) leaching. Broad scale CL mapping for the San Bernardino Mountains using the SMB model resulted in nutrient N CL values that were on average approximately 50 % lower than the empirical CL value for NO_3 leaching (17 kg ha^{-1} year^{-1}) in California mixed conifer forests. Over the range of elevations and vegetation types in the San Bernardino Mountains, SMB CL values ranged from 5.1 to 13.0 kg ha^{-1} year^{-1} for nutrient N. For both the empirical NO_3 leaching CL and the SMB estimate, the CL was generally lower for chaparral vegetation than for forests. The estimated CL for NO_3 leaching derived from the Daycent model was equal to the empirical CL (17 kg ha^{-1} year^{-1}), but the severity and frequency of elevated NO_3 leaching was

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underestimated by Daycent. Statewide empirical CL exceedance maps indicate that 3.3 and 4.5 % of the chaparral and forested areas in California are in excess of the NO_3 leaching CL. Likewise, 23.4, 41.2 and 52.9 % of the mixed conifer forest, oak woodland and chaparral areas are in excess of the empirical N CL for epiphytic lichen community effects, respectively. Eutrophication effects in terrestrial ecosystems of California are widespread, while significant acidification effects are limited to the more polluted sites in southern California.

Keywords Biogeochemical models • Critical load exceedance • Epiphytic lichen communities • Nitrate leaching • Soil acidification

38.1 Introduction

Critical loads (CLs) have been developed as a tool for determining the atmospheric deposition below which significant harmful effects do not occur according to present knowledge. Critical loads can be determined for acidification effects of nitrogen (N) and sulphur (S) deposition, and for nutrient or eutrophication effects of N using models of varying complexity or from field observations at sites with varying levels of atmospheric deposition or nutrient addition studies. The latter two are referred to as empirical CLs.

Modelled CLs can be calculated and mapped across the landscape based on soil mineralogy, chemistry, hydrology and nutrient cycling data. Empirical CLs are determined from field observations under real world conditions. Each approach has its own sources of uncertainty and most appropriate applications. Empirical CLs can be used to evaluate whether modelled CLs are realistic. Moreover, empirical CLs are important because sometimes the important factors controlling ecosystem responses to atmospheric deposition and co-occurring stressors are difficult to model or replicate under experimental conditions. Modelled CLs in conjunction with experimental studies can be useful in determining mechanistic processes and controlling factors affecting the CL and for predicting CLs where empirical data are absent. In this study we compare empirical and modelled CLs for forests, oak woodlands and chaparral ecosystems in California. Both acidification and eutrophication CLs were considered.

38.2 Methods

38.2.1 Study Locations

Critical load calculations were performed using soils data for the San Bernardino Mountains which are located inland from the greater Los Angeles, California urban region. Streamwater samples for nitrate analysis were collected from the San Bernardino Mountains and southwestern Sierra Nevada Mountains in central

California. Lichen community data were collected from the mixed conifer zone of the Sierra Nevada Mountains. Soil parent material in the study sites is weathered or decomposed granitic rock. Soils in the San Bernardino Mountains are generally sandy loam in texture, have weakly developed B horizons and become increasingly coarse textured with depth. Percent base saturation ranges from 70 to 100 %, except in the most polluted western San Bernardino Mountain sites.

38.2.2 Empirical Critical Loads

Empirical CLs for streamwater NO_3 losses were determined across N deposition gradients in the Sierra Nevada and San Bernardino Mountains in California (Fenn et al. 2008, 2010). Nitrogen deposition was measured as throughfall with ion exchange resin collectors (Fenn et al. 2009). In addition, to determine areas in exceedance of the NO_3 leaching CL on a statewide basis, N deposition was estimated using the US/EPA CMAQ model. However, because CMAQ underestimated N deposition in pollution-affected montane regions of California, the CMAQ-simulated N deposition estimates were adjusted based on throughfall N deposition data (Fenn et al. 2010). Empirical CLs for lichen community effects in forests were determined from Forest Inventory and Analysis (FIA) lichen community data and throughfall N deposition data in the Sierra Nevada (Fenn et al. 2008; Jovan 2008). Empirical CLs for lichen community impacts in chaparral/oak woodlands were determined from lichen community surveys in the Greater Central Valley of California (Fenn et al. 2011; Jovan and McCune 2005), which includes the central Coast Ranges and Sierra foothills, in combination with CMAQ N deposition estimates.

The empirical CL for soil acidification was determined from a linear regression ($r^2=0.99$) of throughfall N deposition and soil pH (H^+ concentration) from six sites across a N deposition gradient in the San Bernardino Mountains (Breiner et al. 2007). A soil of pH 4.6 was selected as the threshold pH below which the CL was considered exceeded, based on expert judgment and the study of MacDonald et al. (2002).

38.2.3 Modelled Critical Loads

Critical loads for terrestrial acidification and eutrophication across the San Bernardino Mountains were calculated according to the Steady State Simple Mass Balance (SMB) method as described in the Mapping Manual (ICP Modelling and Mapping Manual 2008). The determination of critical loads for acidification requires the consideration of both S and N deposition on the one side, and plant uptake, weathering, and biochemical immobilization processes on the other side. The deposition of acidifying S and N exceeds a critical value if they alter the chemical characteristics of the soil solution. Indicators for the chemical characterization are (a) aluminum concentration, (b) base cation:aluminium ratio, (c) pH value, (d) base saturation of soils, and (e) acid neutralization capacity (ANC).

The simple mass balance (SMB) equations for the maximum critical load for sulphur-based acidity, $CL_{max}(S)$, and the maximum critical load for N-based acidity, $CL_{max}(N)$, are given by the following equations (ICP Modelling and Mapping Manual 2008):

$$CL_{max}(S) = BC^*_{dep} - Cl^*_{dep} + BC_w - BC_u - ANC_{le(crit)} \quad \text{(Eq. 38.1)}$$

$$CL_{max}(N) = N_u + N_{fire} + N_i + N_{de} + CL_{max}(S) \quad \text{(Eq. 38.2)}$$

with

$CL_{max}(S)$	Critical load for sulphur-based acidity
$CL_{max}(N)$	Critical load for nitrogen-based acidity
BC^*_{dep}	Base cation deposition (sea salt corrected)
Cl^*_{dep}	Chloride deposition (sea salt corrected)
BC_w	Base cation weathering derived from soil type and parent material class
BC_u	Base cation uptake and removal by biomass under steady state conditions
N_u	Nitrogen uptake and removal by biomass under steady state conditions
N_{fire}	Nitrogen loss in smoke by fire
N_i	Long-term immobilization of nitrogen
N_{de}	Denitrification rate
$ANC_{le(crit)}$	Acceptable leaching of acid neutralization capacity

The SMB approach for calculating critical loads for nutrient N assumes steady-state equilibrium of N input, acceptable storage and output. In this case, the N-fixing processes (immobilization, N uptake in the harvested biomass, N loss by fire) and N removal (denitrification, acceptable N leaching) should be in balance with N deposition for steady-state conditions. The mass balance equation to calculate the critical load for nutrient N according to the ICP Modelling and Mapping Manual (2008) is given as:

$$CL_{nut}(N) = N_u + N_{fire} + N_i + N_{le(acc)} + N_{de} \quad \text{(Eq. 38.3)}$$

with

$CL_{nut}(N)$	Critical load for nutrient nitrogen
N_u	Nitrogen uptake and removal by biomass under steady state conditions
N_{fire}	Nitrogen loss in smoke by fire
N_i	Long-term immobilization of nitrogen
$N_{le(acc)}$	Acceptable leaching of nitrogen
N_{de}	Denitrification rate

Nitrogen loss by fire was added to the N uptake term. It was estimated that the annual vegetation loss due to fire at the sites is 0.25 % of the aboveground biomass. Based on estimated plant growth rates and N concentrations in plant tissue, N losses in fire were calculated.

In calculating the acceptable NO_3 leaching for the SMB nutrient N CL [Cl_{nut}(N)], precipitation surplus was determined based on long term streamflow data (Fenn and Poth 1999). The CL for nitrate leaching in mixed conifer forests was also estimated with the Daycent biogeochemical model (Fenn et al. 2008).

38.3 Results and Discussion

38.3.1 Eutrophication Critical Loads: Empirical vs. Modelled

The NO_3 leaching CL derived from the Daycent biogeochemical model simulations (17 kg N ha^{-1} year^{-1}) was equal to the empirical CL based on streamwater NO_3 data collected at sites with varying N deposition, notwithstanding the fact that Daycent underestimated NO_3 concentrations in many years (Fenn et al. 2008). Similar to other reports, we found that the steady state SMB CL values for N as a nutrient effects, determined using the approach of the Mapping Methods Manual (ICP Modelling and Mapping Manual 2008), were lower than the empirical CL. In Table 38.1 the values for the calculated SMB parameters for nine sites in the San Bernardino Mountains are given. The SMB CL for the forested sites ranged from 5.6–13.0 kg N ha^{-1} year^{-1} compared to a CL of 5.1 for a chaparral site (Table 38.1).

Nitrogen immobilization (N_i) and denitrification losses (N_{de}) are considered the most uncertain parameters for calculating the SMB CL in the San Bernardino Mountains. The higher calculated denitrification value of 3.7 kg N ha^{-1} year^{-1} at three of the sites (Table 38.1) is due to soil maps indicating alluvial fine textured soils at these locations that are expected to have higher soil moisture content. We consider that these values may be overestimates, particularly at Barton Flats and Holcomb Valley where N deposition is below 10 kg ha^{-1} year^{-1}. However in a recent study in a Mediterranean shrubland in southern Italy, high denitrification rates, with dinitrogen as the dominant end product, were reported even in relatively dry soils (Dannenmann et al. 2011). Trace gas losses of N in upland forest and chaparral soils in California occurs primarily as nitric oxide from nitrification. Flux rates from low N deposition sites suggest an ecologically acceptable annual trace gas N loss of 0.5–1.0 kg ha^{-1} year^{-1} (Fenn and Poth 2001).

Both the SMB CL and empirical CLs are known to entail considerable uncertainty, and SMB is probably best used for broad scale mapping of CLs to highlight areas at risk, and when overlain with atmospheric deposition maps, to determine areas of likely CL exceedance. Improved mechanistic understanding and definition of the individual terms used to derive the SMB CL is desired because this will improve the reliability and usefulness of the CLs. In addition, a mechanistic understanding would aid the development of management strategies to mitigate the effects of N excess. Empirical data can be useful in field testing and evaluating the SMB CLs and parameters used to calculate the SMB CL.

Table 38.1 Values used to derive the Simple Mass Balance CL for nutrient N [Cl_{nut}(N)] at sites across an air pollution gradient in the San Bernardino Mountains in southern California based on methods of the Mapping and Modelling manual (ICP Modelling and Mapping Manual, 2008). SMB parameters given in the table are: $N_{le(acc)}$, Acceptable N leaching; N_i, N immobilization; N_u, N uptake; N_{de}, Denitrification. Exceedance (Ex) was estimated as the critical load minus deposition. For all parameters units are kg N ha^{-1} year^{-1}

Site	N Dep	Vegetation	$N_{le(acc)}$	N_i	N_u	N_{de}	CL_{nut}(N)	Ex
Strawberry Peak	39	Sierran mixed conifer	1.6	2.0	3.3	1.1	8.0	31.0
Heaps Peak	36	California black oak	1.6	1.4	1.3	1.3	5.6	30.4
Camp Angelus	13	Sierran mixed conifer	1.3	2.5	3.3	3.7	10.8	2.2
Green Valley	9	White fir	1.5	3.1	1.8	1.1	7.5	1.5
Barton Flats	9	White fir	1.1	3.0	1.8	3.7	9.6	−0.6
Converse Flats	6	Interior ponderosa pine	1.1	2.5	4.7	1.9	10.2	−4.2
Holcomb Valley	6	Interior ponderosa pine	1.2	3.4	4.7	3.7	13.0	−7.0
Devil Canyon 3	23	Canyon live oak	1.5	1.0	2.1	1.1	5.7	17.3
Devil Canyon 6	14	Hard chaparral	1.3	2.0	0.5	1.3	5.1	8.9

38.3.2 Critical Loads for Fichen Community Effects

Critical loads for epiphytic lichen community changes in California forests can generally be considered to be based on a eutrophication or nutrient N effect, although lichen responses may be a combined effect of eutrophication and changes in bark pH from ammonia (NH_3) deposition (Sutton et al. 2009). Critical loads for epiphytic lichen responses are not soil-mediated effects, but are based on direct atmospheric deposition to the lichen thallus. In this sense lichen-based CLs are computed from a less complex system, although the community or biodiversity responses can be complex. Lichens are the most sensitive documented terrestrial responders to N in California forests and scrublands, and harmful effects of N to lichen communities are more widespread than other effects of chronic N deposition (Fenn et al. 2010, 2011). The N CL values vary depending on the criterion chosen to make a cut-off:

- initial changes in chemistry and lichen community effects (3.1 kg ha^{-1} year^{-1}),
- shift from acidophyte to nitrophyte lichen dominance (5.2 kg ha^{-1} year^{-1}),
- extirpation of the acidophyte lichen community (10 kg ha^{-1} year^{-1}).

Recent work has demonstrated that the CL for epiphytic lichens is affected by precipitation levels. A simple yet robust model has been developed to determine lichen CLs from N deposition levels and precipitation (Geiser et al. 2010, 2014, Chap. 33: this volume).

Critical levels have been established for lichen community responses to ambient NH_3 air concentrations in some regions (Cape et al. 2009). The critical level of a pollutant gas is defined as 'the concentration in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to present knowledge' (Cape et al. 2009; Posthumus 1988). Although, NH_3 is a major driver of N deposition (often the most important N compound) in

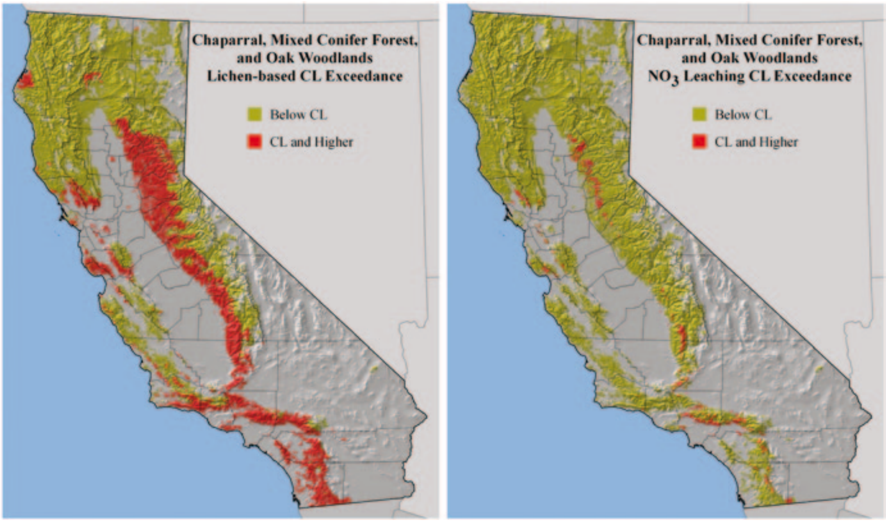

Fig. 38.1 (*Left*) Critical load exceedance map for lichen community changes. Forest CL = 5.2 kg ha^{-1} year^{-1}; chaparral and oak woodlands CL = 5.5 kg ha^{-1} year^{-1}. (*Right*) Critical load exceedance map for NO_3 leaching. Forest CL = 17 kg ha^{-1} year^{-1}; chaparral CL = 14 kg ha^{-1} year^{-1}

much of California, critical levels for NH_3 effects on lichen communities have not been established. Preliminary results in the Sierra Nevada suggest that critical levels for NH_3 effects on lichens may be similar to those reported in Europe (Andrzej Bytnerowicz and Sarah Jovan, unpublished data). Further work is needed however.

38.3.3 Eutrophication Critical Load Exceedance in California Forests and Scrublands

Statewide empirical CL exceedance maps (Fig. 38.1) indicate that 3.3 and 4.5 % of the chaparral and forested areas in California are in excess of the NO_3 leaching CL. By comparison, 23.4, 41.2 and 52.9 % of the mixed conifer forest, oak woodland and chaparral areas are in excess of the empirical N CL for epiphytic lichen community effects, respectively (Fig. 38.1). Ammonia concentration exposure profiles in California indicate that most if not all of the Sierra Nevada from Lake Tahoe southward is in exceedance of the critical level for NH_3 (Andrzej Bytnerowicz, unpublished data). Moreover, the proportional area shown in Fig. 38.1 to be in exceedance of the CL is a conservative estimate. The data used to derive the CL (Fenn et al. 2008) suggest that decreases in the occurrence of sensitive acidophyte species were initiated at N deposition levels below the lower-bound CL of 3.1 kg ha^{-1} year^{-1}, but more data points at low N deposition inputs are needed to better define this relationship. This becomes difficult with throughfall measurements however, because at low N deposition inputs (e.g., 2–4 kg ha^{-1} year^{-1}) forest canopies consume a large fraction of atmospherically-deposited N that is not washed off from tree canopies in precipitation and thus not measured as throughfall; this can result in negative net throughfall values. In these cases calculating N deposition with the inferential method can be an effective alternative approach (Fenn et al. 2009).

A fraction of the N consumed within the canopy is presumably due to N retention by epiphytic lichens. Negative net throughfall is by definition when deposition as bulk precipitation in forest clearings is greater than throughfall deposition measured under tree canopies. The critical level approach avoids this complication of canopy retention of N, because the response is based solely on the relationship between atmospheric concentrations of NH_3 and lichen community changes. However, in California the effects of co-occurring oxidant gases such as nitric acid vapor (HNO_3) and ozone must also be considered when determining the critical level for NH_3 (Riddell et al. 2008). In any case, NH_3 exposure profiles in the Sierra Nevada and unpublished estimates of the critical level for lichen community effects, and CLs for lichen effects (Fenn et al. 2010, 2011), suggest that approximately one-third of the land area of California covered by forests, chaparral and oak woodlands is in exceedance of the critical load for lichen communities.

Because of the capacity of terrestrial watersheds to retain and process significant levels of added N, the CL for NO_3 leaching is much higher than the CL for lichens. Although only an estimated 4.2 % of the combined forest and chaparral areas are projected to be in exceedance of the NO_3 leaching CL, the affected area represents approximately 570,000 ha, including watersheds vital for the water supply to millions of people. The NO_3 leaching CL for forested watersheds is based on a N deposition level of 17 kg ha^{-1} $year^{-1}$. At this deposition level, NO_3 concentrations in runoff from forested or chaparral catchments only begin to exceed background levels. Thus, the significance for areas in exceedance of the CL is that NO_3 levels will be higher than ‘normal’ for varying periods of the year and that the amount of excess NO_3 will vary.

In many chaparral and forested catchments surrounding Los Angeles and adjoining urban centers, NO_3 concentrations are elevated year-round, even during base flow conditions, indicating that groundwater NO_3 is also elevated. Ecological effects of N deposition occur at thresholds of at least an order of magnitude lower than for drinking water effects. However in highly-polluted catchments (e.g., N deposition of 25–70 kg ha^{-1} $year^{-1}$), elevated NO_3 concentrations can also reduce water quality, particularly when water from forests are relied upon as relatively pristine water sources, often blended with lower quality sources before delivery to domestic water supplies.

38.3.4 Acidification Critical Loads: Empirical vs. Modelled

Contrary to eutrophication CLs, the empirical N CL for soil acidification (26 kg ha^{-1} $year^{-1}$; see Breiner et al. 2007) was lower than the SMB N CL values (23–168 kg ha^{-1} $year^{-1}$), although it was within the lower end of the range of the

Table 38.2 Comparison of eutrophication (kg N ha^{-1} $year^{-1}$) and acidification (kg S ha^{-1} $year^{-1}$ or kg N ha^{-1} $year^{-1}$ [meq m^{-2} $year^{-1}$]) critical loads for California mixed conifer forests

	Eutrophication Critical Loads (kg N ha^{-1} $year^{-1}$)				Acidification Critical Loads		
	SMB Mapping	Daycent Model[1]	Empirical NO_3 Leaching[1]	Lichen Comm. Response[1]	SMB Mapping	SMB Site-Specific[2]	Empirical[3]
CL_N	5–13	17	17	3–10	23–168	BF: 32 (228) CF: 37 (266) CP: 46 (328)	26
CL_S					26–59	BF: 29 (183) CF: 35 (217) CP: 44 (273)	n.d.

[1] Daycent model and empirical NO_3 leaching CLs and the lichen CLs are from Fenn et al. 2008
[2] Critical loads for soil acidification $CL_{max}(N)$ and $CL_{max}(S)$ (maximum critical load of nitrogen and sulphur). $CL_{max}(S)$ and $CL_{max}(N)$ were calculated using site-specific mineralogy and soil weathering rates estimated with the PROFILE model to protect ponderosa pine (Bc:Al = 2.0). The three sites in the San Bernardino Mountains are: Barton Flats (BF), Converse Flats (CF), and Camp Paivika (CP)
[3] The empirical CL for soil acidification is from Breiner et al. 2007. The CL was determined by linear regression of throughfall N deposition vs. soil pH at sites across an N deposition gradient in the San Bernardino Mountains in southern California

SMB mapping CL values (Table 38.2). High calculated CLs for acidity are largely due to high soil weathering rates (89–145 meq m^{-2} $year^{-1}$). Historical soil pH data and spatial trends in soil pH across the N deposition gradient in the San Bernardino Mountains demonstrate that soil acidification is occurring in the most polluted sites (Breiner et al. 2007). Over an 18 year period from 1975 to 1993, soil pH decreased from 4.8 to 3.1 at Camp Paivika, a site in the western San Bernardino Mountains (Wood et al. 2007) where current average N deposition is 70 kg ha^{-1} $year^{-1}$ (Fenn et al. 2008). The range of SMB and empirical CLs for nutrient N effects (3–17 kg N ha^{-1} $year^{-1}$) are lower than those reported for acidification effects (23–168 kg N ha^{-1} $year^{-1}$), which highlights the far greater risk of eutrophication effects in California terrestrial ecosystems compared to soil acidification in this semiarid climate. Likewise, in Europe CL exceedance for nutrient N effects are more prevalent than for soil acidification effects (Hettelingh et al. 2008).

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Chapter 39
Source Attribution of Eutrophying and Acidifying Pollutants on the UK Natura 2000 Network

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Abstract Atmospheric nitrogen (N) and sulphur (S) deposition from industrial, transport and agricultural sources may exert a range of different types of impacts on Natura 2000 sites in Europe. The FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model, incorporating emission point sources and sectors, was used to provide footprints of N and S deposition across the UK from 160 sources or groups of sources. The resulting matrix of source attribution by sector, and exceedance statistics for each site, provide a means of impact assessment for the whole UK's Natura 2000 network. For 2005 80 % of Special Areas of Conservation (SACs) in the UK have at least one feature exceeding their minimum N critical load, while the figure for acidity exceedance is 75 %. By 2020, the values are estimated at 74 and 62 %, respectively, indicating that current policies are insufficient to avoid exceedance of the critical loads. Although NO_x emissions are projected to decrease substantially, the modest reduction in exceedance is a consequence of the

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contribution of NH_3 from agricultural sources, which is projected to decrease only slightly between 2005 and 2020. Future analysis should address the spatial importance of source location and site proximity to a source, and examine the relationship between dry and wet deposition by source sector.

Keywords Acidification • Air pollution • Eutrophication • Natura 2000 • Source attribution

39.1 Introduction

Industrial processes may exert a range of different types of impacts on Natura 2000 sites in Europe. The combustion of fossil fuels, in particular, may release large quantities of sulphur (S) and oxidised nitrogen (N) which can then be dispersed and deposited on designated sites, leading to acidification and eutrophication effects. However, deposition of S and N may also arise as a result of releases from other sources such as transport, domestic or commercial activities, the long-range transport of S and oxidised N or more locally as a result of ammonia released from agricultural activities. The output from this research provides useful policy insight into the key sources that are contributing to exceedance at Natura 2000 sites and critical loads for N and acid deposition. Understanding the relative contributions of these different sources can help policy makers decide on the most effective remedial actions that need to be taken to reduce deposition.

39.2 Methodology

The FRAME (Fine Resolution Multi-pollutant Exchange) model, incorporating emission point sources and sectors, was used to provide source footprints of N and S deposition across the UK (Vieno et al. 2009). The modelling was carried out for 2005 and a future emissions scenario for 2020. Using a GIS package, the footprint deposition files were superimposed over the Natura 2000 network boundaries in conjunction with the relevant critical loads for the designated features at each site. The resulting matrix of source attribution by sector and exceedance statistics for each site, provide a status of the whole UK's Natura 2000 network.

39.3 Results

Preliminary results have shown that for 2005 80 % of Special Areas of Conservation (SACs) in the UK have at least one feature where the minimum N critical load is exceeded, while the figure for acidity exceedance is 75 %. By 2020, the percentage of SACs exceeding N and acidity critical loads is predicted to reduce to 74 and

Fig. 39.1 **a** Nitrogen deposition to Beinn Dearg SAC by source sector. This clean site is dominated by long-range transport of pollutants from outside the UK (*Sensitive Habitat: Blanket bogs; CL Exceedance?: Nitrogen:Yes|Acidity:Yes; Dep Stats: 7.5 kg N ha*$^{-1}$ *year*$^{-1}$|*5.6 kg S ha*$^{-1}$ *year*$^{-1}$). **b** Nitrogen deposition to Breckland SAC by source sector. The site is dominated by intensive poultry farming. The site is characterised by 51 % deposition of reduced nitrogen (NH_3 and NH_4) (*Sensitive Habitat: European dry heaths; CL Exceedance?: Nitrogen:Yes|Acidity:Yes; Dep Stats: 20 kg N ha*$^{-1}$ *year*$^{-1}$|*5.2 kg S ha*$^{-1}$ *year*$^{-1}$)

62 % respectively. The scenario for 2020 predicts substantial emission reductions for the major coal fired power stations (reductions of 80 % for NO_x and 90 % for SO_x from 2005). However, despite this, there is not a significant decline in numbers of sites exceeding the critical loads. This is largely because the biggest contribution to exceedance comes from agricultural sources which are predicted to have small emission reductions from 2005–2020.

39.3.1 Nitrogen Deposition and Source Attribution

Nitrogen deposition across the Natura network reflects many different source-pollutant gradients. The corresponding make-up of wet/dry and pollutant species deposited at a Natura site, change across the UK depending on source-sector emissions and distances between sources and sites. For example Fig. 39.1a shows the deposition of N to a Natura site in the north of Scotland. This site is not surrounded by any main point sources nor main transport links, nor is there much intensive livestock production. As a consequence a large proportion of the N being deposited comes from outside the UK as an import. 15 % comes from local livestock production. Point sources (combustion) account for only 13 % of the N deposition. Figure 39.1b, however, shows the breakdown of sources to a site in East Anglia. At this site the livestock sector dominates the N deposition contribution. There is still a strong import from outside the UK (25 %) and transport (12 %) reflects the higher amounts of road traffic in the region. Reduced N, from the agricultural area, makes up over 51 % of the N contribution to this site.

39.3.2 Sulphur Deposition and Source Attribution

Sulphur deposition has similar regional differences based on the relationship between site and source. Figure 39.2a shows the SAC Thorne Moor which is very close to

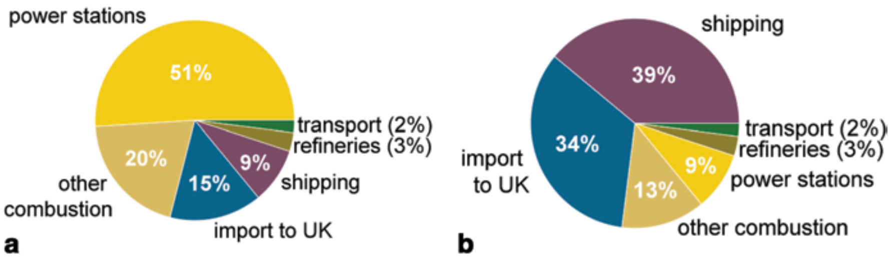

Fig. 39.2 **a** Sulphur deposition to Thorne Moor SAC by source sector. The site is in a area dominated locally by 4 large coal-fired power stations. (*Sensitive Habitat: Active raised bogs; Exceedance?: Nitrogen:Yes|Acidity:Yes; Dep Stats: 16 kg N ha*$^{-1}$ *year*$^{-1}$*|4.7 kg S ha*$^{-1}$ *year*$^{-1}$). **b** Sulphur deposition to Dartmoor SAC by source sector. The site is dominated in the area by sulphur emissions from international shipping lanes (*Sensitive Habitat: Blanket bogs; Exceedance?: Nitrogen:Yes|Acidity:Yes; Dep Stats: 25 kg N ha*$^{-1}$ *year*$^{-1}$*|9.2 kg S ha*$^{-1}$ *year*$^{-1}$)

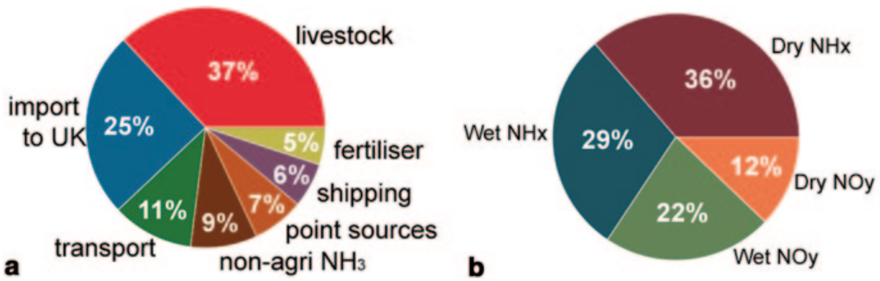

Fig. 39.3 **a** UK source attribution for N deposition. **b** Wet/dry components of N deposition

four large power stations. As a result over 50 % of the deposited S comes from power stations. Other combustion makes up another 20 %. Figure 39.2b shows that shipping makes up a significant part of the S being deposited at this site. This is due to the SAC being in south west of England and close to the coast and the English Channel shipping lanes. The import to the UK is also high at this site possibly indicating south westerly's carrying pollutants from North America.

39.3.3 UK Source Attribution Statistics

The status of N and S deposition across the UK is shown in Figs. 39.3 and 39.4. In the UK, N deposition to the Natura network comes predominantly from livestock practices (Fig. 39.3a) reflecting the fact that SACs are often surrounded by agricultural land and practices. Furthermore, of the total N deposited on Natura sites, 65 % comes from the reduced form of N (Fig. 39.3b), with dry deposition being the main fraction. For S deposition the distribution is shared between four main source-sectors—UK import, shipping, power stations and other combustion. Notably, the majority of S deposition is in the form of wet deposition highlighting the importance

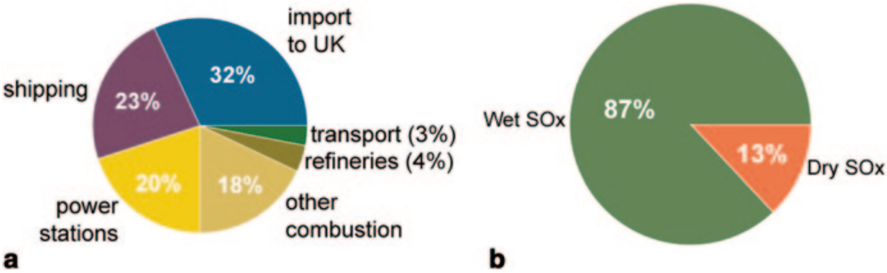

Fig. 39.4 **a** UK source attribution for S deposition. **b** Wet/dry components of S deposition

Table 39.1 Exceedance of critical loads for UK SACs by site and by area

Year	SACs	Exceeds minimum CL(N)[a]	Exceeds maximum CL(N)[a]	Exceeds CL for acidity[a]
2005	n=616 sites	n=452 (73 %)	n=328 (53 %)	n=379 (62 %)
2005	2,621,558 ha	1,351,867 ha (52 %)	846,620 ha (32%)	1,031,340 ha (39 %)
2020	n=616 sites	n=417 (68 %)	n=275 (45 %)	n=343 (56 %)
2020	2,621,558 ha	1,125,265 ha (43 %)	738,930 ha (28 %)	858,483 ha (33 %)

[a] Exceedance is based on the most sensitive Annex 1 habitat feature at any site. For area statistics it is assumed that the habitat is present across the whole site

of long range transport. Geographically most power stations are further than 100 km from most of the SACs resulting in long-range transport of pollutants which are subject to rainfall wash-out and wet deposition.

39.3.4 Exceedance Statistics for the UK Natura Network

Exceedance statistics were calculated for the whole network comparing the source-sector deposition with the critical load of the most sensitive feature at each site (Table 39.1). Exceedance of the critical loads for nutrient N and acidity is high across the Natura network. Over 70 % of the network exceeds the lower critical load for N and 62 % of the sites exceed acidity critical loads. In terms of area, this represents 52 and 39 % of the total network in hectares (assuming the sensitive habitat is found across the whole site). For 2020 the situation has improved although the reductions are small.

39.4 Discussion

Source attribution provides an invaluable method of examining the spatial differences in the pollution climate and pattern of deposition across the UK. This is driven by the location of sources in relation to a site and the meteorological variability across the UK. We can see that sites in different locations around the UK are impacted by different pollutant sources. However, in general, the predominant source of eutrophying and acidifying pollutants comes from agricultural activities. This sector is responsible, on average, for over 40 % of the N deposition, while over 65 % of the total N deposition on to SAC is in the form of reduced N. The future for improving critical load exceedance on the Natura network is uncertain with only small reductions (< 10 %) made for the 2020 scenario. While these scenarios have focused on reducing emissions from power stations and shipping, little headway (beyond national ceiling targets) has been made into reducing agricultural emissions of N.

39.5 Conclusions

- Source attribution provides an invaluable method of examining the spatial differences in the pollution climate and pattern of deposition across the UK.
- Deposition is driven by the location of sources in relation to a site and the meteorological variability across the UK.
- The predominant source of eutrophying and acidifying pollutants comes from agricultural activities, which are responsible, on average, for over 40 % of the N deposition.
- Scenarios for 2020 still show N deposition as a continuing risk to the network of Natura sites.
- Reductions in emissions through pollution control, national emission ceilings, and large power plant directives are making little headway in reducing site exceedance.
- Agricultural emissions still remain the biggest threat to ecosystem health and biodiversity.

Acknowledgments We gratefully acknowledge funding of this research from the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER), Scottish Environment Protection Agency, Northern Ireland Environment Agency, Natural England, Scottish Natural Heritage, the Environment Agency, the Countryside Council for Wales, and the Joint Nature Conservation Committee.

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Chapter 40
Mapping Critical Loads for Nitrogen Based on Biodiversity Using ForSAFE-VEG: Introducing the Basic Principles

Harald Sverdrup, Bengt Nihlgård and Salim Belyazid

Abstract This chapter describes the basic principles inside the VEG extension to the ForSAFE model system. It allows changes in ground vegetation to be calculated, an important part of biodiversity. In the VEG model, the basis for modelling ground vegetation dynamics is a competition strength model based on soil chemistry promoting and retarding factors, nutrients, water and light. The strength is used in a competition model to assign ground area to each plant type considered. The ForSAFE-VEG is freely available from the authors and is used for assessing critical loads for acidity and nitrogen in Europe and United Sates, based on biodiversity criteria.

Keywords Biodiversity • Critical loads • Dynamic modelling • Interspecies competition • Nitrogen

40.1 Introduction

In Europe, work is under way to establish tools for estimating and mapping critical loads (CLs) for atmospheric pollutants, taking account of climate change and land management interactions. The approach is to work directly from limits set for ecological changes to CLs under certain climate change and management assumptions. The models under development represent some of the most advanced ecosystem models that have been useful for setting environmental policies in Europe.

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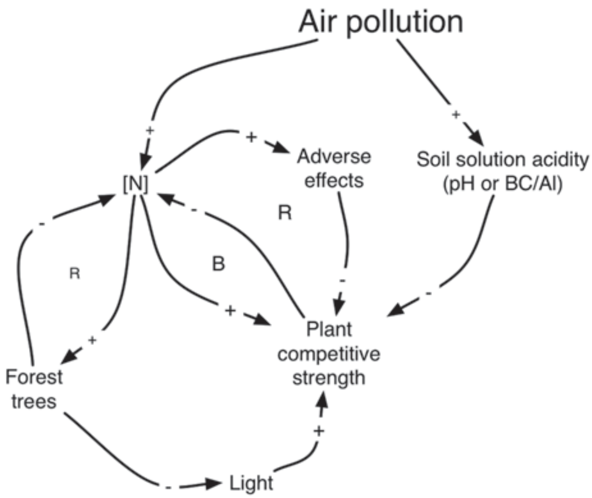

Fig. 40.1 The effect of air pollution and forestry on ground vegetation. The feedback loops are marked *R* or *B* to understand their basic property in the system. *R* represents a reinforcing loop, *B* is a balancing loop

40.2 Purpose

In this chapter we want to explain how nitrogen (N) and other influences affect ground vegetation and the associated plants. We will exemplify the feedbacks within the system with a causal loop diagram, show how the system feedback structure is connected to ecological competition, being the principle behind biodiversity and finally provide guidance on how to interpret field data with respect to the critical load (CL) models used by us.

40.3 Theory

Critical loads or effects assessment of N on ecosystems must consider simultaneously the effects of:

1. Climate change (Change in wind, temperature and water inputs)
2. Forest and land management (Changes in nutrients and water uptake, light conditions, wind exposure, grazing by animals
3. Air pollution; inputs of acidifying compounds (from sulphur (S) and N pollution)
4. Nutrient enrichment (from N pollution)
5. Competition (Internal to the ecosystem the change in competitive balance)

Figure 40.1 shows the effect of N alone on the ground vegetation dynamics within a forest. It can be seen how the effects of forest management and atmospheric pollution interact. Nitrogen has a growth promoting effect when increasing from very low levels. However, high N levels sometimes cause a negative effect, retarding or limiting growth. Acidity has a retarding effect below threshold values, expressed by BC/Al ratio in the soil solution or soil solution pH.

Plants and trees take up N from the soil solution, reducing the availability. Trees also shade light from the ground vegetation and modify the deposition on its way through the overstorey, before it reaches the ground vegetation. There is an important distinction to make between models that operate on the principle of equilibrium ecology (without competition) and those that include competition. The first category of model assumed observed ecological niches to be constant and independent of competition. By contrast the other approach, as implemented in ForSAFE-VEG includes the dynamic force of competition. The field envelope of a plant is system output and includes the effect of competition at the moment of observation.

1. The minimum and maximum value of an observed field envelope for say pH, may be useful input for setting individual plant responses to pH.
2. The "optimal" range is determined by competition between plants at the site and is variable with time, thus using the field "optimal" as input may be misleading.

Imagine you are a small boy, not very strong. And on the bus, you always like to sit on the front row. However, when all the strong boys go to school on the bus, the only seat you will get is the back seat in the bus. For you, the optimal seat is at front, but since the big boys sit there and you cannot take it from them, your 'field envelope' observable for each school day ends up being at the back seat. It is not your optimal choice, but that is what you can get. With plants in nature, competition does the same. So, by observing the field envelope, we must not assume it is the optimal field envelope for that species.

Figure 40.2 shows the causal loop diagram for the competition between plants implemented in the ForSAFE-VEG model.

Figure 40.3 shows how the plant strength is gathered from site conditions. Figure 40.4 shows the slightly simplified version implemented so far in the ForSAFE-VEG system. An ecosystem loaded with N may become self-eutrophying as long as the cycles of the system remains intact. The internal cycle may provide [N] high enough to keep the effects causing vegetation change going for a long time (decades to centuries), even after the external input is turned off. Unless large removals of N from the system are made, recovery may take many centuries. Ecosystems have "memories"; long system delays in biogeochemical and biological systems.

We may in a simple way say that N-pollution loads the gun, land management change, climate change, disasters[1] or acidification may all and each individually pull the trigger causing the system to start leach N. In the computer model, this is solved by combining the soil geochemical model ForSAFE with the vegetation response module VEG as illustrated in Fig. 40.5. Figure 40.5 also illustrates how the ForSAFE-VEG model is used to determine the critical load. The output from the ForSAFE-VEG system is used iteratively to calculate critical loads. In these runs a certain scenario for climate change, forest and land management and evolution of

[1] With disasters we imply relatively unpredictable events such as outbreak of pathogens, attacks by insects, or fire.

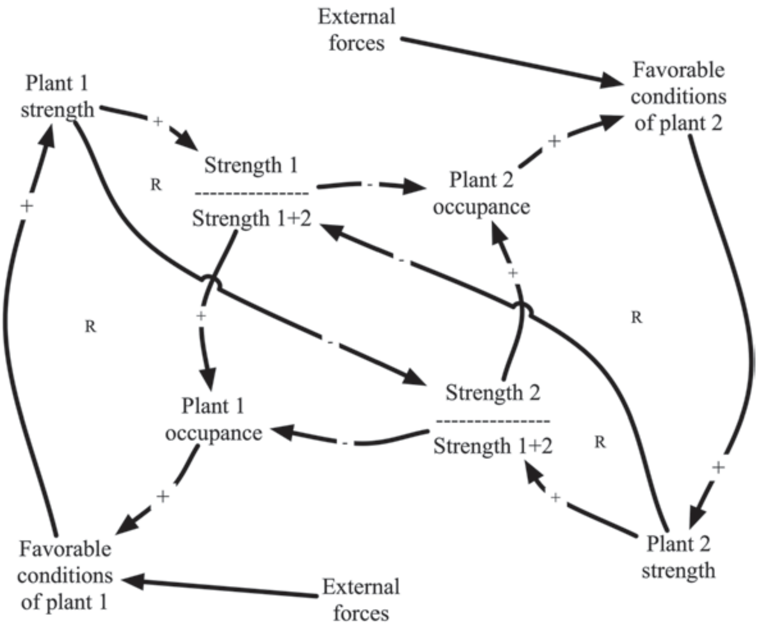

Fig. 40.2 A causal loop diagram for the competition principles inside the VEG model. The plants use their strength to compete for territory. The strength is assembled as illustrated in Fig. 40.3 and realized in the computer model VEG as outlined in Fig. 40.4. Without competition, there would be no ecology in the model. Reproduced with kind permission from Springer Science+Business Media: Sverdrup et al. (2012) Testing the Feasibility of Using the ForSAFE-VEG Model to Map the Critical Load of Nitrogen to Protect Plant Biodiversity in the Rocky Mountains Region, USA, Water, Air, and Soil Pollution, 223, 371–387, Fig. 1, and any original (first) copyright notices displayed with material

other, non-N pollution inputs must be assumed. The state for a certain set of conditions is calculated, then the output is compared to the threshold for response and assessed for exceedance. If necessary, the iteration is continued. Figure 40.6 shows an example of an output plot from the ForSAFE-VEG system, showing the vegetation response 1750–2150 for the Swedish site of Söstared. Each color band represents one of the 43 plant groups used for Sweden. The vegetation plots show from the top downwards 100 % of today's nitrogen input from the air, 66 %, 33 % and background deposition of N as the inputs. The result in plant response is very different. Please also note the very long delay times embedded in the system.

40.4 Conclusions

Three issues are inseparable when discussing critical loads based on biodiversity: (1) Pollution change, (2) Climate change, (3) Management change.

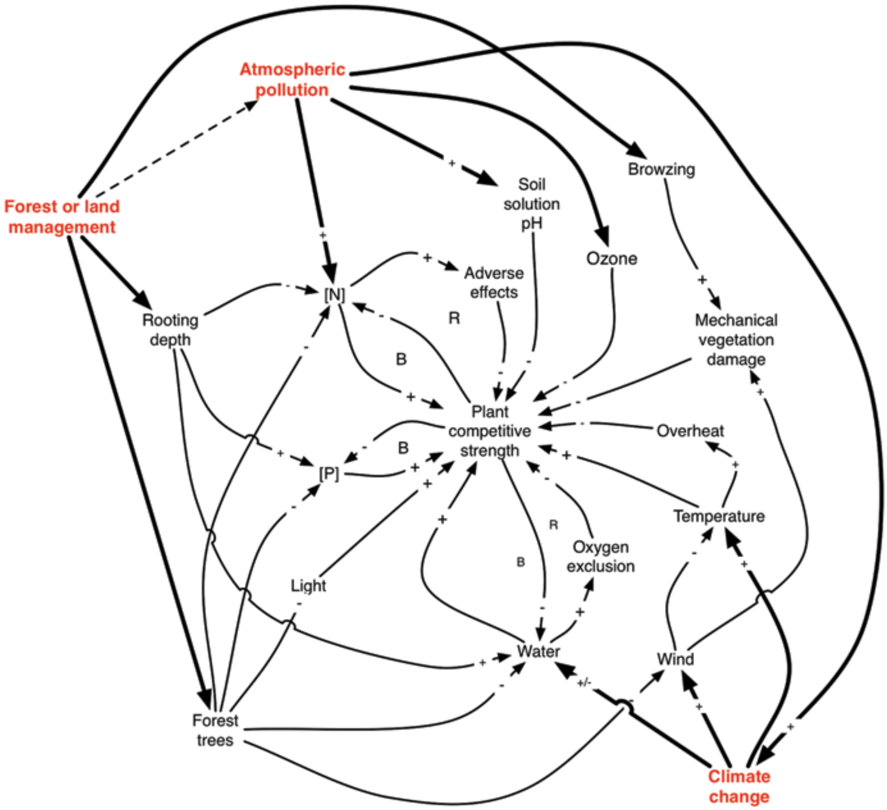

Fig. 40.3 The mental model behind the computer model. A comprehensive causal loop diagram for the interaction between forest and land management, climate change and atmospheric pollution. It can be seen how these affect different system parameters; rooting depth, water, soil solution nitrogen concentration, phosphorus soil solution concentration, light to ground, soil solution, the effect of ozone, mechanical damage, temperature or grazing, all of which affect the competitive strength of each plant species. Reproduced with kind permission from Springer Science+Business Media: Sverdrup et al. (2012) Testing the Feasibility of Using the ForSAFE-VEG Model to Map the Critical Load of Nitrogen to Protect Plant Biodiversity in the Rocky Mountains Region, USA, Water, Air, and Soil Pollution, 223, 371–387, Fig. 2, and any original (first) copyright notices displayed with material

Models VEG is available as an extension to both ForSAFE and VSD. ForSAFE-VEG is available for PC and MAC platforms from the Lund University. With the model, an operational tool for setting CLs based on ground vegetation biodiversity is also available. The tool is field verified for Sweden, Iceland, Denmark, Switzerland, France and tested for the United States (Hubbard Brook, New York, and a site based on data from the sites of Loch Vale and Niwot Ridge, Colorado). The tool is ready for mapping CLs for whole countries.

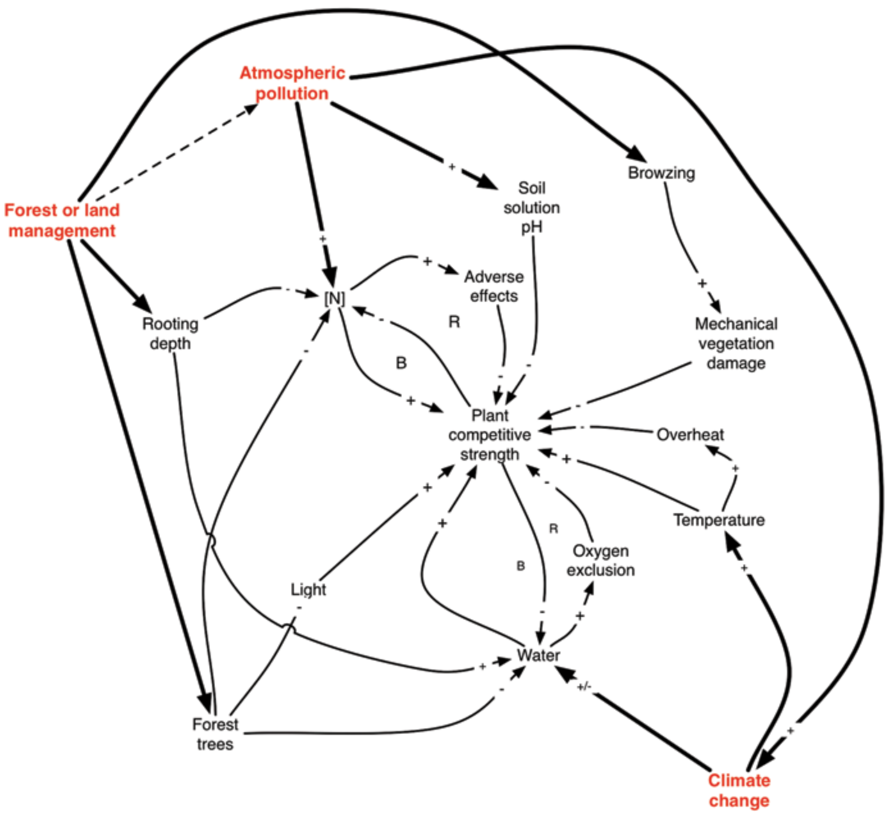

Fig. 40.4 The computer model. In the ForSAFE-VEG model, the system was somewhat simplified. Most importantly, the phosphorus module has still to be added along with the effects of wind, once finance is forthcoming

Setting up for assessment use We are able to parameterize the VEG model for any country, yielding functioning parameter files. It can cover a wide range of biomes, ecosystem types and climate zones. An advisory team is available at Lund University. Good national ecologists should be able to work with the model after initial instruction and training. A training manual and a generic European plant group parameterization table is available from the CCE at Bilthoven. A parameter library derived from Iceland, Denmark, Sweden, Switzerland, France and the Rocky Mountains is already available.

Acknowledgments This study is a part of the Swedish and Swiss critical loads programmes, funded by the Swedish Environmental Agency and the Swiss Ministry of the Environment.

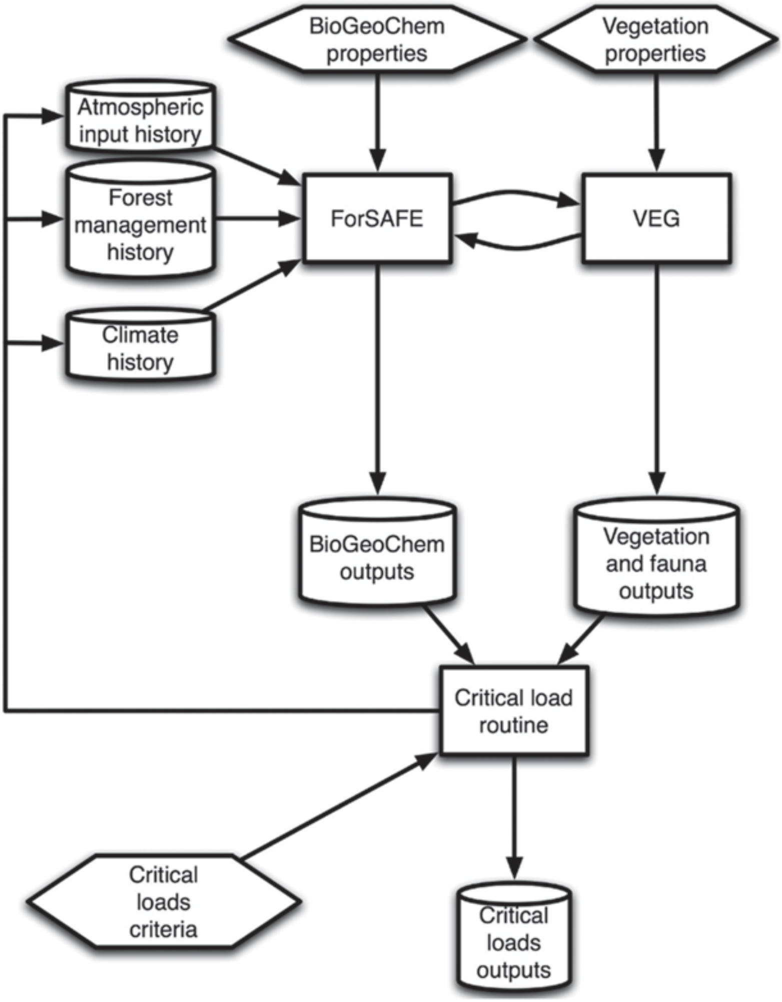

Fig. 40.5 The layout of the ForSAFE-VEG system. The model is supported through input data (soil data) on biogeochemistry, time series with deposition inputs of chemical components and the ground vegetation parameter list. The model is only calibrated by adjusting initial base saturation and the initial soil carbon content, in order to go through the observed values for bases saturation and soil carbon content. Everything from chemistry to vegetation dynamics follows from that, even weathering. No further calibration is required. This makes it the most robust biogeochemical model available in the world today. Reproduced with kind permission from Springer Science+Business Media: Sverdrup et al. (2012) Testing the Feasibility of Using the ForSAFE-VEG Model to Map the Critical Load of Nitrogen to Protect Plant Biodiversity in the Rocky Mountains Region, USA, Water, Air, and Soil Pollution, 223, 371–387, Fig. 3, and any original (first) copyright notices displayed with material.

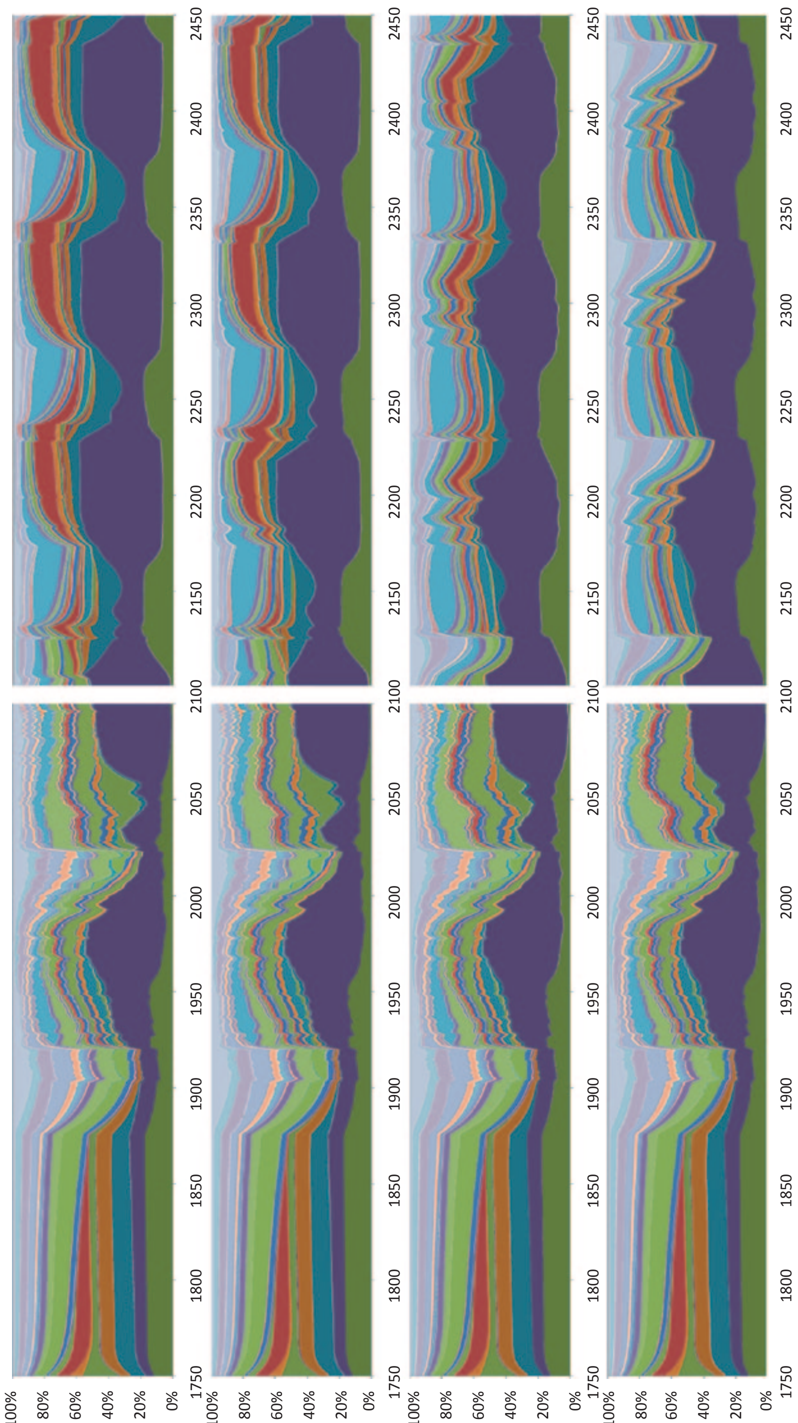

Fig. 40.6 Example of an output plot from the ForSAFE-VEG system, showing the vegetation response 1750–2150 for the Swedish site of Söstared. Each color band represents one of the 43 plant groups used for Sweden. The vegetation plots show from the top and down 100 % of today's nitrogen input from the air, 66 %, 33 % and background deposition of N as input

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Part IV
Nitrogen Deposition, Ecosystem Services and Policy Development

Chapter 41
Impacts of Nitrogen Deposition on Ecosystem Services in Interaction with Other Nutrients, Air Pollutants and Climate Change

Wim de Vries, Christine Goodale, Jan Willem Erisman and Jean-Paul Hettelingh

Abstract Nitrogen (N) deposition affects many ecosystem services, ranging from: (i) provisioning services such as timber/wood fuel production, (ii) regulating services such as carbon sequestration and pollutant filtering leading to the provision of clean air and water, (iii) supporting services such as nutrient cycling and primary production, and (iv) cultural services such as recreation and landscape features or species with aesthetic or spiritual value. This chapter presents discussion of the major relationships between N deposition and ecosystem services as distinguished in the Millennium Ecosystem Assessment. An important issue is how other factors, such as changes in climate, CO_2 and tropospheric ozone exposure and other nutrients, such as phosphate, affect those ecosystem services, and how they should be taken into account in critical load assessments, while accounting for regional

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differences. Another important issue is the linkage between plant species diversity changes, being the main indicator for critical N loads, and ecosystem services, including faunal species diversity and biodiversity-based products, such as impacts on edible wild plants and medicinal plants. Consideration is also given to the implications of these issues for the CBD and LRTAP Conventions.

Keywords CBD • Cultural • Ecosystem services • LRTAP convention • Nitrogen deposition • Provisioning • Regulating • Supporting

41.1 The Concept of Ecosystem Services

An increasing amount of information is being collected on the ecological and socio-economic value of goods and services provided by natural and semi-natural ecosystems. The earliest literature on valuation dates back to the mid-1960s and early 1970s (e.g., Helliwell 1969). More recently, there has been an almost exponential growth in publications on the benefits of natural ecosystems to human society (see for example, Costanza et al. 1997; de Groot et al. 2002).

Inspired by de Groot et al. (2002), who grouped ecosystem services into four primary functions, the Millennium Ecosystem Assessment has made a distinction in provisioning services, regulating services, supporting services and cultural services (Reid et al. 2005). Provisioning services are the products obtained from ecosystems, specifically the provision of food, fibre and wood/fuel. These functions are related to photosynthesis and nutrient uptake. It also includes other products such as the provision of fresh water. Regulating services include the regulation of climate, water quantity (ground water recharge, occurrence of floods etc), water quality and diseases by ecosystems and relate to the impact of ecosystems on greenhouse gas exchange and the buffering and filtering capacity of the soil affecting water and element fluxes. Supporting services relate to the capacity of natural and semi-natural ecosystems to regulate essential ecological processes and life support systems through bio-geochemical cycles. These functions are indirectly related to the provisioning and regulation functions as they affect many services that have direct and indirect benefits to humans (such as clean air, water and soil). Cultural services include for example recreation and landscape features or species with aesthetic or spiritual value.

Ecosystems provide a full suite of services that are vital to human health and livelihood. Important ecosystem services are the provision of wood and carbon storage, an adequate soil and water quality, watershed services and a habitat for a diversity of plants and wildlife. In this context, forests are among the most important ecosystems and their services are also the basis for the "Criteria and indicators for sustainable forest management" as adopted by the Ministerial Conference on the Protection of Forests in Europe. Healthy forests provide a host of watershed services, including water purification, ground water and surface flow regulation and erosion control. Furthermore, biodiversity is high in many forest ecosystems providing habitats for a wide range of animal and plant species. Forests will continue to provide their indispensable ecological and economical benefits only under the condition that they remain healthy, stable and sustainably managed.

41.2 Relationships Between Nitrogen Deposition and Impacts on Ecosystem Services with Other Nutrients, Air Pollutants and Climate Change

Nitrogen (N) deposition affects, amongst others, the following ecosystem services:

- Production of crops and forests (provisioning service of timber/wood fuel) and carbon sequestration (climate regulating service);
- Production of non-CO_2 greenhouse gases (CH_4, N_2O, O_3) and plant albedo (climate regulating services);
- Water quantity by affecting water uptake and thereby ground water recharge and runoff to surface waters (provisioning service of fresh water and water regulating service);
- Water/soil quality by its impact on acidity (pH) and on soil accumulation and leaching of N, aluminium and metals to ground water and surface water (regulating service, i.e. clean soil and water);
- Diversity of plant species by its impact on the habitat function for wild plants (supporting service, recently revised as habitat service) and animals, affecting biological diversity and related products (provisioning service);
- Soil biodiversity and thereby nutrient cycling and primary production (supporting service).

Examples of the causal link between increased N availability and ecosystem services are given in Table 41.1, distinguishing between provisioning services, regulating services and supporting services. There are many uncertainties in the cause–effect relationships, the interactions and the potential feedbacks listed in Table 41.1. Ecosystem services are not only affected by N deposition, but also by changes in the cycling of other nutrients and air quality parameters in interaction with climate change. The pressures to be considered are:

- Nutrient cycling parameters, such as phosphorus (P) and trace elements in agro-ecosystems and forests and silica and P in estuaries;
- Air quality parameters, including exposure to NH_3, NO_x and O_3 and deposition of N and acidity;
- Climatic parameters related to water stress, such as drought; temperature stress, such as late frost; and extreme meteorological events, such as hail and windstorms.

Table 41.1 Major relationships between nitrogen deposition and ecosystem services as distinguished in the millennium ecosystem assessment. (de Vries et al. 2009)

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Provisioning services		
Food/fibre, including:		
Crops	Increase in crop production	N deposition increases crop growth in N limited systems (low N fertilizer inputs)
Wild plants and animal products	Impacts on biodiversity (based products)	N induced eutrophication and soil acidification affects soil, plant and faunal species diversity and thereby biodiversity-based products
Timber/wood fuel	Increase in wood production	In N-limited systems, nitrogen increases forest growth and wood production; in N saturated forests, N can induce mortality
Natural medicines	Impacts on medicinal plants	N induced eutrophication and soil acidification affects plant species, but linkage to medicinal plants is largely unknown
Fresh water	Impacts on ground water recharge and drainage	N induced impacts on growth and plant species diversity also affect water uptake and thereby freshwater supply (see also water quantity regulation)
Regulating services		
Air quality regulation	Decline in air quality	Nitrogen deposition is correlated with increased concentrations of ammonia (NH_3), nitrogen oxides (NO_x), ozone (O_3) and particulate matter (PM_{10} and $PM_{2.5}$), all affecting human health and ecosystems
Climate regulation Greenhouse gas balance	Increased carbon sequestration in forests	In N limited systems, N deposition increases forest growth and related tree carbon sequestration, but can enhance mortality in some species. It also can cause an increased litterfall and reduced decomposition, leading to soil carbon sequestration
	Increased/decreased carbon sequestration in peat lands	At low N deposition, additional atmospheric N deposition may stimulate net primary productivity. At high rates of N deposition, species composition changes lead to loss of peat land forming species and changed microbial activity causing degradation of peat lands
	Increased N_2O production	Ecosystem losses as N_2O increase with increasing N loading
	Decreased CH_4 consumption	Soil microbes decrease CH_4 consumption in response to increased NH_4 availability
	Increased O_3 production	Increased production in tropospheric O_3 from interactions with NO_x and VOC emitted from ecosystems, which serves as GHG and can also inhibit CO_2 uptake through plant damage

Table 41.1 (continued)

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Water quantity regulation	Increased/decreased runoff and ground water recharge	Excess N may cause decreased runoff and ground water recharge due to increased water uptake (elevated growth) but also the reverse because of lower leaf area index due to defoliation caused by pests/diseases. Recharge may in the long term also be affected by impacts on soil carbon content and soil biodiversity, affecting water retention in soil
	Increased drought stress	Excess N causes an increased need for water by an increased growth and an increased sensitivity for drought stress by an increase in the ratio of above versus below ground biomass
Water quality regulation (water purification)	Decline in ground water and surface water (drinking water) quality	Nitrogen eutrophication and N induced soil acidification increases NO_3, Cd and Al availability, leading to:
		− NO_3, Cd and Al concentrations in groundwater and surface water exceeding drinking water quality criteria in view of human health effects
		− Increased Al concentrations in acid sensitive surface waters resulting in the reduction or loss of fish (salmonid) populations and reduction of aquatic diversity at several trophic levels (acidification)
		− Fish dieback by algal blooms and anoxic zones (eutrophication). Eutrophication is also affected by silica and phosphorus in estuaries
Soil quality regulation	Decrease in acidity buffer; change in soil structure	N induced soil acidification decreases the exchangeable pool of base cations, potentially causing reduced forest growth, and decreases the readily available Al pool, affecting soil structure
Pest/disease regulation	Increased human allergic diseases	Increasing N availability can stimulate greater pollen production, causing human allergic responses, such as hay fever, rhinitis and asthma
	Increase in forest pests	Increase in bark or foliar N concentrations can attract higher infestation rates, such as beech bark disease
Supporting services		
Nutrient cycling and primary production	Increases N inputs by litterfall and reduces soil biodiversity	N induced impacts on growth/litterfall and on soil biodiversity (soil mesofauna and bacteria composition) affects decomposition, nutrient mineralization and N immobilization, and thereby impacts nutrient cycling and primary production

Table 41.1 (continued)

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Cultural services		
Cultural heritage values	Impacts on culturally significant species in historically important landscapes	N deposition may change heathlands into grasslands, affecting historically important landscapes
Recreation and ecotourism	Impacts on recreation due to impacts on ecosystems	Nitrogen induces the increase in nitrophilic species like stinging nettles and algal blooms reducing recreational and aesthetic values of nature. Extreme examples include closed beaches due to algal blooms resulting from N-induced eutrophication in estuaries and coastal ecosystems

An illustration showing the major relationships between N deposition and ecosystem services is given in Fig. 41.1, including the interaction with climate change effects and other air pollutants, such as sulphur (acidity) and ozone.

During the breakout session these interactions were further explained and discussed with the aim of extending and prioritizing the list of effects of N in Table 41.1. The outcome of the Working Group discussion is summarized in Erisman et al. 2014 (Chap. 51, this volume).

41.3 Discussion and Recommendations

Table 41.1 establishes the starting point for the discussion of the major relationships between N deposition and ecosystem services as distinguished in the Millennium Ecosystem Assessment (MEA). The focus on ecosystem services especially concerns the further development of tools/indicators for N induced biodiversity loss. Tool/indicator development should ideally take into account impacts of N addition on valuable ecosystem services such as carbon sequestration and regulating services related to soil and water quality, in interaction with climate change and with other nutrients. The challenge is to provide recommendations, referring to the needs identified by the CBD and LRTAP, and by addressing the implications of current knowledge for policy, management and capacity-building needs.

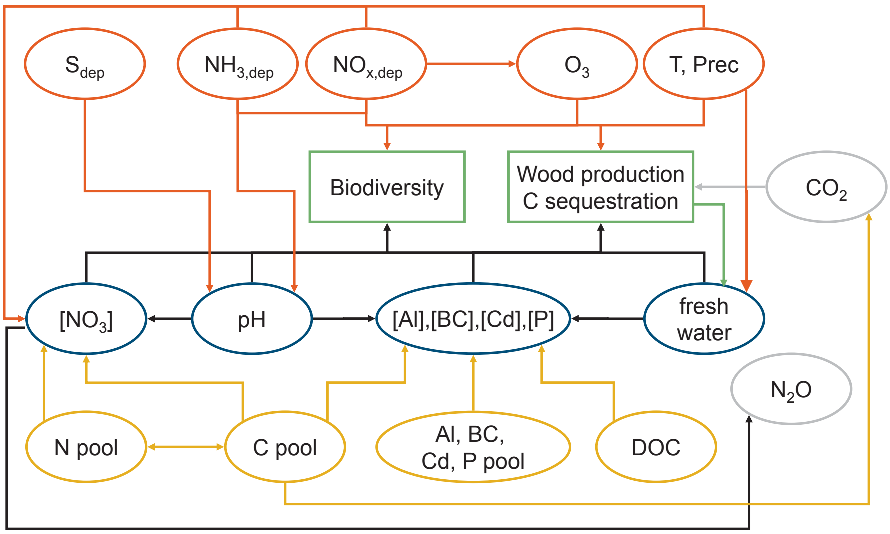

Fig. 41.1 Relationships between N deposition and air quality (*red*), biodiversity and forest growth (*green*), water quality (*blue*), soil quality (*yellow*) and greenhouse gas emissions (*grey*)

41.3.1 Recommendations Referring to Needs Identified by the Convention on Biological Diversity (CBD)

An important aim at EU level was to halt the loss of biodiversity by 2010. This aim required a set of Biodiversity Indicators for assessing the actual change in biodiversity as compared to the 2010 target of no further loss. In this context, the Pan European initiative, SEBI 2010 (Streamlining European 2010 Biodiversity Indicators), was launched in 2004. Its aim was to develop a European set of biodiversity indicators to assess and inform about progress towards the European 2010 targets. In 2005 the Coordination Team and 6 Expert Groups, involving more than 100 experts nominated by European countries as well as non-governmental organisations, started working for the compilation of a First European Set of Biodiversity Indicators for assessing the 2010 target. This has led to a report, describing a proposal for a first set of indicators to monitor progress in Europe (EEA, 2007) (For more information on SEBI 2010 see: http://biodiversity.europa.eu/topics/sebi-indicators).

The 26 indicators proposed by the SEBI 2010 process include (those that are relevant in view of N deposition are shown in italic. Note that even more indicators are important when focusing on farm management and related N emissions, such as 20: Agriculture: area under management practices supporting biodiversity):

1. *Abundance and distribution of selected species*
2. *Red List Index for European species*
3. Species of European interest

4. Ecosystem coverage
5. Habitats of European interest
6. Livestock genetic diversity
7. Nationally designated protected areas
8. Sites designated under the EU Habitats and Birds Directives
9. *Critical load exceedance for nitrogen*
10. Invasive alien species in Europe
11. Occurrence of temperature-sensitive species
12. *Marine Trophic Index of European seas*
13. Fragmentation of natural and semi-natural areas
14. Fragmentation of river systems
15. *Nutrients in transitional, coastal and marine waters*
16. *Freshwater quality*
17. *Forest: growing stock, increment and fellings*
18. Forest: deadwood
19. *Agriculture: nitrogen balance*
20. Agriculture: area under management practices supporting biodiversity
21. Fisheries: European commercial fish stocks
22. Aquaculture: effluent water quality from finfish farms
23. *Ecological Footprint of European countries*
24. Patent applications based on genetic resources
25. Financing biodiversity management
26. Public awareness

The current target of reducing biodiversity loss was not achieved by 2010 (see CBD 2010). Nevertheless, more ambitious targets, for example to halt and/or reverse loss are being proposed for 2020. A broad overall 2020 biodiversity target could be complemented by a set of quantifiable sub-targets. On the basis of the above mentioned list of indicators, it is important to develop recommendations for short listing and further development.

41.3.2 Recommendations Referring to Needs Identified by CLRTAP

The Convention on Long-range Transboundary Air Pollution (CLRTAP) focuses on the combined impacts of NO_x, NH_3, SO_2 and O_3. Until now, critical loads and related emissions ceilings for NO_x, NH_3 and SO_2 are related to impacts of eutrophication and acidification with a focus on biodiversity and undesirable Al to base cation ratios in the soil. Impacts on other ecosystem services such as carbon sequestration and interactions with ozone with respect to impacts are not yet included in the critical load assessment.

National and international policies to control the growth of NO_x emissions will affect future exposure of ecosystems to both ozone and N deposition, but there is almost no basis on which we can currently evaluate the implications of these combined changes in exposure for biodiversity and ecosystem services. Much greater attention needs to be paid to the joint effects of these two major regional pollutants in experimental studies, field observations and model development.

41.3.3 Key Questions

The following questions provided a starting point for discussion at the Workshop:

- Are all possible ecosystem services affected by N deposition mentioned in Table 41.1? If not, which are lacking? Is further description required as to their mechanism of response?
- What are the most important other ecosystem services affected by N deposition. On which services should we focus most attention?
- What is the linkage between plant species diversity changes, being the main indicator for critical N loads, on faunal species diversity and biodiversity-based products, such as impacts on edible wild plants and medicinal plants?
- Is there a linkage between biodiversity changes and the ecosystem services mentioned in Table 41.1, or are most effects due to other more direct pathways?
- Can we come up with other indicators in addition or related to effects on biodiversity that might also be used to assess critical loads?
- How do other factors, such as climate, ozone, other inputs (CO_2, P), affect the ecosystem services mentioned in Table 41.1?
- If so, should they be taken into account in critical load assessments or are the critical limits for other effects less stringent than those for biodiversity (e.g. NO_3 leaching occurs after the biodiversity limits are exceeded)?
- Do we need to take regional difference into account and if so at what scale?

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Chapter 42
The Form of Reactive Nitrogen Deposition Affects the Capacity of Peatland Vegetation to Immobilise Nitrogen: Implications for the Provision of Ecosystem Services

Lucy J. Sheppard, Ian D. Leith, Sanna K. Kivimaki and Jenny Gaiawyn

Abstract Peatlands represent significant carbon (C) reserves accumulated over millennia, as a consequence of slow decomposition rates conditioned by the acidity and anoxia that define these ecosystems. Such conditions are maintained largely through climate but also the activities of peatland 'engineers', vegetation such as *Sphagnum* mosses. Peatlands are hugely valued for C sequestration and the distinct communities they support. However, increased nitrogen (N) availability, from anthropogenic deposition, has been linked to detrimental changes in the vitality of *Sphagnum* and species active in perpetuating peatland processes. The effects of manipulating the form and dose of N to an ombrotrophic peatland, Whim bog in the Scottish Borders, UK, have been studied since 2002. Ammonia is provided by free air release, in response to wind direction and wind speed, and wet deposition, comprising nitrate or ammonium, in response to rainfall. Manipulation has increased the background deposition of 8 kg N ha^{-1} $year^{-1}$ by 2, 4 and 8 times. Responses to the different N forms in terms of species cover, importance of component species in maintaining low nutrient availability through N immobilisation and the implications of breakdown in vegetative cover and species replacement for peatland function are discussed in relation to N fluxes. All forms of N were not equally detrimental: ammonia deposition significantly reduced the vegetative cover, removing the sink

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for N, leading to increased nitrate in soil pore water and nitrous oxide emission whereas effects of wet N deposition, though still detrimental, were more modest. Nitrogen driven reductions in the cover of the keystone *Sphagnum* species and other characteristic mosses and their ability to immobilise incoming N can affect soil chemistry and lead to changes that could compromise C sequestration.

Keywords Ammonia • Ammonium • Nitrate • Nitrogen sinks and losses • Sphagnum

42.1 Introduction

Peat is formed mainly through the incomplete decomposition of vegetation which means that peatlands sustain themselves and grow through carbon (C) sequestration (Charman 2002), providing a vital ecosystem service in today's world. The global extent of peatlands ~400 Mha is equivalent to 3 % of the earth's land surface, predominantly in the northern hemisphere. Northern peatlands store ~450 BtC, approximately 33 % of global C stocks (Strack 2008). In the UK, peat accumulation has been estimated to be 0.7 MtC $year^{-1}$, with losses due to drainage and peat extraction of between 0.5 and 1.0 MtC $year^{-1}$ (Cannell et al. 1999). If decomposition/mineralisation rates start to exceed productivity, gradually their functionality and land cover will decline. Recently, peat soils and bogs in England and Wales have been shown to be losing C at a faster rate than other soil types in response to anthropogenic activities (Bellamy et al. 2005).

Carbon sequestration is probably the most crucial ecosystem service that peatlands provide and it is delivered through factors that influence decomposition. Rates of decay, not production, control peat C accumulation (Clymo 1965). Areas of organic, ombrotrophic peat formation are mostly waterlogged and the combination of anoxic conditions, acidity and low levels of nutrient availability restrict both the plant species and their breakdown, maintaining the *status quo*. Arguably northern peatlands, especially the boreal peatlands draw their characteristic features from the peat mosses, species of *Sphagnum*, they support. *Sphagnum* mosses contribute to maintaining these acidic wet and anoxic conditions and produce compounds that are highly resistant to decay (Rydin and Jeglum 2006). In addition, in common with all lower plant groups bog mosses have at best none or rudimentary access to soil derived nutrients and, aided by the absence of a cuticle, rely for most of their nutrients on atmospheric deposition.

Lower plants such as mosses are highly efficient at immobilising nutrients such as nitrogen (N) that are deposited from the atmosphere (Curtis et al. 2005). This ability together with the niche they occupy, often covering the soil/peat surface enables lower plants to remove atmospheric N before higher plant roots can access it, helping to maintain the low nutrient status and exclude faster growing plants. However, the success of such species under nutrient deprived conditions, in environments that are not conducive to rapid growth, reflects growth strategies that have evolved towards efficient nutrient uptake and use and the production of tissue that is resistant to breakdown, rather than investment in large assimilatory capacity (Aerts 1999). In conditions of enhanced N deposition such life style traits mean peatland vegetation is vulnerable to nutrient accumulation and its toxic effects.

The biogeochemistry of peatlands is highly regulated within a relatively 'self contained cycle' that is reliant on the plant community composition (van Breeman 1995). Pristine bogs are N limited (Aerts et al. 1992). Nitrogen is a key plant and microbial growth nutrient, with the potential to both increase C assimilation and growth and drive changes in species composition (Marschner 1995). Increasing N availability also changes decomposition rates (Charman 2002), although in which direction remains uncertain. Loss of mosses, especially *Sphagnum*, in response to increased N availability, leading to gradual encroachment by higher plants with greater water use and more readily decomposable litter, will challenge the ability of peatlands to sequester C.

Peatlands are widespread in northern regions of Europe with low levels of N deposition, often well below 5, up to 10 kg N ha^{-1} $year^{-1}$, which is the maximum N critical load for bogs (Achermann and Bobbink 2003), so is enhanced N deposition a cause for concern? Evidence suggests that vegetation sensitivity to N is strongly determined by both historic and current N deposition levels (Emmett 2007). Indeed it is possible that some of the sensitivity of plant species to N deposition reflects exceedance of some threshold associated with N accumulation. If this is the case then even areas currently receiving relatively low N deposition loads could be at risk. In the context of peatland ecosystems that have evolved over millennia, the increases in reactive N deposition observed over recent decades (Reay et al. 2008) represent a huge stepwise change, even if the N dose appears very small. Given the tightly closed N cycles these peatland plant communities have evolved under and their limited assimilative capacity, relatively small N doses may still represent an intolerable N burden.

Thus it can be hypothesised that peatland ecosystems are poorly equipped to tolerate elevated N deposition because of the sensitivity of the keystone species composition that underpin the sustainability and function of northern peatlands. However, few studies have tested this view under realistic conditions nor interpreted the responses in terms of their potential effect on the ability to deliver key ecosystem services and none have examined whether the form of N is important. The Centre for Ecology & Hydrology (CEH) Edinburgh has been manipulating N deposition to an ombrotrophic bog in an area of relatively low N deposition since 2002. Realistic deposition scenarios were implemented, so that the wet treatments were coupled to precipitation patterns and dry deposition to wind direction, to increase N deposition by 2, 4 and 8 times the background N deposition of 8 kg N $ha^{-1}year^{-1}$.

This chapter focuses on the significance of increasing N deposition, particularly the form of the deposited N, for species cover and composition, especially of the key bog moss *Sphagnum*, and as a consequence how much of the incoming N is immobilised. This comprises part of the first step to changing peatland characteristics with respect to N cycling and the potential of peatlands to sequester C, its core ecosystem service. The effects of different N forms *per se* on C sequestration are not addressed in this chapter.

Hypotheses Lower plants, mostly the mosses effectively immobilise small amounts of N but as the N dose, especially of reduced N increases, their ability to sequester N declines, as evidenced by increases in the concentration of nitrate in the soil pore-water and thus N losses to the atmosphere as nitrous oxide (N_2O).

42.2 Site Details and Methods

Whim bog, 35 km south of Edinburgh, represents a transition between a lowland raised bog and a blanket bog, 280 m a.s.l., receiving a mean annual rainfall exceeding 900 mm and temperature of 8.2 °C. The experimental site has low background N and Sulphur (S) inputs, <8 kg N (split evenly between wet and dry, reduced and oxidised N), and 4 kg S ha^{-1} $year^{-1}$. The vegetation is unmanaged, NVC M19 *Calluna-Eriophorum* (Rodwell 1991). The surface undulates by up to 0.5 m over 3 to 6 m of acid peat, with pH 3.8 (H_2O), base saturation = 10 %, bulk density between 0.06 and 0.12 g cc^{-1}, and a C:N ratio of 33.

The automated free air ammonia release is controlled by a Campbell 23X data logger which records timing, duration and environmental conditions prevailing during NH_3 release (Leith et al. 2004). The system is activated when wind speed exceeds 2.5 m s^{-1} and direction (sonic anemometer) is aligned with the release transect. Gaseous NH_3, from a pressurised anhydrous NH_3 cylinder, flows via a mass flow controller through a stainless steel pipe at 3.3 g min^{-1} into a fan unit where it is mixed with air. The diluted NH_3 is released from a 10 m perforated pipe, 1 m from the ground. Monthly mean, but not peak, NH_3 concentrations are quantified along the free air release transect using ALPHA (Adapted Low-cost Passive High Absorption) samplers fixed 0.1 m above the vegetation, exchanged monthly for regenerated samplers and the NH_3 concentration measured (Tang et al. 2001). Ammonia concentrations are converted to N dose, taking into consideration plant community type, wind speed, surface wetness, and using a concentration dependent deposition velocity (Cape et al. 2008).

Wet deposition as either oxidised or reduced N as $NaNO_3$ and NH_4Cl respectively, is provided via an automated system, directly coupled to rainfall. Rainwater is collected on site and the treatment concentrate added by diluters, before being transferred along 100 m pipes to a central spinning disc, mounted ~20 cm above canopy height, in each plot (Sheppard et al. 2004a). Treatments are supplied to 4 replicated 12.8 m^2 plots, at a maximum concentration of 4 mM concentration, as and when sufficient rainfall is collected. Thus, the timing, frequency and N concentrations of the wet and dry treatments differ from each other, as they do in the 'real' world.

Vegetation cover was recorded by species in these large plots, after treatments had been running for >7 years. The cover was assessed in two 2*1 m^2 quadrats, at various distances along the ammonia transect, running parallel to the ammonia source. Nutrient N concentrations were measured (CN analyser) in the 2008 annual increment of the most common mosses, *Sphagnum capillifolium*, *Hypnum jutlandicum* and *Pleurozium schreberi*. The annual mass increment was also measured using a modification of the cranked wire method, where moss mass that grew above (*S. capillifolium*), through (*H. jutlandicum* and *P. schreberi*) a reference level, was harvested after 1 year.

Nitrous oxide (N_2O) emissions were measured using static chambers (40 cm diameter) based on four air samples removed over a 30 min period into Teflon bags. The N_2O concentration was measured with a gas chromatograph (ECD, electron capture detector at 350 °C). The values presented represent mean values ($n=4$) from October 2008 to October 2009. Soil water $NH_4^+$and NO_3^- concentrations were measured in water sampled from the 0–10 cm layer of peat using suction samplers (mini rhizon, 20 ml syringe capacity, filter size 0.45 µm, length 10 cm, inserted at 45°). Values represent treatment means of four replicates from May 2006 to May 2008.

42.3 Results

42.3.1 Visible Damage

Differences in the extent of visible damage on key species, associated with the different N forms, were highly visible. Equivalent N doses of dry ammonia gas, when compared with the same N doses applied in rain water, caused damage within one year. The damage occurred on a scale that has still not been replicated 7 years later in the wet plots, even with 56 kg N $ha^{-1}year^{-1}$. The common mat forming lichen *Cladonia portentosa* was killed at NH_3-N deposition equivalent to the 56 kg N ha^{-1} $year^{-1}$ in < one year (Sheppard et al. 2004b). Similar levels of death were also seen amongst *Calluna* (Sheppard et al. 2008) and *S. capillifolium* (Sheppard et al. 2009). By contrast, *Eriophorum vaginatum* has increased its cover along the ammonia transect, compared to the wet treatment plots where there is no obvious change, though a trend toward decreasing cover. The resulting effects of the different N forms on the remaining cover of the key species: *S. capillifolium*, *H. jutlandicum* and *P. schreberi Calluna* and *E. vaginatum* are compared in Fig. 42.1.

42.3.2 Species Cover

In the presence of high ammonia-N doses, > 4 times the ambient N deposition to the site, the cover of all the *S. capillifolium* and pleurocarpous mosses, *H. jutlandicum* and *P. schreberi* has fallen to < 12 %, < half pre-treatment cover levels. The cover of both *S. capillifolium* and *P. schreberi* was also decreased by the wet N dose, but the form of N was unimportant. However, the ~ 10 % increase in dead capitula compared to the start was much smaller than found with ammonia for *S. capillifolium*.

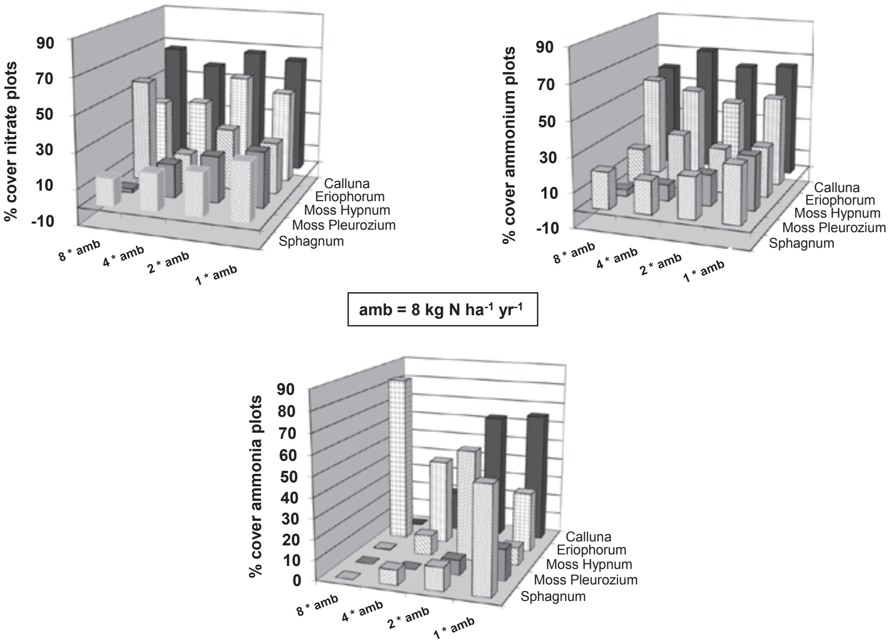

Fig. 42.1 Effect of N form: nitrate, ammonium and ammonia, on the % cover of *Sphagnum capillifolium*, *Pleurozium schreberi*, *Hypnum jutlandicum*, *Eriophorum vaginatum* and *Calluna vulgaris* in 12.8 m^2 plots on an ombrotrophic bog in the Scottish Borders where the forms of N deposition have been experimentally enhanced (wet, $n=4$; ammonia plots $n=2$, cover area for ammonia $=2\times1$ m^2 rectangles). Cover was assessed in 2009 after 7 years of treatment of N doses equivalent to ambient deposition, 8 kg N ha^{-1} $year^{-1}$, 2x ambient, 4x ambient and 8x ambient, in wet deposition (sodium nitrate or ammonium chloride added to ambient rainfall and sprayed onto plots) and as dry deposited ammonia gas

Growth measurements (data not shown) and cover confirm the potency of N for *P. schreberi* with lower cover in respect to N dose, irrespective of form of N. By contrast the other pleurocarpous moss (*H. jutlandicum*) appears to be quite tolerant of wet oxidised N and even stimulated by the high nitrate dose.

Calluna appears to be indifferent to both N dose and N form in wet deposition, but was dramatically reduced along the ammonia transect by NH_3-N deposition of >16 kg $ha^{-1}year^{-1}$. *Eriophorum vaginatum*, by contrast, is also indifferent to N form and dose in wet deposition, but responded positively to high ammonia and the consequent reduction in *Calluna* cover (Fig. 42.1). The loss of *Calluna* cover accounted for 71% of the variation in cover of *E. vaginatum* growing along the ammonia transect. Unlike *Calluna*, *E. vaginatum* appears to tolerate high ammonia concentrations, N dose and the increase in soil pH.

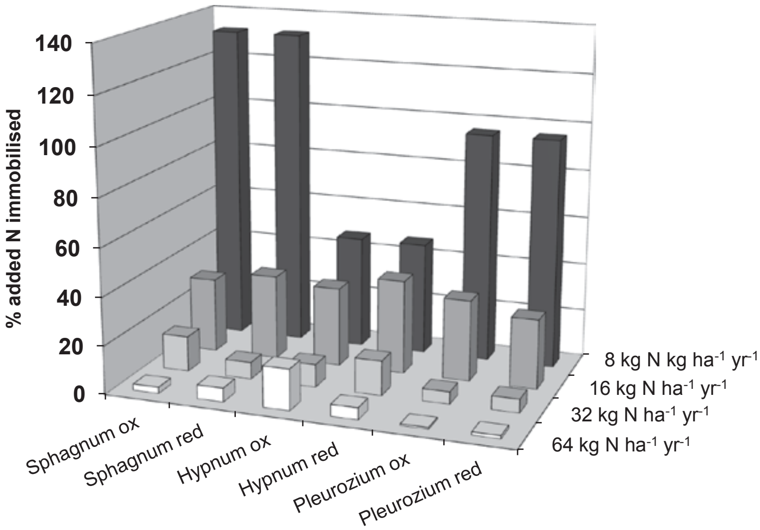

Fig. 42.2 Percentage of N applied as oxidised (*ox*) or reduced (*red*) N immobilised by the main moss species, *Sphagnum capillifolium*, *Hypnum jutlandicum* and *Pleurozium schreberi*. The control receives circa = amounts of both N forms. The percentage has been calculated from the cover of the moss, its annual production per unit area and the N concentration in its annual production

42.3.3 Annual Nitrogen Immobilisation by Moss

This was not assessed along the ammonia transect as there was insufficient moss at the higher NH_3-N dose. In the control treatment, which is sprayed with rainwater providing an extra 10 % precipitation the annual dose is ~ 8 kg N ha^{-1} most N is taken up by *S. capillifolium* (> 120 %) then *P. schreberi* (90 %) then *H. jutlandicum* (40 %) (Fig. 42.2). When the annual deposition is doubled all three mosses immobilised approximately 40 % of the N added, irrespective of N form. Further increases in the N dose, by 4 and 8 times the N dose led to proportionately less of the N dose being immobilised: < 5 % when the total N dose, including ambient, was 64 kg N $ha^{-1}year^{-1}$. Moss N immobilisation was less sensitive to N form although *H. jutlandicum* immobilised more nitrate than ammonium because its cover was much higher with nitrate.

42.3.4 Soil Pore Water Nitrate and Nitrous Oxide Emissions

Soil pore water nitrate was increased by the addition of nitrate > 8 kg N $ha^{-1}year^{-1}$ in response to dose, ~ 4 fold with the highest nitrate-N dose (Fig. 42.3). The ammonium treatment did not include nitrate, but pore water nitrate was slightly raised, though not in response to N dose. Ammonia likewise does not add nitrate but pore-water nitrate increased, especially at the highest N dose, > 20-fold. Nitrous oxide emis-

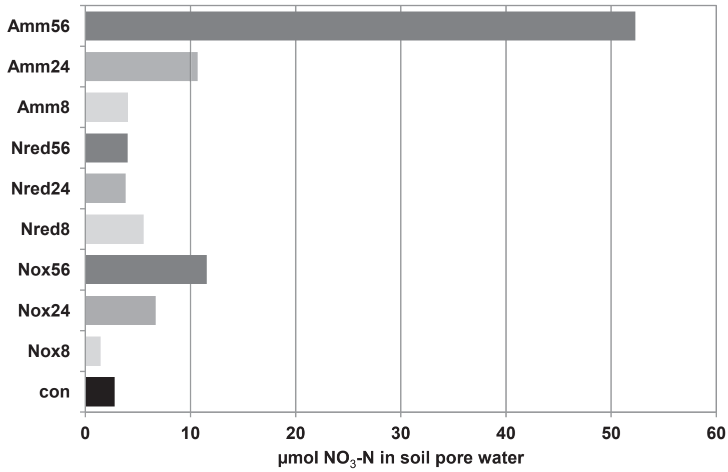

Fig. 42.3 Mean nitrate concentrations (µmol l^{-1}) in pore water, extracted monthly using rhizon suction samplers inserted at 0–10 cm in the peat, after treatment with 8, 24 or 56 kg N $ha^{-1}year^{-1}$ as sodium nitrate (Nox8, Nox24, Nox56) or ammonium chloride (Nred8, Nred24, Nred56) from May 2006-August 2009

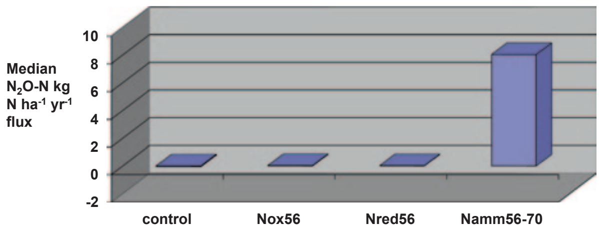

Fig. 42.4 Annual Median nitrous oxide flux kg N ha^{-1} $year^{-1}$ measured in control high ~56 kg N ha^{-1} $year^{-1}$ as nitrate, ammonium and ammonia plots ($n=4$). Flux was measured using static chambers which were closed for 30 min, during which time 4 air samples were removed at 0, 10, 20 and 30 min

sions were only measured in the control and high N treatments and were tiny except in the high ammonia treatment (Fig. 42.4). These high N_2O emissions reflect the high soil pore water nitrate, which is a prerequisite for denitrification.

42.4 Discussion

42.4.1 The Form of Nitrogen Deposition Drives Species Cover Changes

Increasing the supply of mineral N to an ombrotrophic bog changes the relationship between the component species. However, the rate of change per unit N deposited depends on the form of N deposition, dry deposition of NH_3 drives responses much faster than wet N deposition. The change in dominance from *Calluna* to *E. vaginatum* in response to ammonia has not after 8 years, shown any sign of being replicated under the wet treatments. Where there is a strong *Calluna* canopy the cover of *E. vaginatum* appears to be naturally suppressed. *Calluna* cover is negatively correlated with that of *E. vaginatum* and in the dry plots the reduction in *Calluna* cover explained >70% of the *E. vaginatum* cover. In the wet plots *Calluna* cover increased over the first five years time in response to N treatment and *E. vaginatum* cover declined, though not significantly. Sheppard et al. (2008) suggested that ammonia increased the risk of winter desiccation, a 'normal' stressing agent in *Calluna*, by impeding stomatal closure and causing stomata to remain open at lower water contents. Although wet N deposition can also increase winter desiccation, a significant proportion of the canopy recovers (Carroll et al. 1999). Up to the summer of 2009, winter desiccation had not increased in *Calluna* growing in the wet N treatments.

Moss, including *Sphagnum* cover declined in response to N dose, >+8 kg N ha^{-1} year^{-1} and, effects were most pronounced with ammonia. Mosses accumulate N and they accumulated most N when the N form was ammonia. *S. capillifolium*, which was the most sensitive to increased N deposition, accumulated the most N. This may in part reflect the breakdown of the *Calluna* canopy which took up significant amounts of ammonia (Sheppard et al. 2008). In this peatland ecosystem the tolerance of different species to N deposition appears to be linked, with changes in the cover of one species affecting the N tolerance of co-occurring species.

42.4.2 Implications of Nitrogen Driven Changes in Species Composition on Nitrogen Immobilisation

Sphagnum mosses are accomplished at immobilising most of the N in wet deposition when it is supplied in small doses (Lamers et al. 2000). However, this ability declines sharply with increasing N deposition and species effectiveness varies (see Fig. 42.2). In the control plots, the amount of N present in *S. capillifolium* exceeds that provided in ambient deposition, and *P. schreberi* and *H. jutlandicum* also account for substantial amounts of N>90 and 10% respectively. Above the annual ambient deposition at this site, the 'natural filter' begins to fail (Nordbakken et al. 2003), so that less of the N deposition is immobilised in the mosses. *H. jutlandicum* immobilises least N overall, but because it is the most N tolerant species, having the largest moss cover at high N inputs, immobilises proportionally more of the large N dose than the other mosses. These results support the many ^{15}N labelled studies that show the significance of mosses for N immobilisation, providing the N input remains below 5 to10 kg N ha^{-1} year^{-1} (Nordbakken et al. 2003; Curtis et al. 2005).

The repercussions of N saturation and breakdown of the moss flora could potentially contribute to the increases in soil water nitrate (Fig. 42.3) and increased risk of N loss by denitrification (Fig. 42.4) and leaching, which can be associated with surface water acidification (see Curtis et al. 2005). In this study, large N losses have so far only been recorded in response to ammonia (Fig. 42.3) at N inputs above 24 kg N ha^{-1} $year^{-1}$which have significantly reduced not just the cover of key mosses but also that of *Calluna*. Equivalent wet N doses have caused only small increases in soil water nitrate concentrations and denitrification, despite saturating the capacity of key mosses to immobilise N. These differences in the amount of available N in the soil pore water, between dry and wet N deposition plots, probably reflects the large *Calluna* cover in the wet N plots. This implies that *Calluna* also, after 7 years, remains an important sink for wet N deposition.

Where the ammonia deposition exceeded 30 kg ha^{-1} $year^{-1}$ the cover of *Calluna*, *S. capillifolium* and the pleurocarpous (weft like habit) mosses has disappeared and been replaced by *E. vaginatum* and acrocarpous mosses (upright habit) colonising the exposed peat surface. *E. vaginatum*, is a widespread, tussock forming sedge, often described as a perennial graminoid, that flourishes in disturbed, nutrient poor peatlands (Silvan et al. 2004). Despite its low reliance on mineral N (Nordbakken et al. 2003), *E. vaginatum* appears to be quite tolerant of ammonia and the high inputs of mineral N. This is despite increasing its N content by ~45% (data not shown). However, replacement of *Calluna*, *S. capillifolium* and pleurocarpous mosses by *E. vaginatum*, reported to be a strong competitor for nitrate (Silvan et al. 2004) and a thin carpet of acrocarpous mosses has not effectively replaced the function of the *Calluna Sphagnum* moss N sink: the very significant increase in pore water nitrate and N_2O fluxes point to a vastly reduced N immobilisation capacity. A further negative consequence of this species replacement is the contribution *E. vaginatum* can make to increasing methane (CH_4) emissions. *Eriophorum* contain aerenchyma cells which provide a conduit for CH_4, restricting the likelihood of CH_4 oxidation and increasing the potential for CH_4 emission (Greenup et al. 2000). Also, acetate is excreted by the deep roots of *Eriophorum* which can be used by methanogens as an electron acceptor to produce CH_4. Thus ammonia driven increases in the cover of *E. vaginatum* and the decline in *Calluna*, *S. capillifolium* and pleurocarpous mosses will have implications for N immobilisation, and greenhouse gas emissions.

42.4.3 Implications of the Form and Dose of Nitrogen Deposition for Ecosystem Services that Peatlands Provide

We have shown, as hypothesised, that mosses and ericaceous shrubs typifying peatland vegetation can restrict losses of N deposition to water courses and as N_2O to the atmosphere. However, the effectiveness of N immobilisation depends on both the dose and form of N, and after a relatively small cumulative dose over 7 years, we can see that the capacity of the ecosystem for N immobilisation is modest and is declining in response to the accumulating N dose. The high N treatment as ammonia leaked almost 8 times as much N compared with the wet N treatments, with

~30% in the form of nitrate, indicating a high level of nitrification in response to ammonia N deposition. Ammonia deposition has significantly increased the peat pH (+0.5 units, data not shown). These two factors, together with the loss of moss and *Calluna* cover, and the diminished uptake of mineral N by *E. vaginatum* (data not shown) probably explain the relatively high N_2O flux with dry, but not wet, N deposition.

These results demonstrate the importance of the form in which N deposits, as well as the N dose level. With respect to N dose, we have found that effectiveness of the N immobilisation capacity of *S. capillifolium* occurs at similar N doses to those suggested by Lamers et al. (2000) and Blodau et al. (2006) using ^{15}N, ~15–20 kg N ha^{-1} year^{-1}, irrespective of the form of N in wet deposition. The difference in amount of 'leaked' N between dry and wet N deposition was mediated by their respective effects on the amount and quality of the vegetation. Ammonia has changed the vegetation type by killing the *Calluna* and *S. capillifolium*. The loss of the vegetative N sink and the increased pH have contributed to conditions that are now suitable for supporting significant levels of denitrification and N_2O production. Where the cover is dominated by *Calluna*, which constrains *E. vaginatum* growth and appears to protect the moss layer, more of the N is retained.

The effect of N form and dose on the key ecosystem service of C sequestration was not addressed *per se*, but given the importance of *Sphagnum* for peatland C sequestration (Rydin and Jeglum 2006) our observations infer that the effects of enhanced N deposition will be detrimental. *S. capillifolium* was sensitive to even a doubling of the ambient N dose and the increasingly negative effects with the larger N doses suggest the impacts are cumulative. This means that exceeding the present critical N load for bogs could compromise their future potential for C sequestration. Ammonia appears to present the greatest risk to this ecosystem service.

42.5 Conclusions

- Ammonia significantly reduced the cover of *Calluna*, *S. capillifolium*, pleurocarpous moss and lichen, leading to an increase in *E. vaginatum*.
- Wet deposition increased *Calluna* cover and reduced the cover of *E. vaginatum* but not significantly.
- The ammonia-driven loss of higher and lower plant cover reduced the sink for N, leading to an increase in soil pore water nitrate, which led to a significant loss of N as the greenhouse gas N_2O.
- Equivalent N deposition in precipitation has caused some damage to the moss layer, but the higher plant cover has not visibly changed: increases in soil pore water nitrate and N_2O flux were small.
- The loss of key peatland species leads peatlands to become increasingly N leaky.
- Retention of N deposition by *Sphagnum* and other mosses declines between 8–16 kg N ha^{-1} year^{-1}.

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Chapter 43
Quantification of Impacts of Nitrogen Deposition on Forest Ecosystem Services in Europe

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Abstract Important forest ecosystem services are the provision of a habitat for a diversity of plants and wildlife (habitat service), pollutant filtering relevant for an adequate water quality (regulating service) and wood production with the related carbon (C) storage (provisioning/regulating service). Nitrogen (N) deposition affects these ecosystem services as it has an impact on: (i) the habitat for wild plants, reducing plant species diversity, (ii) water/soil quality by its impact on acidity (pH) and on the soil accumulation and leaching of N as nitrate, aluminium (Al) and metals to ground water and surface water and (iii) net primary production and C sequestration. In this chapter, we describe the application of the Very Simple Dynamic (VSD) model, extended with relationships between nitrogen (N) deposition and greenhouse gas emissions, on a European-wide scale to quantify the impact of N deposition on these forest ecosystem services. This includes: (i) potential impacts of N deposition on plant species diversity in terms of excess N deposition compared to critical loads for N, (ii) excess nitrate (NO_3) and Al concentrations in leachate to groundwater and surface water compared to critical limits, (iii) soil acidification, in terms of the depletion of the pools of base cations (BC) and Al, and (iv) C sequestration and related emissions of the greenhouse gases carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). Results show that the N deposition

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reduction measures that have been taken since 1980 have led to a reduction between 10 and 15 % in the areas exceeding critical N loads and critical limits for NO_3 and Al in groundwater or surface water, but the estimated CO_2 uptake is nearly 20 % lower under a reduced N deposition scenario as compared to a constant 1980 N deposition scenario. The N induced N_2O emissions however counteract the N induced C sequestration.

Keywords Acidification • Carbon sequestration • Critical limits • Critical loads • Ecosystem services • Greenhouse gas emissions • Nitrogen • Plant species diversity

43.1 Introduction

43.1.1 The Concept of Ecosystem Services

An increasing amount of information is being collected on the ecological and socio-economic value of goods and services provided by natural and semi-natural ecosystems. The earliest literature on ecosystem service valuation dates to the mid-1960s and early 1970s (e.g. Helliwell 1969). More recently, there has been an almost exponential growth in publications on the benefits of natural ecosystems to human society (see, e.g., Costanza et al. 1997; De Groot et al. 2002; De Groot et al. 2010). Inspired by De Groot et al. (2002), who grouped ecosystem services into four primary functions, the Millennium Ecosystem Assessment distinguished among provisioning, regulating, supporting, and cultural services (Reid et al. 2005). Provisioning services are the products obtained from ecosystems, specifically the provision of food, fibre and wood/fuel. These services also include other products, such as the provision of fresh water. Regulating services refer to the regulation of climate, floods, water quality and diseases. These services are related to the impact of ecosystems on greenhouse gas (GHG) exchange (climate) and the buffering and filtering capacity of the soil, affecting water and chemical fluxes, such as nitrates. Supporting services relate to the capacity of natural and semi-natural ecosystems to regulate essential ecological processes and life support systems through bio-geochemical cycles and other biospheric processes. Supporting services are indirectly related to the provisioning and regulating services as they affect many services that have direct and indirect benefits to humans (such as clean air, water and soil). In the more recent global study entitled ‘The Economics of Ecosystems and Biodiversity (TEEB)’ (TEEB 2010; De Groot et al. 2010), supporting services have been reclassified as ‘habitat’ services which are defined as underpinning almost all other services i.e. ecosystems provide living spaces for plants or animals; they also maintain a diversity of different breeds of plants and animals. Cultural services include for example recreation and landscape features or species with aesthetic or spiritual value.

43.1.2 Qualitative Link between Nitrogen Deposition and Ecosystem Services

Forest ecosystems provide a full suite of services that are vital to human health, livelihood and well-being. Important forest ecosystem services include the provision of adequate soil and water quality, watershed services, carbon (C) storage, and habitat for a diversity of plants and wildlife. Nitrogen (N) deposition affects many ecosystem services, including effects on:

- Diversity of plant species in ecosystems (impact on habitat function for wild plants, reducing biological and genetic diversity; cultural and provisioning services).
- Primary production (provisioning service of wood/fibre and supporting services, as photosynthesis produces oxygen necessary for most living organisms) and C sequestration (climate regulating service).
- Soil and water quality: soil acidification and leaching of N, aluminium (Al) and metals to groundwater and surface water (regulating service, i.e. clean soil and water).

More information on the impacts of N deposition on ecosystem services, including the causal links, is given in de Vries et al. (2009a) and de Vries et al. (2014, Chap. 41, this volume).

43.1.3 Purpose of this Chapter

In this chapter, we describe the application of the Very Simple Dynamic (VSD) model (Posch and Reinds 2009), extended with relationships between nitrogen (N) deposition and greenhouse gas emissions, on a European scale to quantify the impact of N deposition on these forest ecosystem services, i.e. the:

- Potential impacts of N deposition on plant species diversity in terms of excess N deposition compared to critical loads for N (using the steady-state version of VSD, which is equal to the so-called simple mass balance model (SMB), as described in, e.g., Sverdrup and de Vries 1994);
- Water quality regulation: excess nitrate (NO_3) and Al concentrations in leachate to groundwater and surface water compared to critical limits;
- Soil quality regulation: depletion of the pools of base cations (BC) and Al;
- Carbon sequestration and greenhouse gas emissions.

43.2 Quantification of the Link between Nitrogen Deposition and Ecosystem Services

43.2.1 The VSD Model

The VSD model (Posch and Reinds 2009) is based on the soil model SMART, first described by de Vries et al. (1989) and later updated by Posch et al. (1993). It has been simplified, however, by: (i) neglecting the parts related to calcareous soils and aluminium depletion in highly acidified soils, (ii) ignoring sulphate adsorption, (iii) assuming complete nitrification, thus ignoring NH_4 leaching and (iv) lumping the exchange of all BC into one term. Furthermore, it includes some new ideas on N immobilisation. VSD consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing rate-limited and equilibrium soil processes. The soil solution chemistry in VSD depends solely on the net element input from the atmosphere (deposition), net uptake, net immobilisation and denitrification and the geochemical interaction in the soil (CO_2 equilibria, mineral weathering, cation exchange and internal production or organic anions). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g. uptake and weathering) or by equilibrium reactions (e.g. cation exchange). It models the exchange of Al, H and BC = Ca + Mg + K with Gaines-Thomas or Gapon equations. All ions in soil solution are linked via a charge balance equation. Solute transport is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth. Since VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the root zone). The annual water flux percolating from this layer is taken as being equal to the annual precipitation excess. The time step of the model is one year, i.e. seasonal variations are not considered. The model assumes a completely oxidized state of the soil and does not account for upward transport of ions by seepage, implying that it cannot be applied to very wet ecosystems.

Input data for the VSD simulations consist of spatially explicit information on (i) soil and forest data including weathering of BC, nutrient uptake, N transformations and soil properties such as C pool and cation exchange capacity, (ii) climatic variables and (iii) deposition of BC, sulphur (S) and N. The soil and forest data were derived combining European maps and databases of soils, land cover and forest growth regions. A map with computational units (receptors) was created by overlaying maps on land cover, soils and forest growth (Reinds et al. 2008). This results in about 670,000 sites (forests and semi-natural vegetation) covering 3.7 million km^2. Results are also separately presented for forests alone (about 385,000 sites covering about 2.3 million km^2). Time series of temperature, precipitation and cloudiness were obtained from a high resolution European data base (Mitchell et al. 2004) containing monthly values for the years 1901–2100 for land-based grid-cells of $10' \times 10'$ (approx. 15×18 km in central Europe). Deposition data are described below.

43.2.2 Simulation Approach

The VSD model was run for Europe for the period 2000–2050, using deposition data as submitted to the co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP) for NO_x, NH_3 and SO_2. The following scenarios were evaluated:

- Deposition levels for 1980 held constant between 2000 and 2050 (1980 deposition);

- Deposition levels projected to be achieved under the Gothenburg Protocol between 2000 and 2010 and constant thereafter (current legislation);
- Starting with deposition for 2000 and changing N deposition linearly to critical loads for N in view of biodiversity impacts (see Hettelingh et al. 2008) and keeping them constant thereafter (critical loads).

Excess N deposition compared to critical loads of N for biodiversity impacts was assessed by simply taking EMEP model results on N deposition and comparing it with the critical loads submitted by various National Focal Centres under the Convention on Long-range Transboundary Air Pollution (LRTAP).

43.2.3 Quantification and Evaluation of Nitrogen Deposition Impacts on Water and Soil Quality

The water quality regulation function of forest ecosystems is negatively impacted by elevated nitrate concentrations and nitrate-induced acidification, leading to an increase in the concentrations of Al in soil solution. The impacts on water quality and soil quality were derived from the VSD model, implying that the water quality parameters refer to the soil solution draining to groundwater and surface water. The impact of N deposition on the concentrations for Al, NO_3 and N in soil solution draining to groundwater and surface water was evaluated by comparing them with:

- the limits for Al and NO_3 concentrations in groundwater, intended for drinking water, of 0.2 mg Al l^{-1} and 50 mg NO_3 l^{-1} according to the EU Drinking Water Directive (EC 1998);
- a limit of 2.2 mg N l^{-1} for N in surface water in view of eutrophication effects, being a criterion used for the Netherlands (VW 1989).

The impact of N (and S) deposition on soil quality, in terms of depletion of the readily available BC and Al pools, was derived as total BC and Al soil release rates minus BC and Al weathering rates (de Vries et al. 1994). Base cation depletion from the exchangeable BC pool is directly given by VSD. Aluminium depletion was derived by Al leaching, and Al weathering was calculated as twice the BC weathering. Results are given as annual average BC and Al depletions in Eq. ha^{-1} $year^{-1}$.

43.2.4 Quantification and Evaluation of Nitrogen Deposition Impacts on GHG Fluxes

The overall impact of N deposition on terrestrial ecosystems in terms of the net effect on global warming potential (GWP), is mainly determined by the interactions between anthropogenic N deposition and carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) fluxes. Elevated N deposition to N limited systems has three general effects. First, it causes an increase in C sequestration from increased

Table 43.1 Estimated ranges in the impact of 1 kg of N deposition on average annual CO_2, N_2O and CH_4 emissions and on their global warming potential (GWP) in CO_2 equivalents

Greenhouse gas	N deposition impacts in kg ha^{-1} year^{-1} on CO_2-C, N_2O-N and CH_4-C	GWP (kg CO_2 equivalents ha^{-1} year^{-1})
CO_2-C	24.5 ± 8.7 kg CO_2-C ha^{-1} year^{-1}	−89.8 ± 32.0
N_2O-N	0.0087 ± 0.0025 kg N_2O-N ha^{-1} year^{-1}	+4.0 ± 1.2
CH_4-C	−0.015 ± 0.004 kg CH_4-C ha^{-1} year^{-1}	+0.44 ± 0.12
Total		*−85.4 ± 33.3*

wood production and accumulation of soil organic matter through an increase in litter, increased leaf/needle biomass production and a reduced decomposition of organic matter, depending on the stage of humus formation. Second, it causes an increase in N_2O emission due to an elevated nitrification and denitrification and, third, elevated N deposition causes reduced CH_4 uptake in well-drained soils.

Various reviews have assessed the impacts of N deposition on the above GHGs. For this study, we used the results of a recent meta-data analysis by Liu and Greaver (2009) of studies on the GHG flux (CO_2, CH_4, N_2O) from N additions in multiple terrestrial and wetland ecosystems. Their analysis assessed 68 publications containing 208 observations across North and South America, Europe and Asia. We quantified the overall effect of N deposition on GHG fluxes on forests by using the average results from Liu and Greaver (2009) on fertilizer-induced emission/uptake factors per kg N ha^{-1} year^{-1} in terms of CO_2 equivalents. The GWP approach was used, where 1 kg N_2O was assumed to equal 296 CO_2 equivalents and 1 kg CH_4 to equal 23 CO_2 equivalents (Ramaswamy 2001). Results are presented in Table 43.1. The results of Liu and Greaver (2009) for CO_2-C are comparable to ranges given by De Vries et al. (2009b) for C sequestration per kg N addition in above-ground biomass and in soil organic matter for forests. De Vries et al. (2007) also found comparable results for N_2O-N and CH_4-C exchange in response to N deposition based on independent estimates.

The impact of N deposition differences on the GWP at a European wide scale has been estimated by assuming an average impact of 85.4 kg CO_2 equivalents ha^{-1} year^{-1} per kg N (see Table 43.1), using a forested area of 230 million hectare and considering the average increase in N deposition in the period 2000–2050 for the various scenarios compared to the deposition in 1960, which was considered to be a reference situation, before the onset of substantially increased N emissions. Actually, the year 1860 would have been better, but no data were available for this year. Furthermore, de Vries et al. (2007) used this approach to assess the average GWP reduction in the period 1960–2000 as compared to 1960 and we wanted to compare future predictions with this historic approach using the same reference year.

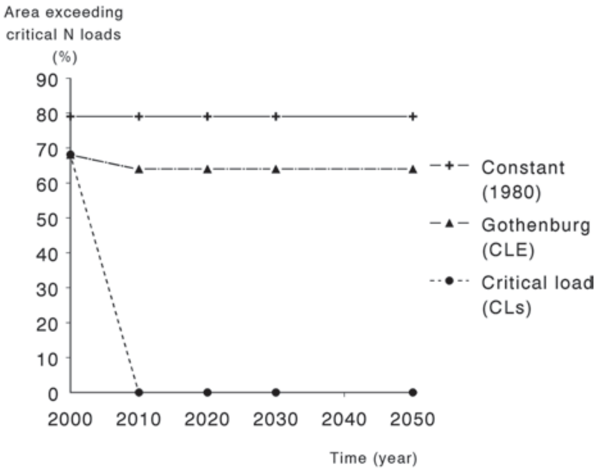


Fig. 43.1 Trends in the exceedance in critical N loads using N deposition values of 1980, the 'Current Legislation' (CLE), and the critical load for N scenarios (see text for details)

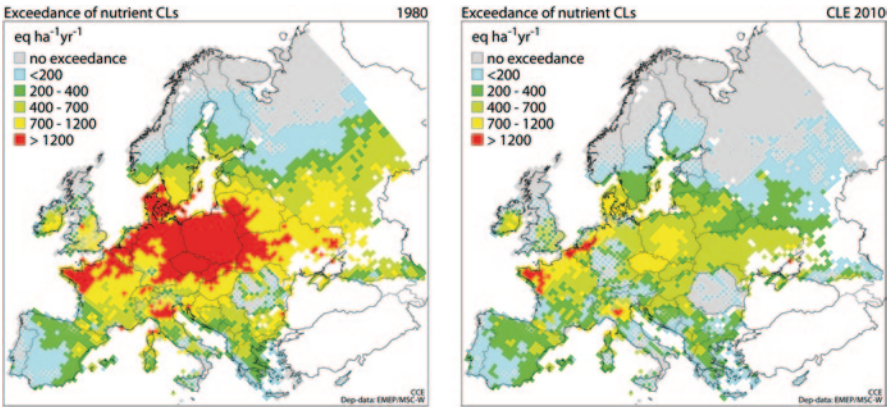


Fig. 43.2 Geographic variation in the exceedance in critical N loads using N deposition values of 1980 (*left*) and according to the 'Current Legislation' scenario (*right*)

43.3 Results

43.3.1 Exceedances in Critical Loads in Relation to Plant Species Diversity Impacts

Exceedances of critical loads according to the three scenarios described above are presented in Fig. 43.1. By definition, the Critical Load scenario (CLs) implies no exceedance of the critical N loads after 2010. The impact of the 'Current Legislation' (CLE) scenario is relatively small compared to constant 1980 deposition with respect to the area exceeding critical loads (Fig. 43.1), but the magnitude of the exceedance differs greatly as shown in Fig. 43.2.

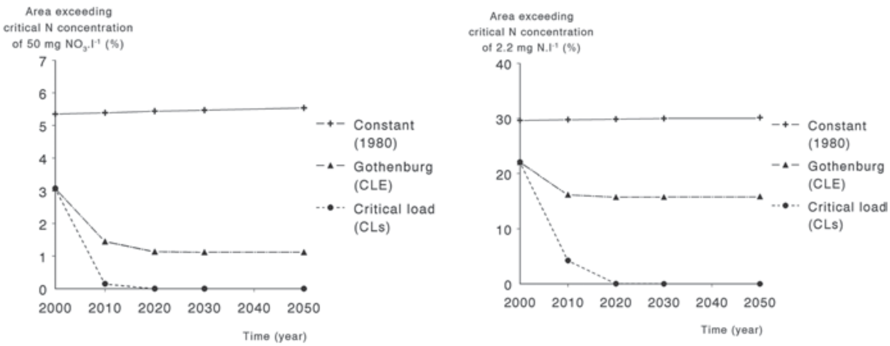


Fig. 43.3 Trends in the exceedance of a critical NO_3 concentration of 50 mg NO_3 l^{-1} in drinking water (*left*) and a critical N concentration of 2.2 mg N l^{-1} for surface water eutrophication (*right*), using N-deposition values of 1980, according to the 'Current Legislation' (CLE) and critical loads for N scenarios

43.3.2 Nitrogen Deposition Impacts on Water Quality

Fig. 43.3 shows the results of the exceedances of the area exceeding a critical NO_3 concentration, either in groundwater (50 mg NO_3 l^{-1}) or surface water (2.2 mg N l^{-1}). Unlike in the biodiversity assessment, results show that the area for which a critical NO_3 concentration is exceeded is larger when comparing the CLE scenario to the constant 1980 N deposition scenario than when comparing the CLE to the CLs scenario, particularly when the groundwater limit of 50 mg NO_3 l^{-1} is used as an additional criterion. This is in line with the much larger reduction in N loads between the 1980 N deposition scenario and the CLE scenario, compared to between the CLE and CLs scenarios. The magnitude of the exceedance of the critical NO_3 concentration also differs greatly between the 1980 deposition and CLE as shown in Fig. 43.4.

Compared to NO_3, results show that the impact of the 'Current Legislation' scenario as compared to constant 1980 deposition on the area exceeding a critical Al concentration of 0.02 mmol Al l^{-1} is much larger than the difference between the CLE and CLs scenario (Fig. 43.5). It is important to realize that the difference is not only caused by the impact of reductions in the deposition of N but also of S. The magnitude of the exceedance of the critical Al concentration also differs greatly between the 1980 deposition and CLE (Fig. 43.6).

43.3.3 Nitrogen Deposition Impacts on Soil Quality

Results of the trends in average BC and Al depletion according to the three scenarios (Fig. 43.7) show again that the impact of the 'Current Legislation' (CLE) scenario as compared to constant 1980 deposition is much larger than the difference between CLE and the critical load scenario (CLs) in line with the much larger reduction in N

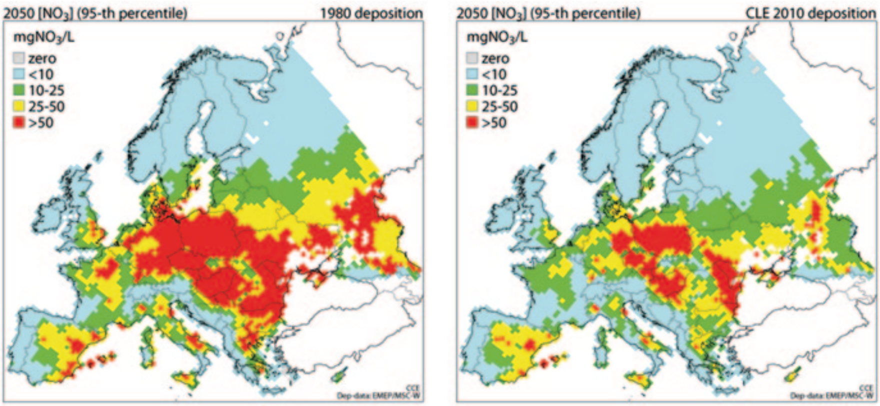
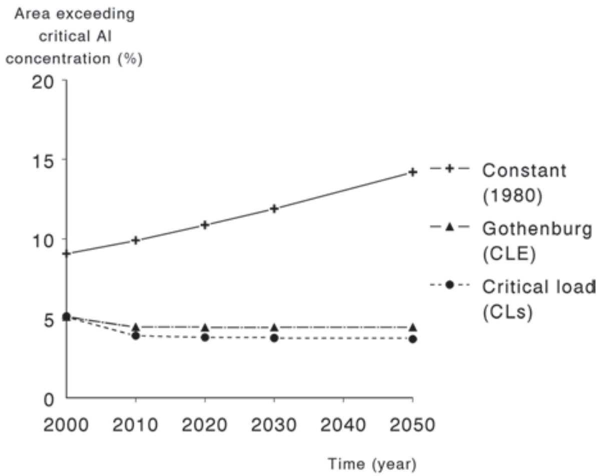


Fig. 43.4 Geographic variation in the exceedance in critical NO_3 concentration of 50 mg NO_3 l^{-1} using N deposition values of 1980 (*left*) and according to the 'Current Legislation' scenario (*right*)

Fig. 43.5 Trends in the exceedance in critical Al concentration of 0.02 mmol Al l^{-1} using N deposition values of 1980, according to the 'Current Legislation' (CLE) and critical loads for N scenarios



and S loads affecting the depletion of both BC and Al. Aluminium depletion is only an issue in central Europe, but BC depletion is more widespread, although the rate of depletion has decreased strongly due to earlier emission reductions.

43.3.4 Nitrogen Deposition Impacts on Greenhouse Gas Emissions

Unlike the other ecosystem services (protected biodiversity, good soil structure, clean water), N deposition has a cooling effect on the GWP since the positive effect on the C sequestration potential of ecosystems overwhelms the warming effect of

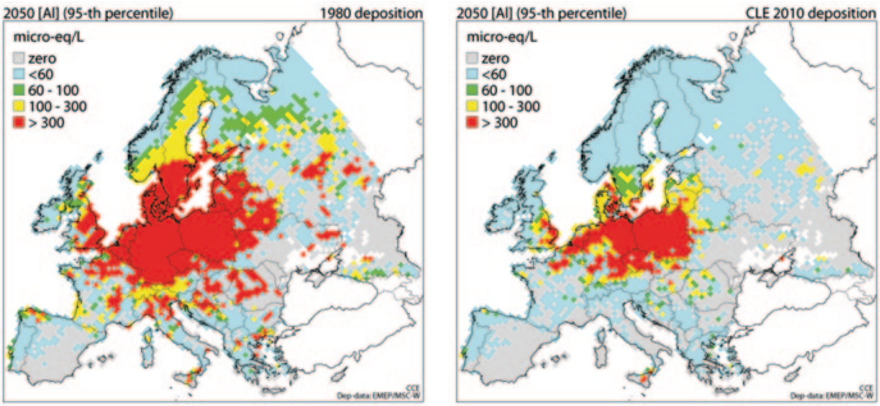


Fig. 43.6 Geographic variation in the exceedance in critical Al concentration of 0.02 mmol Al l^{-1} using N deposition values of 1980 (*left*) and according to the 'Current Legislation' scenario (*right*)

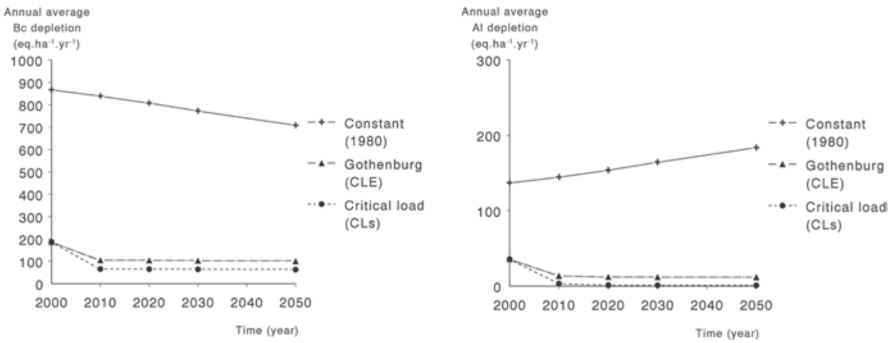


Fig. 43.7 Trends in the annual average BC depletion (*left*) and Al depletion (*right*) using N deposition values of 1980, according to the 'Current Legislation' (CLE) and according to critical N loads

increased N_2O emission and reduced CH_4 oxidation (Table 43.1). Using an average N excess in the period 2000–2050 compared to 1960 of 4.5 kg N ha^{-1} year^{-1} for the CLE scenario and multiplying this with an overall average GWP impact of 85.4 kg CO_2 equivalents ha^{-1} year^{-1} per kg N (see Table 43.1) and a forested area of 162 million ha implies a predicted N induced reduction in annual GWP of 62.0 $MtCO_2$ equivalents. Using the 1980 scenario, the average N excess in the period 2000–2050 is 9.6 kg N ha^{-1} year^{-1} implying a reduction in annual GWP of 132.2 $MtCO_2$, or an extra 70.2 $MtCO_2$. De Vries et al. (2007), who used this approach to assess the average GWP reduction in the period 1960–2000 as compared to 1960 calculated a reduction in annual GWP of 38.6 $MtCO_2$ equivalents

Table 43.2 Predicted areas exceeding critical N loads or critical limits related to water quality in the year 2050 for three scenarios

Model output	Critical limit	Area exceeding critical limits (% of total area)		
		1980 deposition	CLE scenario	CLs scenario
N loads	Critical N loads	79	64	0
NO_3	50 mg NO_3 l^{-1}	30	16	0
N concentration	2.2 mg N l^{-1}	5.2	1.0	0
Al concentration	0.02 mmol l^{-1}	14	4.4	3.7

based on an average increase in N deposition of 2.8 kg N ha^{-1} $year^{-1}$ in 2000 as compared to 1960. Compared to an estimated total carbon CO_2 uptake by European forests of 100 MtC, being equal to 366 $MtCO_2$ equivalents, their results implied that N deposition has increased the CO_2 uptake by approximately 10 % in the period 1960–2000. For the period 2000–2050, we estimate that the increase in CO_2 uptake as compared to 1960 is approximately 17 % for the CLE scenario and 36 % for the constant 1980 N deposition scenario.

43.3.5 Overall Comparison of Effects

A summary of the effects of all scenarios for areas exceeding critical N loads in view of impacts on plant species diversity or limits related to water quality for the year 2050 is given in Table 43.2.

Results show that the N deposition reduction measures that have been taken since 1980 has led to a reduction between 10 and 15 % in the areas exceeding critical N loads and critical limits for NO_3 and Al in groundwater or surface water. The impact of the scenarios on soil quality in terms of changes in Al depletion is comparable to the change in Al concentration, since Al depletion is shown up as leaching of Al. The difference between the CLE and CLs scenarios is much less, except for biodiversity impacts, which is the result of making the N load equal to the critical load at each location. This lower impact is due to the fact that the various water (and soil) quality parameters (BC and Al depletion and Al concentration) are also influenced by S deposition and the difference in S deposition between the CLE and CLs scenario is much less than between the 1980 deposition and CLE scenario.

Unlike biodiversity, soil and water quality, N deposition reduction has a negative impact on the GWP, since the N fertilization effect of forests is reduced, thus reducing C sequestration. For the 2000–2050 period we estimated that CO_2 uptake increased 17 % under the CLE scenario and 36 % under the 1980 N deposition scenario when compared to 1960 levels, implying that the estimated CO_2 uptake is nearly 20 % lower under a reduced N deposition scenario as compared to a constant 1980 N deposition scenario.

43.4 Discussion and Conclusions

In this chapter we quantified the impacts of N deposition on four major ecosystem services, including: (i) an indicator for impacts on the diversity of plant species (critical N load exceedance), (ii) water quality in terms of NO_3 and Al concentrations in leachate to groundwater and surface water compared to critical limits, (iii) soil quality regulation in terms of depletion of the pools of BC and Al and (iv) forest growth and related carbon sequestration, while also accounting for impacts on other greenhouse gases. The results show that there are trade-offs between positive and negative effects of N deposition. N deposition reduction measures lead to a strong decrease in areas exceeding critical loads in view of impacts on plant species diversity and critical limits for NO_3concentration and Al concentrations. Furthermore, soil acidification, in terms of the depletion of BC and Al is reduced. However, these positive effects are counteracted by reduced forest growth and related C sequestration.

The positive effect of N deposition on growth and C sequestration is reduced by the policy objective of bringing N deposition below critical loads (e.g., to protect biodiversity). However, it should be realized that for an overall picture of the effects of N use and N emissions on GWP or radiative forcing, one has to take the complete picture of N induced effects into account. Recently, de Vries et al. (2011) quantified the overall impacts of N use in agriculture at European scale for the year 2000 by multiplying: (i) the anthropogenic N input to agriculture by fertilizer, manure and NH_3-N deposition, the related NH_3-N deposition on terrestrial and aquatic systems and the N runoff to aquatic systems with (ii) "N induced exchange factors", giving responses of CO_2-C, N_2O-N and CH_4-C exchange per kg N input for all ecosystems. Results show that the decrease in GWP caused by elevated C sequestration in non-agricultural systems is completely counteracted by elevated N_2O emission due to N use in agriculture (de Vries et al. 2011). A similar conclusion can be drawn for the overall impact of N emissions on radiative forcing, including (i) the warming effect of NO_x induced formation of tropospheric ozone, being the third most important greenhouse gas, also reducing forest growth and C sequestration and (ii) the cooling effect of the formation of N containing biogenic fine particulates (Butterbach-Bahl et al. 2011). Considering near neutral effects of N on climate change related indicators, the negative effects on biodiversity, eutrophication of surface waters and human health warrant action to reduce N emissions.

The impact of an adequate forest management, focusing on an increase in tree species diversity, may further have a positive impact on all ecosystem services. Although results are not unequivocal, there are strong indications that mixed forests are more resistant against disturbances such as storms and insect pests, and also tend to be more productive than monocultures (Cannell et al. 1992; Kelty 1992; Scherer-Lorenzen et al. 2005). Mixed forests can therefore potentially supply enhanced biodiversity, resilience, productivity and C sequestration and N uptake, thus also reducing the negative impacts of elevated N deposition on water quality.

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Chapter 44
Implications of Current Knowledge on Nitrogen Deposition and Impacts for Policy, Management and Capacity Building Needs: CLRTAP

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Abstract The Convention on Long-range Transboundary Air Pollution (CLRTAP), linking North America, Europe, and large parts of Central Asia, has achieved considerable reductions in air pollution emissions and effects. In addition, CLRTAP has also facilitated political cooperation, international law development, and the use of science to develop and implement policy. For instance, regionalized emission reduction targets of the CLRTAP Gothenburg Protocol minimize environmental effects and abatement costs. However, reductions of nitrogen (N) emissions causing eutrophication effects have not been sufficient to prevent widespread critical load exceedances. CLRTAP has increasingly assessed links between N emissions/effects, climate change and biodiversity but more research is needed. To achieve enhanced capacity building and further emission reduction of N compounds challenges have to be overcome in science (e.g., regarding N effects on ecosystems and feedbacks with climate), policy (e.g., linking CLRTAP with other multilateral and global environmental agreements), and communication between science, policy and the public.

Keywords Atmospheric deposition • CLRTAP • Critical loads • Nitrogen • Science-policy links

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44.1 Introduction

The 1979 Convention on Long-range Transboundary Air Pollution (CLRTAP[1]) addresses major environmental problems caused by transboundary air pollution in the UNECE region (North America, Europe, and large parts of Northern and Central Asia). It has been implemented through eight Protocols[2], two of which deal with reactive nitrogen (N_r). The most recent and important one is the Gothenburg Protocol which aims at simultaneously reducing eutrophication, acidification and tropospheric ozone pollution.

The Convention has been one of the most successful regional environmental agreements ever established:

- Air pollution effects have been reduced considerably especially for acidification, health, vegetation and materials damage due to sulphur dioxide, heavy metal and persistent organic pollution as well as peak ozone concentrations. Reactive nitrogen pollution on the other hand, has improved but not as much as for the other pollutants. The area in Europe with excessive risks of acidification shrank from 139 million ha in 1990 to 23 million ha in 2010. The region with risks of nitrogen (N) deposition leading to eutrophication only fell from 242 million ha in 1990 to 200 million ha in 2010. In addition, the number of days with excessive ozone levels and the exposure of vegetation to excessive ozone levels was significantly decreased (EMEP 2012). The Protocol amendments agreed upon in May 2012 will further reduce these effects until 2020 and beyond (see CLRTAP website for updated information).
- The Convention has connected different political systems with similar environmental problems. This has been very important in the last decades of the past century, and still applies in linking North American, EU and Eastern European, Caucasian and Central Asian countries. In addition, the Convention has linked with countries and other regional environmental agreements outside the UNECE region, especially in Asia.
- The Convention has helped to develop international environmental law, especially on air pollution. For instance, the 1999 Gothenburg Protocol has influenced in many ways the development of the EU Directive on National Emission Ceilings[3].
- The Convention has provided an institutional framework[4] facilitating the use of science to develop and implement policy. It comprises large unique networks for scientific monitoring, modelling and research, with a strong interface to policy making. The database and methodologies (and the networks producing them) have ensured a direct transformation of scientific evidence into policy of not

[1] http://www.unece.org/env/lrtap/.

[2] http://www.unece.org/env/lrtap/status/lrtap_s.htm.

[3] http://ec.europa.eu/environment/air/pdf/nec_eu_27.pdf.

[4] http://staging.unece.org/fileadmin/DAM/env/documents/2013/air/CLRTAP_Structure_July_2013.pdf

only CLRTAP but other processes as well. The scientific results have been be used to define limit values, best available techniques and economic instruments in the annexes to protocols and guideline documents, and to develop and implement the effects-based approach (see next section, 44.2) to set targets. This institutional framework has set an example for other regions that are developing air pollution controls.

44.2 Critical Loads in Air Pollution Policies: The Effects-Based Approach

The effects-based approach developed in the Convention minimizes environmental and health risk indicators, such as critical loads exceedances (= deposition minus critical load), and abatement costs to design regional emission reduction requirements. In other words, emission reduction requirements are derived from environmental and health targets using integrated assessment models (see below). Such models derive national emission ceilings for individual pollutants, which also include nitrogen oxides (NO_x) and (in Europe) ammonia.

National critical load data for European and in Canada are generated by a network of National Focal Centres (NFCs) under the International Cooperative Programme on Modelling and Mapping (ICP M&M, www.icpmapping.org). NFCs cooperate with the Coordination Centre for Effects (CCE)[5] to develop modelling methodologies and European databases for critical loads. The CCE reports on this work to the Task Force of the ICP M&M which in turn transmits it to the responsible CLRTAP bodies. The methodology is constantly updated in the CLRTAP's Modelling and Mapping Manual[6]. The organization of effects-based air pollution work under the Convention is described, e.g., by Spranger et al. (2008) and Johansson et al. (2004).

Exceedances of the critical load of acidity and of nutrient nitrogen, among other effects, have been used in European pollution abatement policy for defining emission reduction requirements in CLRTAP as well as in the European Union (National Emission Ceilings Directive 2001[7]; Thematic Strategy Air 2005[8]).

Integrated assessment models (e.g. the RAINS/GAINS model[9] in Europe and RAISON (Lam et al. 1998) in Canada) use these data and methods in analyses of future scenarios. They take into account regionally variable critical loads, emission sources, atmospheric transport and depositions, abatement technologies with related costs, and activity projections (agriculture, traffic, energy use etc.). Such models link pollution sources and effects, allocate costs and benefits and advise policy on prioritizing emission abatement.

[5] http://www.rivm.nl/en/Topics/Topics/C/Coordination_Centre_for_Effects_CCE.

[6] http://www.rivm.nl/en/Topics/Topics/I/ICP_M_M/Mapping_Manual.

[7] http://ec.europa.eu/environment/air/pdf/nec_eu_27.pdf.

[8] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2005:0446:FIN:EN:PDF.

[9] http://www.iiasa.ac.at/rains/ciam.html.

In Canada, critical loads assessment of sulphur (S) deposition effects have been used by Environment Canada (Dupont et al. 2005; Jeffries and Ouimet 2004; Ouimet et al. 2006) and provincial jurisdictions to set S emission levels and help evaluate emission control policies such as the Canada-Wide Acid Rain Strategy for Post 2000 (CCME 1998[10]). Critical load (CL) approaches are currently not being used to assess N emission policies however.

In the United States, the critical loads approach is not an officially accepted approach to ecosystem protection and is not specifically required in the Clean Air Act. Nevertheless, recent activities within federal and state agencies, as well as the research community, indicate that critical loads may be emerging as a useful ecosystem protection, communication and program assessment tool (Porter et al 2005; Burns et al 2008).[11]

Within the U.S. National Atmospheric Deposition Program, an ad hoc critical loads committee[12] was formed which coordinates efforts to explore the potential uses of critical loads in policy development and program implementation.

The ninth biennial progress report completed under the 1991 United States–Canada Air Quality Agreement (Canada-United States Air Quality Agreement. 2008), prepared by the bilateral U.S.-Canada Air Quality Committee[13], included for the first time estimates of critical loads in acid-sensitive lakes in the northeastern United States.

44.3 Policy Outcomes

The application of the effects-based approach in the Gothenburg Protocol has resulted in emission ceilings for 2010 for four pollutants: S, NO_x, volatile organic compounds excluding methane (VOC), and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options as described above. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. Europe's emissions were reduced considerably between 1990 and 2010, even more than envisaged when the Gothenburg Protocol was agreed in 1999: sulphur emissions were cut by almost 80 % NO_x by ca. 45 %, VOC by almost half, and ammonia by ca. 35 % (see http://www.emep.int for up to date emission data).

[10] http://www.ccme.ca/assets/pdf/1998_acid_rain_strategy_e.pdf.

[11] In 2004, the National Research Council recommended that the U.S. Environmental Protection Agency (EPA) consider using critical loads for ecosystem protection. In 2005, EPA included a provision in its Nitrogen Dioxide Increment Rule that individual states may propose the use of critical loads information as part of their air quality management approach, in order to satisfy requirements under Clean Air Act provisions regarding "prevention of significant deterioration." Federal land management agencies, such as the National Park Service and the U.S. Forest Service, developed specific recommendations for using the critical loads approach as a tool to assist in managing federal lands.

[12] http://nadp.sws.uiuc.edu/clad/.

[13] http://nepis.epa.gov/EPA/html/DLwait.htm?url=/Exe/ZyPDF.cgi?Dockey=P1002RGK.PDF.

However, N deposition has remained much higher than critical loads in large parts of Europe, and it has barely changed over the last decade, causing widespread eutrophication of terrestrial ecosystems and causing (or slowing down recovery from) acidification. The Gothenburg Protocol has therefore not been sufficient to significantly reduce risks from N deposition, including nutrient imbalances and biodiversity degradation, and more N emission reductions are necessary (see e.g. analyses of the CLRTAP Working Group on Effects from 2007[14], 2009[15]). CLRTAP has reacted to this and other air pollution related threats by amending the Gothenburg Protocol. Parties agreed in May 2012 to further reduce emissions of the above pollutants and of (especially fine) particulate matter until 2020 and thereafter (see http://www.unece.org/index.php?id=29858 and http://www.unece.org/env/lrtap/welcome.html for details). For instance, the EU as a whole is going to reduce its emissions of SO_2, NO_x, NH_3, VOC and $PM_{2.5}$ by 59, 42, 6, 28 and 22 % respectively, from 2005 levels.

The EU established in 2005 the Thematic Strategy on Air Pollution (Commission of the European Communities: TSAP 2005; Commission of the European Communities, 2005). Its objectives are inter alia to reduce by 2020 the ecosystem area with excess of critical loads of eutrophication by 43 % from the 2000 level. According to more recent analyses, this would need a reduction of NO_x emissions by about 58 % and NH_3 emissions by about 22 % from the 2000 level. This means that in 2020 most N_r emissions within the EU will be NH_3 emissions from agriculture.

Nitrogen deposition in North America has also not declined over the previous decades; in some regions it has increased, in others it has remained unchanged (Galloway et al. 2003; National Atmospheric Deposition Program; http://nadp.sws.uiuc.edu/). The Clean Air Act (CAA) and CAA Amendments led to substantial decreases in SO_2 but not NO_x emissions; NH_3 emissions are not covered by the CAA (CAA 2011). In Canada, the pattern of NO_x emissions has changed over the past decade, with significant reductions occurring in the eastern part of the country, and increases in Alberta due to increasing oil sands extraction activity.

44.4 Science and Policy Developments in CLRTAP and Beyond Relating to the Link Between Nitrogen, Biodiversity and Climate Change

The Millenium Ecosystem Assessment (2005) has established the strong link between air pollution (especially by N) and biodiversity on the global level. Two chapters of the European Nitrogen Assessment have built on this by describing the risk and the policy response (Dise et al. 2011) and establishing scenarios of possible future developments (Winiwarter et al. 2011).

[14] http://www.unece.org/env/documents/2007/eb/WGE/ece.eb.air.wg.1.2007.14.e.pdf.

[15] http://www.unece.org/env/documents/2009/EB/wge/ece.eb.air.wg.1.2009.15.e.pdf.

The exceedance of critical loads of N is used as an indicator of risk to biodiversity by the European Environment Agency (EEA 2007). Cooperation at national and European levels has explored improved relationships between critical load exceedances, N impacts and objectives set according to the EU Habitats Flora Fauna Habitat (FFH) directive and comparable national legislation. This applies to all areas, including the Natura 2000 areas in EU Member States.

It is necessary to consider local biodiversity action plans in larger scale modelling. Strategies exist to integrate them into the European scale, e.g. via the FFH Directive and the Natura 2000 network. However, the role of air pollution effects is often not explicitly taken into account even though N inputs have a large effect on biodiversity: there is room for improvement on local, national and European levels (Hicks et al. 2011; Spranger et al. 2009).

The effects of air pollution on materials, health and ecosystems are also affected by climatic conditions. Monitoring and modelling of effects has taken them into account, however, formal collaboration is in an initial phase only between air the pollution and climate change communities (including Intergovernmental Panel on Climate Change and UN Framework Convention on Climate Change).

CLRTAP has, among many several other science/policy developments in recent years, increased its work to link and assess nitrogen effects to climate change and biodiversity. Critical loads and dynamic models have been further developed and are increasingly used as risk indicators for biodiversity loss in ecosystems (see Hettelingh et al. 2008, 2014; Chap. 30, this volume).

In response to the increasing effects of anthropogenic changes of the nitrogen cycle on the environment (including air pollution and biodiversity), CLRTAP established the Task Force on Reactive Nitrogen (www.clrtap-tfrn.org) in 2007 under the Working Group on Strategies and Policies. Its tasks include the collaboration with other CLRTAP bodies to produce, inter alia:

- a better understanding of the integrated, multi-pollutant nature of reactive nitrogen (air pollution in context of the N cycle),
- comprehensive assessment of emissions, budgets, fluxes and effects of N;
- a review of agricultural ammonia emissions (control techniques, good agricultural practice, etc.).

The links between air pollution with N compounds and biodiversity are being dealt with jointly by the Working Group on Effects and the Task Force on Reactive Nitrogen.

A similar development is expected concerning the relation of air pollution and climate change. Synergies between air pollution and climate change policies are increasingly being analyzed and applied to define emission reduction targets. Until recently, the focus has been to assess the co-benefits in emission reductions. According to first analyses, the implementation of climate and energy policies in combination with most technically advanced emission abatement techniques would result in the reduction of SO_2 and particulate matter emissions which are larger than needed to reach sustainable conditions with respect to health and ecosystems (e.g. critical loads) in 2050. In contrast, the resulting NO_x and ammonia emissions would not be sufficient to reach such conditions. This means that air pollution abatement policies should increasingly focus on NO_x and especially on ammonia.

While emission co-control is now in the policy focus, co-benefits, antagonisms and feedbacks concerning air pollution and climate change effects have until recently not been used for policy development. Links have been established and their development and use in policy have been recommended (Pleijel 2010).

44.5 Challenges and Outlook

The challenges and needs in capacity building on the global level relate to three fields: science, policy and communication.

44.5.1 Science

As described in Bobbink et al. (2010), de Vries et al. (2010), Dise et al. (2011) and documents and presentations during this conference, there exist huge knowledge gaps on N effects on ecosystems including biodiversity loss, on feedbacks with climate, and on how to model these effects. There is a clear need to improve on this especially for ecosystems outside northwestern Europe and parts of northern America.

44.5.2 Policy

The effects-based approach is one of the most important strengths of CLRTAP. The effects-oriented activities are, and will continue to be in the near future, important, particularly in evaluating the adequacy and effectiveness of emission reductions in the Gothenburg Protocol and its possible amendment, as well as to explore links between air pollution, climate change and biodiversity. CLRTAP needs to retain a strong effects-science base, coordinated by the Working Group on Effects, and to retain the focus on N effects.

Bull et al. (2011) analyze options for coordinating European nitrogen policies between international treaties. Any global and/or multi-regional environmental agreement on nitrogen, be it via United Nations Environment Programme (UNEP), the International Nitrogen Initiative (INI) or other routes, will most likely have a strong biodiversity effects component. To help this development, CLRTAP needs to further develop its outreach on nitrogen/biodiversity links to other regions and possibly on the global scale. This includes links to the Convention on Biological Diversity at the convention level and possibly in addition between the newly established Intergovernmental Platform on Biodiversity and Ecosystem Services (IPBES) and the CLRTAP Working Group on Effects.

44.5.3 Communication Between Science, Policy and the Public

Science has strongly influenced the formulation of various policies relevant to biodiversity in Europe and elsewhere. As described above, an example is the effects-based approach to air pollution abatement. The use of critical loads in that framework has been successful in summarizing scientific risk information for policymakers and the public, and has provided a quantitative estimate of the need for political action.

To continue this path for more complex issues such as feedbacks between nitrogen inputs, biodiversity and climate change, there is a strong need for good communication: shared understanding of problems and methods to solve these problems, interchange of individuals between the different arenas and, as a consequence, credibility and trust between science, policy, and the public (Grennfelt et al. 2005).

Indicators are an important communication instrument. The further development of indicators linking nitrogen pollution and biodiversity loss is dealt with by J.-P. Hettelingh et al. (2014; Chap. 30, this volume).

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Chapter 45
The Convention on Biological Diversity: How does Nitrogen fit into the Plans?

James M. Williams

Abstract The Convention on Biological Diversity (CBD) recognises five direct drivers of biodiversity loss: habitat change, climate change, invasive species, over-exploitation, and pollution, including by excessive nitrogen (N) and phosphorus (P) nutrients. Nitrogen was part of the flexible framework of indicators, under the 'threats' focal area, established to measure progress towards the CBDs target of achieving a 'significant reduction in the current rate of biodiversity loss' at global, regional and national level by 2010. Nitrogen indicators were established at various scales, including N deposition at global scale and critical loads at European scale. The target was not reached for almost all the indicators. Measuring, and addressing changes in, ecosystem services is likely to be a key aspect of any post-2010 target, and is an area in which this workshop could help the CBD: by providing ideas on how N inputs can be effectively measured at a variety of scales, and critically, what the impact of different levels of N (in its various forms) is on biodiversity, at a variety of scales.

Keywords Biodiversity • Biological diversity • Convention • Global • Nitrogen deposition • Policy • Threats

45.1 Background

The Convention on Biological Diversity (CBD) was negotiated at the Earth Summit in Rio in 1992. It entered into force on 29 December 1993, and there are now 193 Parties (168 signatures). The Convention has three main objectives:

1. To conserve biological diversity;
2. The use of biological diversity in a sustainable fashion;
3. To share the benefits of biological diversity fairly and equitably.

To focus effort, the Convention works to achieve its vision and mission through a strategic plan containing sub-targets, delivered through programmes of work on a thematic basis, all organised through a multi-year programme of work. A key part

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of the Convention's work was the 2010 target on biodiversity: "to achieve by 2010 a significant reduction of the current rate of biodiversity loss at the global, regional and national level as a contribution to poverty alleviation and to the benefit of all life on Earth". It is worth emphasising that this was adopted not just by parties to the CBD, but by the World Summit on Sustainable Development, and as part of the Millennium Development Goals—it was given a big political emphasis.

Most countries are implementing the Convention through national biodiversity strategies and action plans (NBSAP). Most Parties have an NBSAP, and with the newer and revised NBSAPs we see a more strategic focus on policy and institutional change and greater emphasis on mainstreaming; integration into local level planning. We now have a wealth of experience and good practice to build on and much to learn through exchange of this experience and expertise.

The information discussed here summarises what has been achieved towards the 2010 target and is based on the second edition of Global Biodiversity Outlook (CBD 2006) and the Millennium Ecosystem Assessment (2005). Information updated through country reports and global analyses has contributed to the third edition of Global Biodiversity Outlook (CBD 2010).

45.2 Nitrogen and Biodiversity Indicators

To measure progress towards the 2010 target, the CBD created a flexible framework of indicators. Nitrogen (N) was part of that framework, under the 'Threats' focal area. Indicators have been created at a variety of scales—at Global, European, National and country level, enabling policy makers to use evidence to explore whether the pressures are continuing or declining. It is worth noting that the different indicators are actually measuring slightly different things at different scales—for example NO_2 at the Scottish level, and critical loads in Europe. It is important to understand what each of them is saying at the scale at which it is being used, but it is not necessary that they are the same—the key point is that they show whether the pressure is reducing or increasing.

Almost all the indicators in the 2nd edition of Global Biodiversity Outlook (CBD 2006) show trends reflecting a worsening situation. The picture in the 3rd edition of Global Biodiversity Outlook (GBO-3) is broadly the same (CBD 2010). One outcome of the Millennium Ecosystem Assessment (MA) was to identify five principal factors which lead directly to change in biodiversity, and therefore to the services provided by ecosystems. These direct drivers, as they are known, are: habitat change, climate change, invasive species, over-exploitation (for example hunting or fishing beyond replacement rates), and pollution, including by excessive N and phosphorus (P) nutrients.

The impact of each of these drivers is either constant or increasing in every type of ecosystem on the planet, with the exception of temperate forests where habitats are being created. The result is that the 2010 target was not achieved. If there is to be any prospect of slowing biodiversity loss, policies must squarely address these drivers and reduce their impacts.

One of the areas which has started to get more attention over the past few years is ecosystem services. Ecosystem services are defined as services provided by the natural environment that benefit people, for example by providing food, clean air and clean water (see De Vries et al. 2014; Erisman et al. 2014; Chaps. 41 and 51: this volume). While there is no single, agreed method of categorizing all ecosystem services, the MA framework is widely accepted and is seen as a useful starting point. The MA reviewed the state of 24 services and found that 15—three quarters of them—are in decline. Measuring, and addressing changes in, ecosystem services is likely to be a key aspect of any post-2010 target, and is an area in which this workshop could help the CBD: by providing ideas on how N inputs can be effectively measured at a variety of scales, and critically, what the impact of different levels of N (in its various forms) is on biodiversity, at a variety of scales.

45.3 Outlook

The 10th CBD Conference of the Parties in Nagoya Japan, October 2010, can be considered as a milestone for biodiversity in a milestone year. Key activities included:

- Countries, through their fourth National Reports, assessed the state of biodiversity and progress towards the 2010 target. The results were synthesised in the 3rd edition of Global Biodiversity Outlook—GBO-3.
- A new framework of goals and targets was agreed—the Strategic Plan for Biodiversity, containing 20 Aichi Targets (Aichi Targets 2010), to measure progress towards 2020 targets within a 2050 vision. Within Goal B, Target 8 is specifically focused on pollution, including those from excess nutrients.
- The Nagoya Protocol on Access and Benefit-sharing (Nagoya Protocol 2010) was adopted—an international agreement which aims at sharing the benefits arising from the utilisation of genetic resources in a fair and equitable way.

2010 was the International Year of Biodiversity. Reflecting the importance of achieving the Aichi Targets, 2011–2020 has been designated the United Nations Decade on Biodiversity. It is an opportunity for the whole world to recognise the importance of biodiversity for all life on Earth, to reflect on our achievements to safeguard biodiversity, and to focus on the urgency of our challenge for the future.

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Chapter 46
Agriculture and the Nitrogen Problem in India: Environmental Implications

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Abstract Much of the excess nitrogen (N) inputs in the Indian region are from agriculture. We quantified soil surface N loads for agro-ecological zones (AEZs) in India using a mass balance approach. We estimate nearly 35.0 Tg of N inputs from different sources, with output N from harvested crops of about 21.0 Tg. The soil surface N balance, estimated as inputs minus outputs, is found to be about 14.4 Tg surpluses from the agricultural land of India. Livestock manure constituted a major percentage of total inputs (44 %), followed by inorganic fertilizer (32.4 %), atmospheric deposition (11.86 %) and N fixation (11.58 %). Nitrogen balance varied from deficit to surplus for different Indian states and AEZs. The lowest N loads were found for AEZs in the Eastern Himalaya, with 19 kg ha^{-1} surplus, and highest surplus in AEZs with >111 kg ha^{-1} in areas such as the Deccan plateau and southern India. Environmental implications of these excess N loads in India are discussed, in addition to some best management practices to reduce the loads from agricultural sources.

Keywords Agriculture • Nitrogen budgets • Agro-ecological zones • India

46.1 Introduction

Since pre-industrial times, food production has been the major source of reactive nitrogen (Galloway and Cowling 2002). It is estimated that 20 % of the global total anthropogenic nitrogen (N) emissions come from Asia (Oliver et al. 1998). A nearly 4.7-fold increase in reactive nitrogen (N_r) in the Asian region has been reported from 1961–2000, primarily due to increasing food and energy demands (Zheng et al. 2001). Agriculture is estimated to be the largest source of N_r, accounting for about 50 % of the global nitrogen budget. Further, on a global basis, the rate of N_r

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has been estimated to be increased from nearly 15 Tg N year^{-1} in 1890 to nearly 140 Tg N year^{-1} in 1990, while natural terrestrial biological N fixation decreased from nearly 100 Tg N year^{-1} to nearly 89 Tg N year^{-1} (Galloway and Cowling 2002). The extent to which agricultural inputs have contributed to these global N changes is tied to the N cycle.

India is predominantly an agricultural country with 70 % of its people living in villages. Agriculture and animal husbandry dominate in several regions of India. Though India is self-sufficient in agricultural production, with a population of about 1.13 billion (World Bank 2009) accounting for about 16 % of world population and only 2.42 % of the total world area, sustaining agricultural production without degrading land resources and the environment is a challenging task. In India, the net sown area has increased from about 118.7 Mha in 1950–51 to current levels of about 162 Mha. Because the cropped area has remained more or less static at around 140 Mha during the last 25 years, the increase in production has been achieved by increasing productivity. The increasing productivity is clearly suggested by the trends in food production, primarily cereals (rice, wheat and maize) which form more than 70 % of the dietary energy of Indians, along with increased nitrogenous fertilizer consumption, which has increased massively by ~47 fold (Prasad et al. 2003). With the introduction of such intensive agriculture and adoption of modern farming techniques involving the application of agricultural chemicals, the problem of N losses has been increasing. Further, India's massive population base, potential for future growth and relatively small scope for further expansion of agricultural land make land and water resources highly vulnerable to pollutant loads. Quantifying the N sources within the agriculture sector and agro-ecological zones can help policy makers to focus on mitigation options for effective N management. Nutrient balance calculations provide a useful framework for understanding the rate of nutrient depletion or accumulation. In this study, we discuss the agricultural N cycle using a mass-balance approach and explore the relationships between agricultural production and N loads in the Indian region. Using the mass-balance calculations we show the reducing the N loads in some of the agro-ecological regions can significantly reduce N loads to the environment.

46.2 Methods and Approach

We used a mass balance approach for estimating the soil surface N budgets. The soil surface N balance is calculated as the difference between the total quantity of N inputs entering the soil and the quantity of N outputs leaving the soil. Individual crop cover datasets were generated by integrating state-level planted area data, production and yield data for various crops, into a Geographic Information Systems (GIS) database. The aggregate input of N sources for the entire country, such as inorganic fertilizers, was calculated by summing the area-weighted portion of fertilizer sold for each state and multiplying by the N content of the fertilizer. The sum in each unit was divided by the total area of the agricultural production to obtain unit-area values for fertilizer applied per agricultural area for each state.

Livestock manure N production from different states was calculated as the number of live animals distinguished in terms of general species (sheep, goats, cattle, buffaloes, horses, mules, donkeys, camels, methuns, pigs, poultry, and yaks) multiplied by respective N excretion coefficients. Because country-specific coefficients were absent in our study, we used the N excretion factors suggested by the IPCC for the Asian region. The factors range from 0.6 kg animal^{-1} year^{-1} (for poultry) to 40 kg animal^{-1} year^{-1} (non-dairy cattle).

Nitrogen input from biological N fixation (field beans, soybeans, clover, alfalfa, pasture) has been obtained from dry biomass production multiplied by the fraction of N in N fixing crops. Crop production data have been converted to crop biomass data prior to calculation. Nitrogen inputs from atmospheric deposition were calculated from volatilization and subsequent atmospheric deposition of ammonia and nitrogen dioxide resulting from fertilizer inputs and livestock excretion products (Burkart and James 1999).

Nitrogen uptake per unit of harvested yield from different crops (e.g., Rice, Wheat, Jowar, Bajra, Maize, Pulses, Gram, Tur, Lentils, nine different oil crops, soybeans, sunflower and sugarcane) were derived from crop N concentrations and moisture contents. Finally, the soil surface N balance from agriculture has been calculated as N inputs minus N outputs. If the balance is positive, there is a N surplus and if the balance is negative, there is a N deficit (Parris and Rielle 1999).

Mass-balance calculations were performed for agro-ecological regions throughout India. During the late 1980s, the concept of geographic mapping units referred to as Agro-Ecological Zones (AEZs) was developed by the Food and Agriculture Organization of the United Nations (FAO). Distinct AEZs are based on climate conditions, land forms, and homogenous crop growing environments. Characterization of AEZs permits a quantitative assessment of the biophysical resources upon which agriculture and forestry research depends. The classification system distinguishes between tropical regions, subtropical regions with summer or winter rainfall, and temperate regions. In India, the National Bureau of Soil Survey and Land Use Planning (NBSS & LUP) (Sehgal et al. 1992) developed distinct AEZs for the Indian region. India was categorized into 21 AEZs on a 1:4 million scale, based on superimposition of three basic maps (soil-physiography, bioclimate, and length of growing period) for regional level planning and resource allocation and to establish 60 agro-ecological sub regions. State and district level agro-ecological maps were generated by narrowing down the limit of the attributes used for distinguishing AEZs at the sub region level and adding the local soil condition as additional parameters. In this study, we used the above agro-ecological region boundaries for calculation of soil surface N budgets.

46.3 Results

Our results for India as a whole, show nearly 35 Tg of N as inputs from different sources, with output N from harvested crops of about 21.2 Tg. Soil surface N balance, estimated as inputs minus outputs, was found to be about 14.4 Tg. Livestock manure constituted the major percent of total inputs (44.06%), followed by

Table 46.1 Soil surface nitrogen balance in the agro-ecological zones of India

AEZ No.	Agro-ecological zones of India	N kg ha^{-1}
1	Western Himalayas, cold arid ecoregion with shallow skeletal soils	25.6
2	Western Plain, hot arid ecoregion with desert and saline soils	32.0
3	Deccan Plateau, hot arid ecoregion with mixed red and black soils	48.3
4	Northern Plain and Central Highlands, hot semi-arid ecoregion with alluvium-derived soils	53.5
5	Central (Malva) Highlands and Kathiawar Peninsula, hot semi-arid ecoregion with shallow and medium (inclusion of deep) black soils	46.7
6	Decaan Plateau, hot semi-arid ecoregion with shallow and medium (inclusion of deep) black soils	82.5
7	Decaan Plateau and Eastern Ghats, hot semi-arid ecoregion with red and black soils	110.7
8	Eastern Ghats (TN Uplands) and Deccan Plateau, hot semi-arid ecoregion with red loamy soils	220.5
9	Northern Plain, hot sub-humid ecoregion with alluvium-derived soils	100.5
10	Central Highlands (Malwa and Bundelkhand), hot sub-humid ecoregion with medium and deep black soils	67.0
11	Deccan Plateau and Central Highlands (Bundelkhand), hot sub-humid ecoregion with red and black soils	99.6
12	Eastern Plateau (Chattisgarh region), hot sub-humid ecoregion with red and yellow soils	85.2
13	Eastern (Chotta Nagpur) Plateau and Eastern Ghats, hot sub-humid ecoregion with red loamy soils	116.1
14	Eastern Plain, hot sub-humid ecoregion with alluvium-derived soils	53.5
15	Western Himalayas, warm sub-humid (inclusion of humid) ecoregion with brown forest and podzolic soils	104.3
16	Assam and Bengal Plains, hot humid (inclusion of sub-humid) ecoregion with alluvium-derived soils	19.2
17	Eastern Himalayas, warm perhumid ecoregion with brown hill soils	19.0
18	North-eastern Hills (Purvachal), warm perhumid ecoregion with red and lateritic soils	131.2
19	Eastern Coastal Plain, hot sub-humid ecoregion with alluvium-derived soils	111.6
20	Western Ghats and Coastal Plains, hot humid-perhumid ecoregion with red lateritic and alluvium-derived soils	−40
21	Islands of Andaman-Nicobar and Lakshadweep, hot perhumid ecoregion with red loamy and sandy soils	−87

inorganic fertilizer (32.48 %), atmospheric deposition from agricultural sources (11.86 %) and N fixation (11.58 %). It should be noted that these N loads are specifically from agriculture sector. Including the N loads from others (fossil fuels, sewage, mobilization of N, etc.) may significantly add to the total N budget. Further, our study is also limited by the availability of data such as on N-excretion factors of animals and other coefficients used in calculations. Thus, the results may be viewed with caution as we have followed the generalized IPCC default coefficients, which are not country specific. Using this approach, the N balance from Indian agriculture was found to be negative in some of the states, due to aggregation of different states under a particular agro-ecological region. However, all the regions showed surplus N loads, with a range of about 19–110 kg ha^{-1} (Table 46.1). The lowest loads are found for AEZ 17 (Eastern Himalayas, warm perhumid ecoregion with brown hill soils) with a 19.2 kg ha^{-1} surplus, followed by AEZ 16 (Assam and Bengal Plains, hot humid ecoregion with alluvium-derived soils) with a 19 kg ha^{-1} surplus. The highest surplus N loads are found for AEZ 7 (Deccan Plateau and Eastern Ghats, hot semi-arid ecoregion red and black soils), AEZ 8 (Eastern Ghats (TN Uplands) and Deccan Plateau, hot semi-arid ecoregion with red loamy soils), AEZ 15 (Western Himalayas, Warm Sub-humid ecoregion with brown forest and podzolic soils), 18 (North-eastern Hills (Purvachal), warm perhumid ecoregion with red and lateritic soils) and AEZ 9 (Northern Plain, hot sub-humid ecoregion with alluvium-derived soils) (Table 46.1).

State level results for the N balance varied from deficit to surplus for different states. The highest surplus N loads (110.7 kg ha^{-1}) found in AEZ 7 covers nearly six states, extending throughout Madhya Pradesh, Orissa, Maharastra, Andhra Pradesh, Karnataka and Tamilnadu. All of these states are characterized by the presence of relatively high amounts of fertilizer use per ha as well as N livestock excretion, which contributed to relatively high surplus loads. For individual states, the highest N surplus was found for Uttar Pradesh (2.50 Tg) followed by Madhya Pradesh (1.83 Tg), Andhra Pradesh (1.79 Tg), Bihar (1.54 Tg), and Maharastra (1.45 Tg). However, N surplus in kg per hectare has been found to be high for Kerala (556 kg ha^{-1}), Tamil Nadu (279 kg ha^{-1}), Andhra Pradesh (170 kg ha^{-1}), and Bihar (167 kg ha^{-1}). A negative N balance was found for Orissa, Andaman Nicobar Islands and for some of the northeastern states.

46.4 Discussion and Conclusion

In several regions of India, the timing of N application to fields seems important. Several farmers apply the N during the beginning of the growing season, with only 30 % absorbed and the rest leached or lost in gaseous form. While the production of major crops (e.g. rice and wheat) reached a plateau, N fertilizer application has been constantly increasing. One way to decrease N loss through leaching is to adjust fertilizer inputs to site-specific conditions (Ersahin 2001). Strategies to reduce NO_3-N are primarily associated with conditions that allow NO_3-N accumulation in the soil profile. However, this can mean that NO_3-N accumulation is translocated to the lower depth of soil profile; it becomes unavailable for plant uptake and poses a threat to the quality of the underlying water systems (Agrawal 1999). Balanced use of nitrogen, phosphorus and potassium (N-P-K) is suggested as a practice to improve N use efficiency. Results from numerous on-farm treatments by the Indian Council of Agricultural Research (ICAR) indicate that the average wheat grain yield response to N could be increased by 67 % by including P, and 90 % by including both P and K with N fertilizer (Fixen and West 2002 and references therein). Further, to balance the current N use in India, P and K use in India were projected to increase to increase by 21 % and 71 % respectively. Development of more efficient sources of N for use on crops in order to prevent effectively the release of gaseous N_r and dissolved inorganic N from agricultural systems is considered a major mitigation option at the farm level (Singh and Singh 2008). Further, in order to develop environmentally sustainable farming systems, it is important to consider the effects of interactions between N application rate and water table depth on NO_3-N accumulation in the soil profile and NO_3-N losses to subsurface drainage (Narain et al. 1998).

Our present estimates of N mass balances for AEZs help to identify 'hotspot' areas of excess N loads. For example, AEZ 7 had the highest surplus N loads (110.7 kg ha^{-1}) where mitigation actions can be focused. Further, our results on nutrient balance estimates in AEZs can be aggregated with more mechanistic models to investigate the changes caused by both natural and human perturbations. Furthermore, such studies will improve our ability to predict N export to streams and will help identify areas that may be sensitive to conditions of N saturation, particularly the AEZ regions of 7, 15 and 9, the hotspots of surplus N loads. It should be understood that the N surplus estimates presented in the study indicate the maximum potential nutrient load for a given agro-ecological region; however, the actual nutrient load carried to the rivers and streams is likely to be substantially less than total estimated nutrient loads, due to processes of loss or storage that occur before nutrients reach the river. Losses may include ground water and riparian zone storage, in-stream sedimentation, and denitrification (Stow et al. 2001). In addition, N losses through leaching vary across a field due to differences in soil physical properties and N status of soil (Ersahin 2001). The uncertainties in the results are mainly attributed to the conversion factors which may be different for different agricultural systems, soils, climate conditions, crop types, and management practices. Thus, measurements relating to N leaching rates and fluxes to the atmosphere in different agro-ecosystems would greatly improve our understanding of N loading to surface and sub-surface waters. This may further help in adopting sustainable best management strategies for minimizing nutrient losses from agriculture.

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Chapter 47
Mitigating Increases in Nitrogen Deposition: The Challenge of Extending Symbiotic Nitrogen Fixation to Cereals and Other Non-legume Crops

Edward C. Cocking and Philip J. Stone

Abstract Extending the symbiotic nitrogen-fixing capability of legume crops with nitrogen-fixing bacteria to non-legume crops, particularly the cereals, would increase the extent of biological nitrogen (N) fixation and reduce the need for synthetic N fertilizers; excess N from N fertilizers causes many environmental impacts including a contribution to the greenhouse effect, acid rain and biodiversity loss. The first step required to achieve symbiotic N fixation in non-legume crops is to establish N-fixing bacteria intracellularly within cytoplasmic vesicles in their roots. By inoculating seedlings of maize, rice, wheat, oilseed rape and tomato grown aseptically in sucrose-containing culture media with very low numbers of *Gluconacetobacter diazotrophicus* we have shown that this N-fixing bacterium is able to intracellularly colonise the meristematic cells of their roots. Dark blue histochemically stained *G. diazotrophicus* were visible within the cytoplasm of meristematic cells of root tips and also within their cell walls. Electron microscopy confirmed that *G. diazotrophicus* was within membrane-bound vesicles in the cytoplasm. Field trials of cereals and other major non-legume crops will now be required. Within a timeframe of 5–10 years it should be possible to determine the extent to which symbiotic N fixation resulting from this bacterial intracellular colonisation will enable reductions in the use of synthetic nitrogen fertilizers.

Keywords Diazoplasts • Intracellular colonization by *Gluconacetobacter diazotrophcius* • Over-use of synthetic nitrogen fertilizers • Symbiotic nitrogen fixation in cereals

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47.1 Introduction

The major detrimental effects on the environment from the over-use of synthetic nitrogen (N) fertilizers in agriculture are the resulting pollution of the atmosphere by nitrous oxide, which has a global warming potential 293 times that of CO_2, and of water by nitrates. Such effects underline the need for more efficient and/or reduced use of fertilizers (Galloway and Cowling 2002), since their use also adds generally to the eutrophication problem and acidification of soils and water (Cassman et al. 2002). The need to mitigate increases in reactive nitrogen (N_r) in Europe is well documented (Boyer et al. 2004); and China for instance is also having problems of a similar or even worse nature (Guo et al. 2010).

In legume nodules, N-fixing rhizobia present intracellularly, supplied with energy derived from photosynthesis, fix N symbiotically. The nodulated legume plant is supplied with biologically fixed N, usually as ammonia (Mylona et al. 1995). This minimises or eliminates the need for inputs of synthetic nitrogen fertilizers. If a large proportion of synthetic N fertilizer could be substituted by biological N fixation considerable mitigation of increases in N deposition would be realised and impacts on the environment and human health would be minimised. The challenge of establishing a N-fixing symbiosis in cereals and other major non-legume crops is seen as basically the challenge of establishing an adequate level of plant cell intracellular colonization and N fixation without necessarily the need for nodulation. For the foreseeable future cereals will continue to supply much of our increased food demand, both for direct human consumption and as livestock feed. The annual world consumption of synthetic N fertilizers, manufactured with fossil fuels by the Haber-Bosch process has averaged 83 to 85 million MgN in recent years, with nearly 60 % of that amount applied to cereal crops (Dobermann 2007); application rates in North America are 112 kg N^{-1} ha^{-1} and 113 kg N^{-1} ha^{-1} in Europe and a large proportion of this N_r is lost to the environment (Dobermann and Cassman 2005). Any intracellular symbiotic N fixation in cereals from inoculations with N-fixing bacteria is likely to result in an ability to reduce inputs of synthetic N fertilizers and mitigate current increases in N deposition (Cocking 2009).

47.2 Method and Results

47.2.1 Inoculation of Cereals and Other Non-Legume Crops with Gluconacetobacter Diazotrophicus

We have investigated the interaction of *Gluconacetobacter diazotrophicus*, a non-nodulating N-fixing bacterium isolated from the intercellular juice of sugarcane, with seedlings of the cereals maize, rice and wheat and other non-legume crops. An aqueous suspension of *G. diazotrophicus* (5 colony forming units) was used for the inoculation of surface sterilised seeds germinated aseptically on Murashige

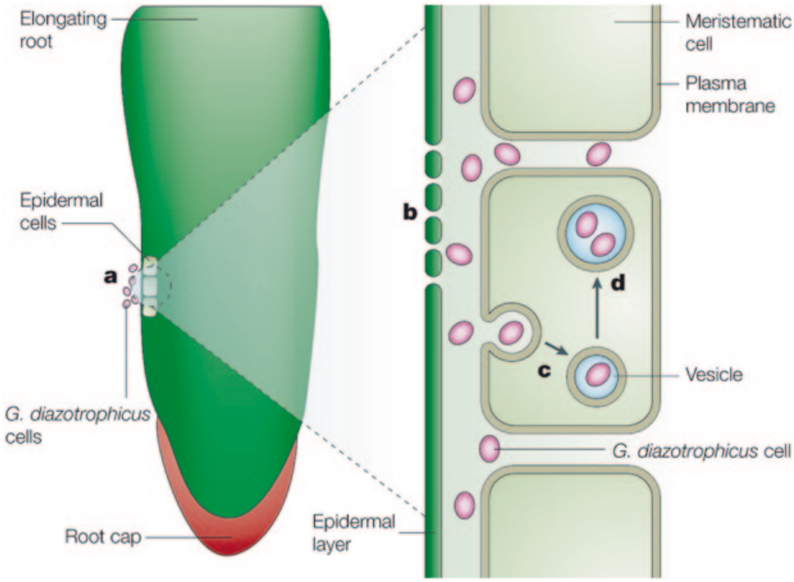

Fig. 47.1 Schematic representation of the interaction of *Gluconacetobacter diazotrophicus* with cereal roots: **a** Meristematic zone of elongating root, **b** *G. diazotrophicus* penetrates the epidermal cell wall by secretion of cellulase enzymes, **c** The plasma membrane pinched off via endocytosis forms a membrane surrounding vesicles containing *G. diazotrophicus*, **d** vesicles with *G. diazotrophicus* (diazoplasts) are surrounded by a membrane analogous to the symbiosome membrane of rhizobia. From Cocking et al. 2006 (copyright 2006 by the Society for In Vitro Biology, formerly the Tissue Culture Association). Reproduced with permission of the copyright owner

and Skoog medium containing 3 % (w/v) sucrose and vitamins but lacking growth regulators. Following inoculations with *G. diazotrophicus* containing a constitutive expressed *gus* A gene, the bacteria colonization of roots was visualised by light microscopy of the dark blue precipitate resulting from the degradation of the histochemical substrate X-Gluc by bacterial β-glucuronidase encoded by the *gus* A gene. For observations on sections of roots, samples exhibiting blue-staining GUS activity were fixed in glutaraldehyde, dehydrated with ethanol and embedded in LR White acrylic resin. Sections of 1 μm were cut and counterstained with safranin (0.01 % w/v) for light microscopy.

47.2.2 Demonstration of Intracellular Colonization by G. Diazotrophicus

Following inoculation of maize, wheat, rice, oilseed rape and tomato, *G. diazotrophicus* was detected intracellularly microscopically within the cytoplasm of the cells of the root tips of all these inoculated non-legume crops at 7 days post inoculation. A schematic representation of the interaction is shown in Fig. 47.1. In maize,

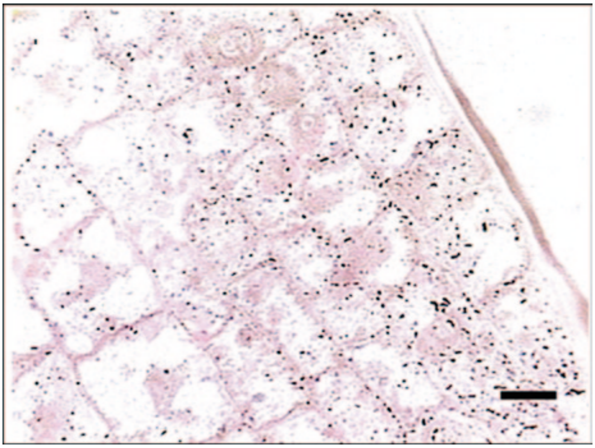

Fig. 47.2 Light micrograph of maize inoculated with *Gluconacetobacter diazotrophicus*: section of region of root tip showing blue-staining *Gus* A-G. diazotrophicus bacteria within cells and in cell walls (scale bar = 10 µm). Reproduced from Cocking et al. 2009, with permission of the copyright owner, the American Societies of Agronomy, Crop and Soil Sciences

for example, dark blue stained *G. diazotrophicus* was clearly visible within the cytoplasm of meristematic cells of the elongating region of the root, and also within their cell walls (Fig. 47.2) (Cocking et al. 2006). Electron microscopy of ultrathin sections of the same roots confirmed that the *G. diazotrophicus* bacteria appeared to be within membrane-bound vesicles in the cytoplasm. Similar results using inoculation with *nif*H promoter-GUS-labelled *G. diazotrophicus* showed blue-stained *G. diazotrophicus* within the cytoplasm of root cells indicating that intracellular conditions were suitable for the expression of nitrogenase, the bacterial enzyme complex that forms ammonia from gaseous nitrogen (N_2) and hydrogen.

47.3 Discussion

47.3.1 Establishing Symbiotic Nitrogen Fixation in Cereals to Mitigate Increases in Reactive Nitrogen Deposition

The fact that *G. diazotrophicus* is able to become established in symbiosome-like compartments in the meristematic root cells of cereals and other non-legume crops (Fig. 47.1) indicates that there is likely to be no need for nodulation to achieve symbiotic N fixation. If stably transmitted from cell to cell fixing nitrogen, these symbiosome-like membrane-bound compartments containing *G. diazotrophicus* could become diazoplasts, a new type of organelle analogous to chloroplasts and acquired in a like manner by accretion of an endosymbiotic prokaryote into the plant's genome (Postgate 1992).

We are investigating by N balances and ^{15}N methodology whether this non-nodular intracellular colonisation by *G. diazotrophicus* results in symbiotic N fixation of benefit to plant growth. Field trials will need to be performed under a range of environmental and soil conditions to establish reductions possible in synthetic N fertilizer application, while maintaining or increasing yields. There is an ever increasing urgency to do so not only to mitigate increases in N_r deposition and GHG fluxes but also for Global Food Security. The Royal Society report on 'Reaping the Benefits: Science and the Sustainable Intensification of Global Agriculture' (Royal Society of London 2009) has highlighted the need for research on high-return topics such as N fixation in cereals to provide the dramatic, but sustainable, improvements in crop production that are urgently required. Food Security and the challenge of feeding 9 billion people (Worldwatch Institute 2010) requires a multi-faceted and linked global strategy including how to optimise the use of nitrogen to not only produce enough food to meet the demand from population increase and the expansion of biofuel production, but also to minimise the impacts of synthetic N fertilizers on the environment and human health (Godfray et al. 2010).

47.3.2 Future Possibilities

Currently there is a resurgence of interest in sustainable practices to decrease the use of synthetic N fertilizers, including the further development of cereals and other crops with endosymbiotic nitrogen-fixing bacteria to supply their N needs (Canfield et al. 2010). Estimates of the time frame required to genetically engineer non-legume crops to fix their own N, that would require the co-ordinated and regulated expression of the 16 genes of the nitrogenase enzyme complex, have been given as long term and greater than 20 years (Godfray et al. 2010). Our demonstration of non-nodular intracellular colonisation of cereals and other non-legume crops by the naturally occurring N-fixing bacterium *Gluconacetobacter diazotrophicus* (Cocking et al. 2006) has increased the possibility of achieving symbiotic N fixation within a short term of 5 to 10 years.

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Part V
Conclusions and Outlook

Chapter 48
Progress in Nitrogen Deposition Monitoring and Modelling

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Abstract The chapter reviews progress in monitoring and modelling of atmospheric nitrogen (N) deposition at regional and global scales. The Working Group expressed confidence in the inorganic N wet deposition estimates in U.S., eastern Canada, Europe and parts of East Asia. But, long-term wet or dry N deposition information in large parts of Asia, South America, parts of Africa, Australia/Oceania, and oceans and coastal areas is lacking. Presently, robust estimates are only available for inorganic N as existing monitoring generally does not measure the

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complete suite of N species, impeding the closing of the atmospheric N budget. The most important species not routinely measured are nitrogen dioxide (NO_2), ammonia (NH_3), organic N and nitric acid (HNO_3). Uncertainty is much higher in dry deposition than in wet deposition estimates. Inferential modelling (combining air concentrations with exchange rates) and direct flux measurements are good tools to estimate dry deposition; however, they are not widely applied. There is a lack of appropriate parameterizations for different land uses and compounds for input into inferential models. There is also a lack of direct dry deposition flux measurements to test inferential models and atmospheric model estimates.

Keywords Inorganic • Modelling • Monitoring • Organic • Wet and dry deposition

48.1 Introduction

This chapter reports the findings of a Working Group to address progress in monitoring and modelling of atmospheric nitrogen (N) deposition at regional and global scales. A background paper by Dentener et al. (2014, Chap. 2, this volume), presentations, and posters set the stage for Working Group discussions. The group focused on current knowledge in modelling and measurements of N deposition, identification of important gaps, and recommendation for future needs, including capacity-building at a regional level, assessing scientific uncertainties, understanding co-benefits beyond N deposition, and identifying links with other processes. The spatial and temporal trends of N emission and deposition around the world are described for inorganic and organic N.

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48.2 Status of Monitoring

The World Meteorological Organization's Scientific Advisory Group in Precipitation Chemistry (WMO SAG PC) is currently working on an assessment to review and synthesize the state of the science on the chemical composition of precipitation and deposition of major ions for the period 2000–2008. The regional presentations and posters further emphasized the different regional challenges regarding the understanding of key processes and sources as well as the quality assurance of the measurements. As an example, 90 % of precipitation in India occurs from June to September, meaning that dry deposition is of much more importance in major parts of the year, in contrast to high precipitation regions in Northern Europe and parts of North America.

The observations show these general patterns:

- The highest levels of total nitrogen (N) deposition occur in China and India with much lower values in Africa. The Arctic and Antarctic represent the cleanest regions, depending on long-range transport for deposition inputs.
- Preliminary estimates of wet deposition show a range of 4–7 kg N ha^{-1} $year^{-1}$ in eastern North America, 5 to > 7 kg N ha^{-1} $year^{-1}$ in Europe, while sites in East Asia experience wet deposition between 2 and 60 kg N ha^{-1} $year^{-1}$. In Africa the estimated total deposition (dry plus wet) is typically between 7–10 kg N ha^{-1} $year^{-1}$.
- The emissions of NO_x and NH_3 have been increasing dramatically in Asia since the 1980s, and leading to increased N deposition which is of great concern both on a regional and global level. NO_x emissions have on the other hand decreased in North America and Europe.
- Organic N deposition is not routinely measured in all regions and the quality of measurements is often dubious; however the organic N contribution may be high (10–40 %) in some areas (i.e. in parts of China).

Knowledge of the data quality of the measurements is certainly of great importance when comparing measurements within and across networks. In many regions, the recommended measurements guidelines (i.e., by WMO) are not followed, decreasing confidence in these measurements. Examples of measurement issues include improper sampling method and storage, and delay in chemical analysis. This may cause degradation of samples, which is especially important for N species. For example, ammonium in stored rainwater samples may oxidize to nitrate. Furthermore, many sites are not always representative for a large region (e.g., urban sites) and these have limited value especially for model validation (see also Dentener et al. 2014, Chap. 2, this volume).

48.3 Gaps and Recommendations for Monitoring

Several necessary improvements were identified during the workshop. Priorities vary by region and the intended use of data, whether it is for compliance monitoring to identify and quantify sources for better abatement strategies, or to better understand key atmospheric processes and/or to validate regional and global models. The most important gaps which are important for all these aspects include:

- Long-term monitoring sites for routine air concentration and wet N deposition measurement are lacking in several regions in the world; most evident are South America, large parts of Africa, and Central Asia.
- Several networks do not measure all species and it is recommended to increase the number of N species routinely measured to close the atmospheric N budget, most notably to include organic N, NH_3, HNO_3 and NO_2 in atmospheric concentration measurements, as the basis for estimating dry deposition more comprehensively.
- Greater attention must be paid to monitoring of organic N, which may be of significant importance in several regions. Furthermore, there is a need to develop a standard harmonized method for measuring organic N to improve the quality of the data and for comparability between regions/sites.
- In light of the relative importance of dry deposition to total deposition loads, it is highly recommended that more long-term direct flux measurements are established in major parts of the world, and to use recommended methods for partitioning of gaseous and particulate N (i.e., by using denuder sampling methods).
- The diurnal variation may vary considerably for several N species, and daily or weekly measurements will not capture these variations. It is therefore recommended that a few supersites in each region measure with higher temporal resolutions (i.e., hourly).
- The data quality is not always satisfactory, and there is a need to continue to increase capacity building for measuring wet and dry deposition in the developing world. The Working Group encouraged participation in WMO quality assurance programmes and further interaction and cooperation between regional networks and programmes.
- The Working Group recommended assessment of uncertainty in the deposition estimates to be used either for model validation or critical load assessment.

48.4 Status of Modelling

As a general statement, it is necessary to emphasize that models are essential additions to measurements as they provide evidence of source attribution and chemistry and transport pathways, and can be used for emissions scenario analysis. Models can also help to fill gaps in areas where monitoring is limited (chemically and geographically). However, it is important to note that the models are no better than the inputs included. Thus, high quality input data (i.e., spatial and temporal emission data) and good validation tools (measurement networks) are a necessity for having confidence in the results. Therefore, the confidence in the model results is very much reflected in the measurement gaps described above. Generally, it can be said that:

- Regional and global model representation of wet deposition is reasonable in Europe and the US, but still very uncertain in other parts of the world.
- Preliminary global model estimates show the highest levels of total N deposition (wet + dry, oxidized N + reduced N) occur in China (15–45 kg N ha^{-1} $year^{-1}$) and India (15–35 kg N ha^{-1} $year^{-1}$), followed by Europe (15–25 kg N ha^{-1} $year^{-1}$) and eastern North America (10–20 kg N ha^{-1} $year^{-1}$), with the lowest values in Africa (5–15 kg N ha^{-1} $year^{-1}$), South America (5–15 kg N ha^{-1} $year^{-1}$) and Oceania (< 5 kg N ha^{-1} $year^{-1}$); typical ranges are given.
- The relative contribution of oxidized N to total is dominant in North America, Europe, northern Asia and northern Africa. Reduced N is dominant in South America, Asia and Africa.
- Dry deposition dominates in California, northern Africa, parts of South America, Africa and Oceania.
- Modelled dry deposition fluxes are very uncertain, and can seldom be compared to measurements, due to many factors including incompleteness of observations, uncertainties in chemistry schemes, and sparseness of measurements.
- The confidence level in model outputs increases with accurate emissions data and available data for validation.

48.5 Gaps and Recommendations for Modelling

In addition to problems with high quality measurement data to validate the model output and good emission data, more specific challenges in the model parameterizations exist and necessary improvements were identified by the Working Group:

- Chemical transport modellers should closely follow improvements in meteorological parameterization coming from the meteorological community. Currently, the global and regional chemical transport models have problems characterizing the hydrological cycle (precipitation amounts), especially in situations with complex orography. Further, the night time boundary layer representation must be improved and cloud/fog deposition approaches should be developed.
- Land use data included in models vary between groups, and the Working Group recommended harmonizing land-use between atmospheric and ecosystem models and further development of the sub-grid scale representations.
- The dry deposition processes described in the models need to be developed; bi-directional exchange of NH_3 should be incorporated, and unidirectional deposition of oxidized N and sulphur (S) species should be updated further.
- Since there is a serious lack of wet and dry deposition measurements, models need to be verified and improved utilizing alternative datasets as much as possible, such as ambient concentrations, dedicated field study data and model intercomparisons. Promising datasets are becoming available from satellites, but more work must be done to consistently combine the model and measurement frameworks.

- New emission datasets are becoming available, and should be checked using knowledge in countries and regions i.e. 'ground-truthing'. For instance, NO_x emission estimates from lightning and ships are important sources for some regions and must be addressed in the models.
- In order to obtain accurate spatial and temporal emission estimates, especially for NH_3, meteorology driven modules should be applied.
- Capacity for modelling wet and dry deposition should be increased in the developing world.
- Understanding of the sources of bias should be developed further. Areas that must be addressed include missing sources, such as lightning NO_x and NH_3 emissions from soil and organic N; uncertain processes like dry deposition/air surface exchange; and occult deposition (cloud droplet deposition), wintertime photochemistry/free troposphere chemistry.
- There are uncertainties in the split of coarse and fine nitrate aerosol that have implications for dry deposition processes. The Working Group recommended using intensive campaign data to further improve the parameterization of gas/particle phase of N, as well as the size distribution of aerosols species.

48.6 Conclusions

- The Working Group expressed confidence in the inorganic N wet deposition estimates in U.S., eastern Canada, Europe and parts of East Asia. We are lacking long-term wet or dry N deposition information in large parts of Asia, South America, parts of Africa, Australia/Oceania, and oceans and coastal areas.
- Presently, robust estimates are only available for inorganic N as existing monitoring generally does not measure the complete suite of N species, impeding the closing of the atmospheric N budget. The most important species not routinely measured are nitrogen dioxide (NO_2), ammonia (NH_3), organic N and nitric acid (HNO_3).
- Uncertainty is much higher in dry deposition than in wet deposition estimates.
- Inferential modelling (combining air concentrations with exchange rates) and direct flux measurements are good tools to estimate dry deposition; however, they are not widely applied. There is a lack of appropriate parameterizations for different land uses and compounds for input into inferential models. There is also a lack of direct dry deposition flux measurements to test inferential models and atmospheric model estimates.

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Chapter 49
The Effects of Atmospheric Nitrogen Deposition on Terrestrial and Freshwater Biodiversity

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Abstract This chapter reports the findings of a Working Group on how atmospheric nitrogen (N) deposition affects both terrestrial and freshwater biodiversity. Regional and global scale impacts on biodiversity are addressed, together with potential indicators. Key conclusions are that: the rates of loss in biodiversity are greatest at the

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lowest and initial stages of N deposition increase; changes in species compositions are related to the relative amounts of N, carbon (C) and phosphorus (P) in the plant soil system; enhanced N inputs have implications for C cycling; N deposition is known to be having adverse effects on European and North American vegetation composition; very little is known about tropical ecosystem responses, while tropical ecosystems are major biodiversity hotspots and are increasingly recipients of very high N deposition rates; N deposition alters forest fungi and mycorrhyzal relations with plants; the rapid response of forest fungi and arthropods makes them good indicators of change; predictive tools (models) that address ecosystem scale processes are necessary to address complex drivers and responses, including the integration of N deposition, climate change and land use effects; criteria can be identified for projecting sensitivity of terrestrial and aquatic ecosystems to N deposition. Future research and policy-relevant recommendations are identified.

Keywords Biodiversity • Flora • Fauna • Ecosystems • Nitrogen effects • Policy

49.1 Introduction

Reactive nitrogen (N_r), by virtue of being an essential nutrient for life, exerts a major influence on ecosystem structure and function. Human activities now convert more atmospheric nitrogen (N) to reactive plant-available forms than all natural sources combined and this has resulted in N becoming abundant in many ecosystems where it has been historically scarce. Inputs of N_r to the Earth's ecosystems have increased 20-fold since 1860 (Galloway et al. 2008). Rockström et al. (2009) conclude that the human interference with the global N cycle has already crossed a threshold leading to an unacceptable level of environmental change. Interestingly, these authors posit the threshold for the rate of biodiversity loss (defined as shifts in species composition, loss of individual species, and reduced richness) has also been crossed, and it is most likely that human impacts on N cycling and biodiversity loss are, in part, connected.

Nitrogen has the potential to be transported through the atmosphere and deposited many kilometers from its source area, and atmospheric N deposition has become a major force of ecological change in areas both adjacent to and remote from sources of emissions (Sutton et al. 2011). Large areas of industrial nations, and increasingly large areas of developing nations, now receive N_r from atmospheric deposition in amounts that are orders of magnitude greater than from naturally fixed N.

The following report summarizes the results of a Working Group on the consequences of atmospheric N deposition on biodiversity. We describe a continuum of effects of atmospheric N deposition on species and ecosystems from low, initial increases in N deposition on natural undisturbed areas to high levels of atmospheric N to historically altered and managed landscapes. We summarize known consequences of N for biodiversity, point out information gaps, and make suggestions for research and ways that policy could be altered to protect it. Our conclusions are as striking for what we do not know as for what we know and can document. Records of global N deposition and biodiversity response are sparse, and many regions of the world have little or no information on historic deposition, current deposition, biotic inventories, or susceptibility of native species to N. Much of what we understand about N deposition impacts on biodiversity has been extrapolated from N fertilization experiments, with limited studies along N deposition gradients.

49.2 Ecosystems, Communities and Organisms at Risk from Nitrogen Deposition

Terrestrial and aquatic ecosystems can respond rapidly to increased N from atmospheric deposition if they are N-poor initially, or have or are surrounded by soils of low to moderate buffering capacity. If nutrient poor, N contributes to eutrophication, and if soils have low buffering capacity, they are susceptible to acidification from strong acid anions, including nitrate. Oligotrophic freshwater ecosystems may be eutrophied or acidified by nitrate or ammonium deposition to surrounding soils with poor buffering capacity (Baron et al. 2000; Rabalais 2002). Evidence from monitoring, paleoecological reconstructions, and experiments show that oligotrophic arctic, alpine, temperate grasslands, heathlands, deserts, Mediterranean vegetation, and lakes are sensitive to slight increases in N availability (Gordon et al. 2001; Wolfe et al. 2001; Fenn et al. 2003; Bowman et al. 2006; Rao et al. 2010; Bobbink et al. 2010; Dias et al. 2014, Chap. 27, this volume). Experimental and observational results indicate the loss of species is nonlinear; the greatest decline in species richness occurs with slight increases of N above a natural, or experimental control deposition rate, and there is less change in diversity at higher depositions (Bobbink et al. 2010; Emmett 2007; Dise et al. 2011). The biodiversity of undisturbed landscapes with background levels of N deposition is, therefore, theoretically at high risk from N deposition.

Certain types of terrestrial organisms will be more susceptible to increased N deposition by virtue of their low stature, higher N accumulation rates, or specialized structures or hosts; these include bryophytes, oligotrophic lichens, insectivorous plants, those with N-fixing nodules and mycorrhizal fungi (Gordon et al. 2001; Bobbink et al. 2010). Specialist herbivorous insects on susceptible plants will be vulnerable (Throop and Lerdau 2004). While N impacts can be predicted for taxa or functional groups based on knowledge of the generalized response to N of some members of the groups, and these are summarized in Bobbink et al. (2010), there is a dearth of information on many particular species or guilds. While some research has addressed the biodiversity of free-living microorganisms in response to N deposition, this literature body has not been synthesized, yet these organisms constitute most of the biodiversity of all ecosystems.

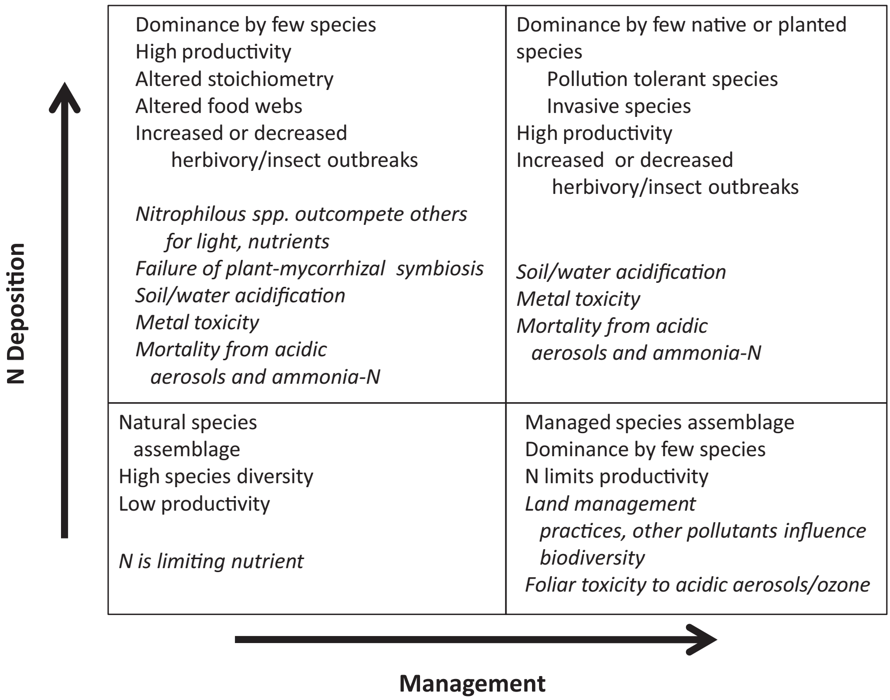

Fig. 49.1 Conceptual depiction of the causes (*italics*) and effects of N_r deposition to ecosystems ranging from minimally disturbed to highly managed

49.3 Mechanisms by Which Nitrogen Deposition Affects Biodiversity

Atmospheric N deposition alters species composition, richness, and productivity in terrestrial and freshwater environments via many pathways (Fig. 49.1). The physical mechanisms, such as eutrophication-induced competition for light and soil acidification, can be described as “bottom-up” processes. Species losses can also be hypothesized to occur from “top-down” ecological processes including increased herbivory and insect outbreaks. Different species are likely to be differentially sensitive to different processes, but there is some evidence that both processes are relevant (e.g. Hautier et al. 2009).

49.3.1 Physical Mechanisms

Eutrophication is a cascade of events that is triggered by relief from N limitation in individual plants. Rates of native biodiversity loss due to eutrophication will be greatest at the lowest and initial stages of N increases in the most oligotrophic environments (Baron et al. 2000; Bowman et al. 2006; Emmett 2007). Nitrogen deposition continues to reduce plant diversity at higher deposition amounts (Clark and Tilman 2008). Mechanisms include soil acidification which lowers pH, depletes soils of nutrient base cations, and allows toxic metals such as aluminum to become soluble (Bowman et al. 2008). Direct toxicity from gases, acidic aerosols and reduced N (ammonia and ammonium) in heavily polluted industrial or agricultural areas can lead to plant and animal mortality (Riddel et al. 2008; Kronzucker et al. 2003; Wallace et al. 2007; Bobbink et al. 2010). Soil fauna are negatively affected by N deposition through changes in soil acidity (Xu et al. 2009).

Eutrophication reduces the heterogeneous distribution of soil N and gives nitrophilous plants with high maximum growth rates a competitive advantage over others; faster growing and large species outcompete slower growing and smaller stature neighbours for light, water, and other nutrients (Egerton-Warburton and Allen 2000; Feest 2006; Gilliam 2006; Hautier et al. 2009; Bobbink et al. 2010; Dise et al. 2011). Grasses, sedges, and ruderal species, some of which may have invasive characteristics, are successful when N is abundant (Clark and Tilman 2008).

Elevated N availability also disrupts the symbiotic relation between soil mycorrhizae and their host plants, which has evolved to provide N or phosphorus (P) to plants when the availability is low in exchange for a supply of carbon (C) from plants. The loss of symbiosis leads to reduced fungal associations and increased parasitism (Johnson et al. 2003). Where N was previously limiting to growth, increased primary productivity occurs with N deposition or experimental N additions, but productivity occurs at the expense of biodiversity (Wolfe et al. 2001; Hautier et al. 2009). Reductions in richness have been observed in response to N addition experiments and across continental gradients from low to high atmospheric N deposition in North American, European, and tropical Asian ecosystems (Gordon et al. 2001; Stevens et al. 2010; Clark and Tilman 2008; Bobbink et al. 2010; Lu et al. 2010). The decline in richness is attributed to both eutrophication and acidification in temperate and tropical systems (Stevens et al. 2010; Lu et al. 2010).

There are many studies that document increases in biomass and shifts in dominant taxa when oligotrophic waters became enriched with N, but surprisingly few studies of the effect of N additions on algal species richness (Wolfe et al. 2001; Nydick et al. 2004; Bergström and Jansson 2006; Lewis and Wurtsbaugh 2008; Elser et al. 2009). An increase in eutrophic algae has the potential to alter food webs and community structure. The concentrations of N and P drive productivity, but the stoichiometric relation of N:P determines the abundance or dominance of individual taxa (Rabalais 2002). High N, low P phytoplankton make poor food for P-rich zooplankton that consume them. Alterations in zooplankton size and abundance in turn affect higher trophic levels, such as fish (Elser et al. 2009).

49.3.2 Ecological Mechanisms

The effects of changing plant and fungal mycorrhizal communities can propagate through the food web to influence animal behavior and abundance. Fungi can be important foods for small mammals, and their absence can affect both plant and mammal fitness (Myers et al. 2000). For herbivorous insects, the N concentration of host plants strongly controls processes such as growth, survivorship, population levels and outbreak frequency (Throop and Lerdau 2004). High N accumulation in plants can promote large insect outbreaks that have the potential to damage their host plants, thereby affecting ecosystem structure and function (Kerslake et al. 1998). Changes in plant community composition may affect herbivore community composition. Some insects are host-specific and may decline along with their host plant. Invasions of Mediterranean annual grasses under N deposition in California have reduced densities of the host plant of the rare Bay Checkerspot butterfly in California, and caused local extirpations (Weiss 1999). Nitrogen deposition favors plants with N-based defenses, such as members of the Solanaceae (Throop and Lerdau 2004). Few herbivores are able to consume solanaceous plants, thus a shift toward plants with N-based defenses will cause a shift in the herbivore community.

49.4 Mechanisms by Which Nitrogen Deposition Affects Ecosystem Function

Alteration of food webs is one important way that N deposition affects how ecosystems operate and the services they provide to society. Nitrogen deposition affects decomposition rates, substrate quality, and can enhance terrestrial C sequestration in some circumstances (Knorr et al. 2005; Hobbie 2008; Goodale et al. 2009). Increased N availability can also increase N_2O emissions from soils and freshwaters and lower CH_4 uptake (Goodale et al. 2009; Sutton et al. 2011). The occurrence of N saturation in terrestrial systems adversely affects downstream water quality. When excess N accumulates in freshwater and estuarine environments (from raised primary productivity) this promotes the development of noxious algal blooms, decreased water clarity, decreased levels of dissolved oxygen, and lower diversity (Rabalais 2002; Rockström et al. 2009). The role of N in water eutrophication depends on its relative availability with respect to other elements, such as C, P and silica (Billen and Garnier 2007). The anthropogenic increase of N and P in lakes, reservoirs, rivers and coastal waters is the main cause of eutrophication (Sutton et al. 2011).The ultimate consequence of reduced biodiversity is a more homogeneous biotic environment, and recent studies document homogenization and loss of structural diversity, in part due to N deposition (Bobrovsky 2010; Britton et al. 2009; Keith et al. 2009).

49.5 Interactions of Nitrogen Deposition with Other Human-Induced Stresses

Nitrogen deposition adds an additional stress to many, if not all, ecosystems already affected by climate change, land use, other air pollutants, invasive species, and habitat fragmentation. In arctic and montane systems warming is compounding the effects of even slight increases in atmospheric N deposition for both terrestrial and aquatic habitats (Wolfe et al. 2006; Baron et al. 2009). Nitrogen oxide and sulphur dioxide emissions are the major precursors of acid rain; their deposition has brought about dramatic changes to soil base cation availability and is, or may be, responsible for long-term trends in forest vegetation structure, songbird breeding success, and food web dynamics in lakes of temperate Europe and North America (Bowman et al. 2006; Long et al. 2009; Hames et al. 2002; Jeziorski et al. 2008).

In Californian Mediterranean-type and desert ecosystems, N deposition contributes to a positive feedback between loss of native plants, increases in annual grass invaders, and the frequency of fire that transforms native communities, perhaps permanently (Talluto and Suding 2008; Allen et al. 2009; Rao et al. 2010); in semi-arid European ecosystems, plant community responsiveness to N addition could be mediated by forbs (Ochoa-Hueso and Manrique 2010). A decline in tropical forest floor diversity appears to be due to N deposition-induced soil acidification alone (Lu et al. 2010), but in many areas of the tropics undergoing rapid land use change and industrialization there is the potential for interaction of N deposition with other stress factors.

49.6 Visualizing the Connectivity Between Nitrogen Deposition and Biodiversity

Bobbink et al. (2010) map the overlay of current and potential future N deposition with the Global 200 Ecoregions (Olson and Dinerstein 2002) that represent areas of distinct assemblages of natural communities and species, and are recognized as priority conservation areas for protecting a broad diversity of the Earth's ecosystems. Areas of concern include much of Southeast Asia, Mexico and Central America, southern Brazil and Central Africa. Such maps are particularly effective at illustrating regions where investigation is greatly needed to document current species composition and atmospheric deposition, and where monitoring for trends in cause and effect needs to be conducted. Additional visual portrayal is needed for at least two resolutions of scale. General global maps depicting biomes of known concern are important for illustrating the wide extent of N deposition effects (e.g., Fig. 49.2). Refinements of maps like this to portray finer-scale, or more targeted resolution of specific areas of concern or species of concern will be a useful tool for identifying specific areas for either research or conservation.

Phoenix et al. (2006) noted that analyses of the impacts of N deposition on biodiversity have occurred mainly on terrestrial landscapes of northern Europe and North America. What is lacking is a global-scale description, and analysis of the role of N deposition in 'biodiversity hotspots' (defined by high levels of plant species endemism, as well as threat; Myers et al. 2000). The average deposition rate across hotspots was 50% greater than the global terrestrial average in the mid-1990's and could more than double by 2050. A comparison of patterns of global N deposition with the recently defined set of freshwater ecoregions of the world (Abell et al. 2008) is also required.

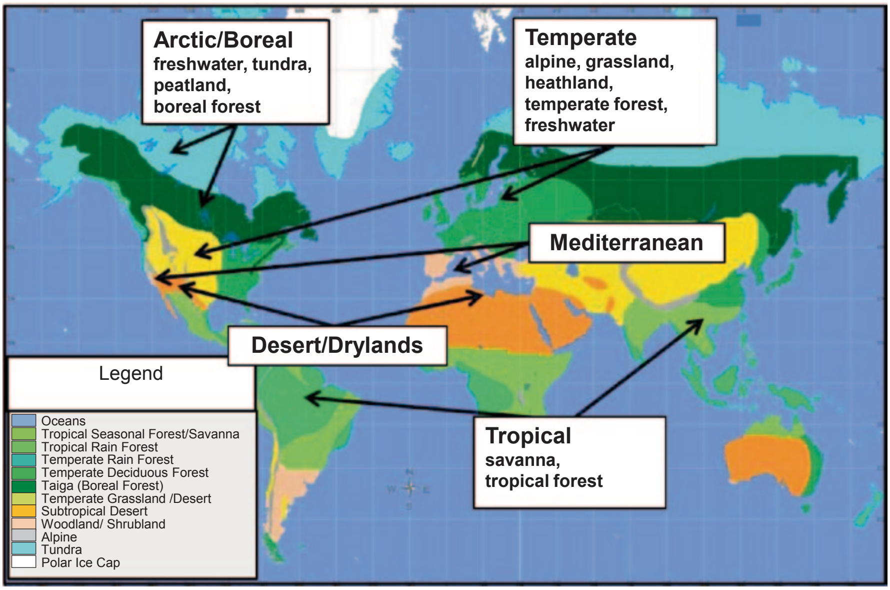

Fig. 49.2 Biomes of known N deposition effects on biodiversity

Further, it is essential to compare patterns of N deposition with patterns of species irreplaceability (high endemism) and vulnerability (high threat). This can be done relatively easily, at a regional or global scale, for some taxonomic groups. Regional species distribution and conservation status information is available for many types of animals (e.g. IUCN 2009, www.iucnredlist.org; NatureServe 2009, www.natureserve.org/explorer/). These data provide the capacity to compare distributions of range-restricted or threatened species overlain with current or projected future N deposition maps, providing powerful visual images of where to conduct research on biodiversity and N deposition, or where critical loads for N deposition have been exceeded. Similar distribution maps for fungi, plants, insects, and algae, which are not available, will be needed for this approach to add substantially to the effort already found in Bobbink et al. (2010). Much of this spatial information is available via public databases and portals such as the Integrated Biodiversity Assessment Tool (http://www.ibatforbusiness.org).

49.7 Conclusions and Recommendations

Specific conclusions were reached regarding the state of the knowledge of regional and global impacts on biodiversity, as well as potential indicators of these impacts:

- There is a spectrum of responses to N deposition, for example, rates of loss in biodiversity are greatest at the lowest and initial stages of N deposition increase;

- Changes in terrestrial species compositions are related to the relative amounts of N, C and P in the plant soil system;
- Enhanced N inputs have implications for both the freshwater C cycle and global C cycle;
- Nitrogen deposition is having a negative effect on European and North American vegetation composition;
- While very little is known about tropical ecosystem responses, tropical ecosystems are major biodiversity hotspots and are increasingly recipients of very high N deposition rates;
- Nitrogen deposition dramatically alters forest fungi and mycorrhyzal relations with plants; the rapid response of forest fungi and arthropods makes them good indicators of change which should receive more attention;
- Nitrogen deposition increases sensitivity to climate change and other stresses;
- Climate change, air pollution, and land use must be addressed as integrated problems;
- Predictive tools (models) that address ecosystem scale processes are necessary to address complex drivers and responses;
- Criteria can be identified for projecting sensitivity of terrestrial and aquatic ecosystems to N deposition:
  - Nutrient poor conditions (flora adapted to low nutrients and low to moderate buffering capacity);
  - Highly weathered soils (high Ca/Al ratio in soil);
  - Sensitive sites typically have one of more of these characteristics: a high proportion of N-fixers, potential for increases in ruderal species, insectivorous plants, high bryophyte cover (often sites with communities of high potential significance); seasonally dry climates.

Research recommendations that follow from the scientific evidence to date are to:

- Expand empirical information about, and theoretical underpinnings of, ecosystem and food web responses to increasing N deposition. Identify which changes are important and potentially irreversible. Investigate responses to the reduction of N deposition. Can recovery occur?
- Conduct assessments of the distribution, ecology, conservation status, threats, and risk of extinction for species of different taxonomic groups, especially freshwater species and many terrestrial invertebrates, in order to make meaningful comparisons and models of the relationship between species composition in ecosystems, N deposition, and resultant compositional change of the species diversity over time.
- Conduct an assessment of understudied regions of the world, such as the tropics and developing regions of Asia. Which ecosystems, communities, and organisms are vulnerable to atmospheric N deposition? What are current deposition amounts and trends? What risks do future N deposition amounts pose to natural areas and their species?
- Quantify the connections between N deposition effects on biodiversity and subsequent change in ecosystem services.

- Develop and apply more modeling capability related to N deposition effects on ecosystems/biodiversity, particularly for aquatic systems, non-temperate forest or alpine ecosystems.

Based upon the scientific evidence to date, the policy implications are to:

- Protect highly vulnerable ecosystems that are still unaffected by N deposition impacts;
- Where current or future N deposition overlaps with areas of high biodiversity conservation value (in terms of numbers of endemics- ecoregions etc), conduct inventories of species and implement monitoring of changes over time;
- Consider N deposition effects in conjunction with other human-caused drivers of climate change and land and water use;
- Build on existing knowledge to define connections between biodiversity and ecosystem services;
- There are different pathways by which N deposition affects biodiversity, which policy making should consider including:
  - Competitive advantage of some species over others;
  - Enhancement of invasive species over natives (which in some places can alter disturbance cycles such as fire return frequency);
  - Nutrient imbalance propagated up the food chain;
  - Acidification through loss of ANC or base cations.

Overall, the workshop recommended that:

- The CBD continue to recognize that excessive N affects biodiversity;
- The LRTAP Convention continues to recognize that loss of biodiversity is an important adverse effect of N transport and deposition;
- A combined approach to the problem by both Conventions might be a productive means to address the impacts of N deposition on biodiversity.

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Chapter 50
The Critical Loads and Levels Approach for Nitrogen

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Abstract This chapter reports the findings of a Working Group to review the critical loads (CLs) and levels approach for nitrogen (N). The three main approaches to estimating CLs are empirical, mass balance and dynamic modelling. Examples are given of recent developments in Europe, North America and Asia and it is concluded that other countries should be encouraged to develop basic assessments using soil, land cover, and deposition map overlays in order to determine what regions might exceed nitrogen CLs. There is a need for increasing the certainty of critical load

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(CL) estimates by focusing on empirical data needs, especially for understudied ecosystems such as tropical or Mediterranean, high elevation environments, and aquatic systems. There is also a need to improve steady-state mass balance parameters, especially soil solution terms, such as nitrate leaching, used to determine the

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CL, and denitrification, which is an equation parameter. Improved dynamic models are needed for predicting plant community changes, and work should continue on existing models to determine CL values. Dynamic models require more data and are more complex than simple calculated CLs but offer more information and allow the development of 'what if?' scenarios. Optimal use of CLs requires expert knowledge of ecosystem values to provide reference states so that safe deposition amounts can be determined. Increased interaction between CL and biodiversity specialists to identify critical biodiversity limits would help provide better CL assessments.

Keywords Critical loads • Empirical • Exceedance • Modelling • Nitrogen deposition

50.1 Introduction

The main purpose of the Working Group was to assess the state of the art for the setting of regional critical loads (CLs) for reactive nitrogen (N_r) as a cause of eutrophication and acidification. Critical loads are a well established, effects-based approach to evaluating emission reductions in the analysis of the effects of air pollutants, as they are used to determine "tolerable" deposition amounts (see also Hettelingh et al. 2014, Chap. 30; this volume). For example, sulphur (S) and nitrogen (N) CLs are currently used by policy makers for objectively setting emissions reduction targets for sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ammonia (NH_3) in the Gothenburg Protocol. Setting CLs can be challenging, however, as calculating them requires knowledge which can change with improvements in the

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science, thus sometimes making CLs moving targets. Critical loads can also be difficult to develop and apply because the data required are not always available.

The Working Group reviewed where current N critical load (CL) approaches for eutrophication and acidity were lacking and how improvements could be made. Five main questions were identified for discussion:

a. Can existing CL approaches be improved? There has been extensive use of N_r CLs in the past 10 years, particularly in European countries, so what have practitioners learnt from that experience?
b. Could new, simplified approaches be developed for estimating CLs in regions where there is little information?
c. How could the CL approach be used to assist policy makers in better dealing with issues relevant to the Convention on Biological Diversity (CBD)?
d. Currently, all inorganic N_r species (especially NO_x, NH_3) deposited into landscapes are lumped together to produce total N deposition estimates. Is it necessary to separate reduced from oxidized species in the calculations? Do we have the knowledge to do this? Critical loads have usually been set as deposition values. Should more work be done estimating critical levels for air concentrations relevant to sensitive taxa such as lichens?
e. Currently, all N_r critical load maps are calculated for terrestrial ecosystems. Is there a need to develop freshwater CLs for N?

50.2 Review of Critical Load Approaches

There are three main approaches for estimating CLs which are described here: empirical, mass balance and dynamic modelling. Empirical CLs are based on knowing the deposition or ambient N_r levels below which specific detrimental effects do not occur according to current knowledge. These are based on field or experimental observations of direct impacts to biota, such as changes in tree growth or changes in vegetation (biodiversity). These values can be estimated over large areas from map layers, if adequate information exists on soil chemistry and plant communities. However, the data required can sometimes be taken from examples collected elsewhere and may offer a relatively easy way to get a first approximation of N sensitivity of catchments. A number of reports have summarized tolerances to N_r of plant species, such as Bobbink et al. (2003) and Pardo et al. (2011), and these form the basis for maps describing ecosystem N tolerances in Europe and the United States (USA). More detail and examples of how critical loads can be calculated are found in Hettelingh et al. (2008).

Mass balance CLs are based on equations which assess the ability of a landscape to retain deposited N. A formal definition was provided by the German Ministry of the Environment (UBA 2004) where critical loads of nutrient N are defined as 'a quantitative estimate of an exposure to deposition of N as NH_3 and/or NO_x below which no harmful ecological effect is detected'.

This can be stated quantitatively from the N balance:

$$N_{dep} = N_i + N_u + N_{de} + N_{le} \quad \text{(Eq. 50.1)}$$

where N_{dep} is total deposition of N, N_i net immobilization, N_u removal by plant biomass, N_{de} denitrified to N_2 or N_2O gases and N_{le} is N leaching from soils (Hettelingh et al. 2008). The critical N load for the soil can thus be described as:

$$CL_{nut}(N) = N_i + N_u + N_{de} + N_{le,crit} \quad \text{(Eq. 50.2)}$$

where $N_{le,crit}$ is the acceptable leaching level. When N deposition exceeds N removal plus soil immobilization, the CL is said to be exceeded and a problem is identified.

Simple mass balance (SMB) CL approaches for both NO_3 leaching and changes to biodiversity have been applied in the European context. Nitrogen CLs are related to other stressors, such as pH and sulphur (S) from acidification. Critical loads can be calculated using dynamic geochemical models. These require more data and are more complex than simple calculated CLs but offer more information and allow the development of 'what if?' scenarios. Chemical CL critical limits or criteria need more research regarding specific ecosystem effects to allow more accurate assessments. In view of biodiversity issues, the distinction between acidity and nutrient N critical loads should be abandoned as it is potentially misleading, with eutrophication and acidification effects on biodiversity often difficult to disentangle (see Baron et al. 2014, Chap. 49; this volume). Moreover, multiple critical limits, which allow the assessment of multi-pollutant effects, can and should be constructed when the situation requires it, such as areas receiving both S and N deposition.

Dynamic CL models based on plant competition and succession have been run in polluted areas. Using estimated relationships between site-specific plant N, S and climate tolerances, Sverdrup et al. (2014, Chap. 40; this volume), have reconstructed historical plant communities in areas which are now affected by atmospheric pollution. Using plant-nutrient-climate relationships, predictions have been made of future plant community composition based on potential future climate and nutrient addition scenarios. Using this approach, other environmental stressors, such as fire and browsing animals can also be taken into account. The approach requires good quality information on plant-environment interactions, but has the ability to show the dynamic nature of plant communities over time.

Current knowledge of ecosystem responses to N inputs for the USA has been compiled by Pardo et al. (2011). The report synthesizes research collected in order to estimate N critical loads for ecoregions across the USA. The synthesis includes information from refereed as well as technical publications and could be used to identify ecosystems at risk for land managers and policy makers. The data are organized by ecoregions and include changes in biodiversity and species composition and in tissue N concentration, as well as N leaching from soils. The approach allowed the identification of receptors, responses, and thresholds, and the extrapolation to other regions or ecosystems. This allowed the estimation of empirical N CLs relevant to the major USA ecoregions. More data are continually being collected and synthesized in order to improve the assessment of atmospheric N pollution effects on USA ecosystems.

Efforts to coordinate CL research as a tool for supporting policy development and assessment in the USA are being developed. The objectives of these efforts are to: (a) facilitate sharing of technical information; (b) identify gaps in CL development, and develop strategies to fill them; (c) provide consistency in development and use of CL in the USA and (d) develop communications tools to help those working on or interested in CLs, to share a common understanding about CL terms and goals. It is hoped that these efforts will ultimately result in the USA being able to develop CL maps using commonly understood protocols, and share them with the UNECE and other interested groups. An overview of organizational models used to develop national N critical loads in other jurisdictions has been developed in order to see what would work best in the USA situation. The USA scientific expertise and funding is more widely dispersed than in most other countries and thus requires a new collaborative model for assembling the data needed to produce a coherent picture for a very large country.

Empirical CL maps for two typical Chinese ecosystems have been developed (Duan et al. 2014, Chap. 35; this volume). Sulphur dioxide emissions have increased in China over the past two decades to the highest levels in the world. The trend was subsequently reversed with a 4% reduction in 2007, 6% reduction in 2008 and a 10% reduction goal from 2005 levels was set for 2010 by government authorities. Despite reductions in S, NO_x and NH_3 emissions are rapidly increasing. In order to assess N_r effects on Chinese ecosystems, the SMB soil model has been used to calculate CL for NO_x and a large exceedance hot spot was identified in north-central China. Before there can be greater confidence in the data, more work must be carried out on longer time scales, and taking S deposition into consideration. China is a large country which also contains ecosystem types, such as sub-tropical regions, where no CLs have yet been estimated, again pointing out the unique situations which have to be understood. Moreover, large areas of China currently receive high N deposition, making it difficult to estimate pre-pollution conditions.

The view was expressed by some experts that globally land use and climate change present the greatest threats to biodiversity, even when N deposition is an important stressor. Moreover, the impacts of nutrient N on biodiversity may be assessed using critical load approaches. From this it was clear that there is currently considerable focus on developing empirical and dynamic approaches. Despite being the basis of 'acidification' assessments, mass balance approaches have fallen by the way-side in the race to determine CLs for nutrient N (Posch et al. 2011). Nonetheless, they may be the most practical (higher-level) approach for large regions, such as Canada. Currently, empirical approaches are the only viable option for large regions, despite there being a clear need to harmonize land cover maps between regions or jurisdictions. There is also a need for the development of more empirical critical limits (i.e., relationship between N deposition and receptor response), especially for low deposition areas.

Measurements and model-based assessments (Julian Aherne, personal communication) indicate that approximately 10% of Canada receives N deposition

>10 kg N ha^{-1} $year^{-1}$ (with the caveat that ammonia deposition may be greatly underestimated in some regions). Moreover, empirical assessments suggested that exceedance of CLs for nutrient N may be confined to a few regions across Canada: south-western British Columbia, northern Alberta, southern Ontario and Quebec where agricultural and industrial activities are intense.

50.3 Discussion and Recommendations

It is clear that the context for CL science is different than 10 years ago: (i) Climate change has a much higher profile, (ii) science and modeling methods have improved, (iii) linking environmental stressors to changes in biodiversity is very important, (iv) more regions of the world (USA, Canada, China, Brazil, India) are involved in CL science, in addition to Europe. Taking these points into consideration, the participants arrived at several conclusions.

50.3.1 How Can Existing Critical Load Approaches Be Improved?

Using empirical and modelling approaches (meso-modelling) in a combined way rather than in three separate approaches (empirical, steady state, dynamic modelling) will most likely create the most informative results. Dynamic modelling identifies what factors may be most important in empirical studies. Moreover, modelling results can be used when no field measurements are available.

More information is needed on the soil geochemical dynamics of N_r, in particular N loss by denitrification, immobilization and leaching. Any improvement in quantifying individual model terms will be useful in improving models, especially as denitrification is sometimes ignored or identified as “retained in the catchment”. More information is also needed on the climate variables which should be measured to improve our understanding of N soil chemistry.

Current models use and predict average values. How can we deal with deviations in extreme events such as significant storms which are important but are not well modelled? Is there a way to deal with this? We also need better spatial data for more ecosystems, such as Mediterranean, tropical and sub-tropical areas, polar and semi-desert ecosystems.

50.3.2 Can Simplified Models Provide Useful Information to Policy Makers and Scientists?

Despite the need to increase the sophistication of CL approaches, there is still a large need for robust tools which can give reasonable approximations of conditions when few data are available. The Working Group agreed that it is important to encourage countries to develop rough map overlays for use with the 'Simple Mass Balance' model (for example) and to encourage development of empirical relationships relevant to their regions. It is important to manage expectations, but primitive models can be useful to identify problems and future data needs, as well as providing information on which areas are most likely to be adversely affected. This approach is especially useful to engage countries where currently little information is available (e.g., countries in South America and Asia).

For countries where more empirical data is available, but where spatial regions covered are very large (e.g., USA, Canada, and China), simple models allow scientists and managers to identify region which need further attention. It is important to note that low deposition areas are very important in developing empirical data and mass balance critical load values.

50.3.3 How Could the Critical Load Approach be Used to Better Deal with Issues Relevant to the Convention on Biodiversity (CBD)?

Air pollution causes acidification as well as eutrophication and both are factors potentially modifying biodiversity. Thus, CL and vegetation dynamic modeling approaches are useful tools for predicting potential changes in biodiversity. However, the CL community lacks sufficient understanding of specific CBD goals or biodiversity limits, which are required to better link CL studies to CBD needs. Meetings like the INI Edinburgh Workshop are a good way to build the links between CBD and the LRTAP Conventions.

An important step in linking CL approaches to biodiversity is identifying reference states. What are the desired ecosystem states? What are the historical references? What are expected future reference states? In Europe, for example, plant community reference states have been identified for a year 2000 condition by EU scientific committees. Scientists can define probable CL levels in general, but it is most important that a more widely held consensus be developed to define biodiversity reference goals. We must better understand how to define desired characteristics of a reference state before we can calculate the CL necessary to achieve that state. Plant dynamic models should continue to be developed or improved to better assist in this task.

With good information on CLs, biodiversity specialists can support policy makers in setting priorities on where to spend resources to greatest effect for protecting key ecosystems or ecosystem components. The issue is further complicated by the fact that a number of regions, such as the Netherlands and parts of Great Britain may not be able to return to 'pristine' conditions for the foreseeable future. For example, central Britain lost most of it natural lichen communities 160 years ago. Is it reasonable to assume that we could ever return to that state? The interaction between CL and biodiversity specialists will be most important in addressing such highly subjective scientific issues.

50.3.4 Is There a Need for Calculating Separate Critical Loads for Oxidized and Reduced Nitrogen?

Evidence for differential effects of reduced and oxidized species is beginning to appear, but is not well developed, as only a few grassland and heathland experiments have been conducted that show differences. The feeling of the Working Group was that it may be premature to set separate limits for reduced and oxidized N at this stage. However, there are some ecosystems where NH_4^+ is important (acid soils, poorly buffered grasslands); in those cases, it may make sense set CLs at the lower end of the deposition range (see Dise et al. 2011 for latest information).

There is sufficient information on the other hand, to set gaseous concentration NH_3 critical levels (as opposed to critical loads). Lichen studies in California and in the UK have developed good concentration-effects relationships which can be used to assess whether existing plant communities are damaged by airborne N. Moreover, relative NO_3 and NH_4 concentrations in air, soils and water are not static, as there are a number of chemical conversion pathways possible. Further, the NH_3 and NO_3 impact on plants in soils solution is governed by soil pH, so that acidification must be considered together to some extent. Nevertheless, NH_3 CLs are beginning to be used in the European government agencies to assess the impacts of changes in agricultural zoning and practices.

50.3.5 Is There a Need to Develop Nitrogen Critical Loads for Freshwater Systems?

There is a great need for improvement in this area. In particular, empirical CLs for nutrient N in high elevation montane regions as well as estuarine/coastal areas currently need to be addressed. Phosphorus also needs to be included as a eutrophication driver, just as N and S are considered together for acidification modelling in surface waters. There is some empirical data available to assess aquatic N CLs in high elevation systems in the USA, but it is only available for limited geographic areas. A major shortcoming in this field of study is that no predictive modelling tools are currently available for nitrogen CL in freshwater systems.

50.4 Conclusions

The consensus was that first approximation empirical CL maps for nutrient effects are useful. Countries should be encouraged to develop basic assessments using soil, land cover, and deposition map overlays in order to determine what regions might exceed N CLs. There is a need for increasing the certainty of CL estimates by focusing on empirical data needs, especially for understudied ecosystems such as tropical or Mediterranean, high elevation environments, and aquatic systems. There is also a need to improve steady-state mass balance parameters, especially soil solution terms, such as nitrate leaching, used to determine the critical load, and denitrification, which is an equation parameter. There is also a need for improved dynamic models for predicting plant community changes, and work should continue on existing models to determine CL values.

Nitrogenous air pollution is one of the many threats to natural plant and animal communities, along with factors such as climate change, land-use change, overexploitation and invasive species. CL science can be most useful once biodiversity reference goals are identified. Therefore, we need assistance from ecosystem value specialists to determine what future states are "desirable" in order to determine what N pollution pressure is 'tolerable'. Though the stressors and their effects are often difficult to separate out, CL analysis provides a tool which can help sort out the contribution of air pollutants to community disturbance. Increased interaction between CL and biodiversity specialists to identify critical biodiversity limits would help provide better CL assessments.

Generally, expert soil chemistry opinion was that, under most conditions, the nitrification of NH_4 to NO_3 occurs very rapidly in most soils and that the long-term biological effects of these two ions could not be separated from each other. Exceptions might occur under wet, anoxic conditions, but these would be locally, not regionally important. However, differences in effect have been observed in the few available experimental studies, while the concentrations of different atmospheric species of N are important for direct effects on lichens and mosses.

The CL approach has shown itself to be a useful tool for assessing the ability of current ecosystems to deal with N_r. There is still room for improvement in the formulation of the approaches or the assessment of limits, but the approach still can be a useful exploratory tool even when little data is available. Optimal use of CLs does require expert knowledge of ecosystem values to provide reference states so that safe deposition amounts can be determined.

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Chapter 51
Nitrogen Deposition Effects on Ecosystem Services and Interactions with other Pollutants and Climate Change

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Abstract Ecosystem services are defined as the ecological and socio-economic value of goods and services provided by natural and semi-natural ecosystems. Ecosystem services are being impacted by many human induced stresses, one of them being nitrogen (N) deposition and its interactions with other pollutants and climate change. It is concluded that N directly or indirectly affects a wide range of provi-

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sioning, regulating, supporting and cultural ecosystem services, many of which are interrelated. When considering the effects of N on ecosystem services, it is important to distinguish between different types of ecosystems/species and the protection against N impacts should include other aspects related to N, in addition to biodi-

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versity. The Working Group considered the following priorities of ecosystem services in relation to N: biodiversity; air quality/atmosphere; ecosystem changes; NO_3 leaching; climate regulation and cultural issues. These are the services for which the best evidence is available in the literature. There is a conflicting interest between

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greenhouse gas ecosystem services and biodiversity protection; up to some point of increasing N inputs, net greenhouse gas uptake is improved, while biodiversity is already adversely affected.

Keywords Air quality • Biodiversity • Climate change • Ecosystem services • Interactions • Leaching • Nitrogen deposition

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51.1 Introduction

It has been acknowledged, as in the Millennium Ecosystem Assessment (MA) that ecosystem services are essential for life on earth and for human well being (Reid et al. 2005). Ecosystem services are defined as the ecological and socio-economic value of goods and services provided by natural and semi-natural ecosystems. Literature on valuation of ecosystem services has grown over the years (e.g. Helliwell 1969; Costanza et al. 1997; de Groot et al. 2002; Reid et al. 2005). The MA distinguished four types of ecosystem services: provisioning services, regulating services, supporting services and cultural services (Reid et al. 2005). Provisioning services are the products obtained from ecosystems, specifically the provision of food, fiber and wood/fuel. These functions are related to photosynthesis and nutrient uptake, and also include other services, such as the provision of fresh water. Regulating services refer to the regulation of climate, water quantity (ground water recharge, occurrence of floods etc), water quality and diseases, and is related to the impact of ecosystems on greenhouse gas exchange and the buffering and filtering capacity of the soil affecting water and element fluxes. Supporting services relate to the capacity of natural and semi-natural ecosystems to regulate essential ecological processes and life support systems through bio-geochemical cycles. These functions are indirectly related to the provisioning and regulating functions as they affect many services that have direct and indirect benefits to humans (such as clean air, water, and soil). Cultural services include for example recreation and landscape features or species with aesthetic or spiritual value.

Nitrogen (N) deposition has an effect on ecosystem services as distinguished in the MA through many relationships which vary in importance and magnitude. The background document for the workshop (see also de Vries et al. 2014, chapter 41, this volume) included a table which was modified and extended as part of the discussions in this Working Group and is provided here as Table 51.1.

51.2 Discussion and Recommendations

The focus of the breakout group on ecosystem services was on further development of tools/indicators for N induced biodiversity loss (Bobbink et al. 2010), which should ideally take into account impacts of N addition on valuable ecosystem services such as carbon (C) sequestration and regulating services related to soil and water quality, in interaction with climate change and with other nutrients. The aim was to provide conclusions and recommendations, referring to needs identified by the CBD and LRTAP Convention, and evaluate the implications of current knowledge for further policy, management and capacity-building needs.

Table 51.1 Major relationships between nitrogen (N) deposition and ecosystem services as distinguished in the Millennium Ecosystem Assessment (extended after de Vries et al. 2009), modified and extended by the working group

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Provisioning services		
Food/fiber, including:		
– Crops (food and bioenergy)	Increase in crop production	Nitrogen deposition increases crop growth in N limited systems (low N fertilizer inputs)
– Wild plants and animal products	Impacts on biodiversity (based products)	Nitrogen induced eutrophication and soil acidification affects soil, plant and faunal species diversity and thereby biodiversity-based products
Timber/wood fuel	Increase/decrease in wood production	In N-limited systems, N increases forest growth and wood production; in N saturated forests, N can induce mortality.
Natural medicines	Impacts on medicinal plants	Nitrogen induced eutrophication and soil acidification affects plant species, but linkage to medicinal plants is largely unknown.
Fresh water	Impacts on ground water recharge and drainage	Nitrogen induced impacts on growth and plant species diversity also affect water uptake and thereby freshwater supply (see also water quantity regulation).
Regulating services		
Air quality regulation	Change in air quality through primary emissions, atmospheric chemistry (including aerosol & cloud interactions) & ecosystem interactions	Nitrogen deposition is correlated with increased concentrations of ammonia (NH_3), nitrogen oxides (NO_x), ozone (O_3) and particulate matter (PM_{10} and $PM_{2.5}$), all affecting human health and ecosystems. The response of ecosystems to N deposition can help regulate air quality.
Climate regulation Green house gas balance	Increased carbon sequestration in forests	In N limited systems, N deposition increases forest growth and related tree carbon sequestration, but can enhance mortality in some species. It also can cause an increased litterfall and reduced decomposition, leading to soil carbon sequestration.
	Increased/decreased carbon sequestration in peat lands	At low N deposition, additional atmospheric N deposition may stimulate net primary productivity. At high rates of N deposition, species composition changes lead to loss of peat land forming species and changed microbial activity causing degradation of peatlands.
	Increased N_2O production	Ecosystem losses as N_2O increase with N loading.
	Decreased CH_4 consumption	Soil microbes decrease CH_4 consumption in response to increased NH_4 availability.
	Increased O_3 production	Increased production of tropospheric O_3 from interactions between NO_x and VOC emitted from ecosystems, which serves as GHG and can also inhibit CO_2 uptake through plant damage.

Table 51.1 (continued)

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Water quantity regulation	Increased/decreased runoff and ground water recharge	Excess N may cause decreased runoff and ground water recharge due to increased water uptake (elevated growth) but also the reverse because of lower leaf area index due to defoliation caused by pests/diseases. Recharge may in the long term also be affected by impacts on soil carbon content and soil biodiversity, affecting water retention in soil.
	Increased drought stress	Excess N causes an increased need for water by an increased growth and an increased sensitivity for drought stress by an increase in the ratio of above versus below ground biomass.
Water quality regulation (water purification)	Decline in ground water and surface water (drinking water) quality	Nitrogen eutrophication and N induced soil acidification increases NO_3, Cd and Al availability, leading to: – NO_3, Cd and Al concentrations in groundwater and surface water exceeding drinking water quality criteria in view of human health effects – Increased Al concentrations in acid sensitive surface waters resulting in the reduction or loss of fish (salmonid) populations and reduction of aquatic diversity at several trophic levels (acidification) – Fish dieback by algal blooms and anoxic zones (eutrophication). Eutrophication is also affected by silica and phosphorus in estuaries.
Soil quality regulation	Decrease in acidity buffer; change in soil structure	Nitrogen induced soil acidification decreases the exchangeable pool of base cations, potentially causing reduced forest growth, and decreases the readily available Al pool, affecting soil structure.
Pest/disease regulation	Increased human allergic diseases	Increasing N availability can stimulate greater pollen production, causing human allergic responses, such as hay fever, rhinitis and asthma.
	Increase in forest pests	Increase in bark or foliar N concentrations can attract higher infestation rates, such as beech bark disease.
Crop Pollination	Timing and occurrence of flowers affected	Both vegetation composition and flowering intensity can be affected.
Supporting services		
Nutrient cycling and primary production	Increases N inputs by litterfall and reduces soil biodiversity	Nitrogen induced impacts on growth/litterfall and on soil biodiversity (soil mesofauna and bacteria composition) affects decomposition, nutrient mineralization and N immobilization, and thereby impacts nutrient cycling and primary production.

Table 51.1 (continued)

Ecosystem services	Examples of nitrogen effects	Causal link with nitrogen deposition
Cultural services		
Cultural heritage values	Impacts on culturally significant species in historically important landscapes.	Nitrogen deposition may change heathlands into grasslands, affecting historically important landscapes; very important for 'healthy species and cultural landscape', which are affected when biodiversity decreases.
Recreation and ecotourism	Impacts on recreation due to impacts on ecosystems	Nitrogen can be important for recreation (fisheries, heathland); it induces the increase in nitrophilic species like stinging nettles and algal blooms reducing recreational and aesthetic values of nature. Extreme examples include closed beaches due to algal blooms resulting from N-induced eutrophication in estuaries and coastal ecosystems.

51.2.1 Effects of Nitrogen on Ecosystem Services

Based on presentations to the Working Group, it appeared that there is a wide range of ecosystem services directly or indirectly affected by N. For these effects, it is relevant in some cases to distinguish between the forms of N. Furthermore, knowledge of inputs is important to establish cause-effect relationships. Organic N is an overlooked N input that can range from 20 % (land-based) to 40 % (oceans) of total N input and is important for ecosystem functioning (Cornell 2011 and 2014, chapter 12, this volume). Nitrogen budgets in ecosystems are essential to determine the cycling and effects of N. Such budgets can serve as an important indicator of the N threats to ecosystems. There is, however, large uncertainty in the different terms of the N budgets. This is particularly true for N inputs, such as organic N and total N deposition. Further understanding of the uncertainty in N deposition estimates is a key to untangling different threats to ecosystem services (e.g., climate, land use, GHG fluxes). An important indirect effect of N is ecosystem exposure to ozone (O_3), which often has a negative impact on Net Primary Production (NPP). However, the Working Group concluded that N and O_3 interactions are unclear. The most important effect of N discussed by the Working Group involved the effect of N inputs on greenhouse gas emissions and sinks. Nitrogen inhibits methane (CH_4) uptake and increases nitrous oxide (N_2O) emission (especially through nitrate (NO_3) inputs) in forests. Nitrogen increases the C sink in forests, but approximately 5–10 % of this effect is counteracted by N_2O and CH_4 fluxes to the atmosphere (see Butterbach-Bahl et al. 2011).

The overview of provisioning, regulating, supporting and cultural services affected by N deposition in Table 51.1 is extended with: atmosphere services (aerosol, clouds), cultural (tourism, recreation, fishing, 'healthy species'), bioenergy, and pollination. Nitrogen affects most of these in varying degree. There is strong evidence for cause-effect relationships for most important ecosystem services. The focus should be on (semi) natural systems in relation to N deposition for:

- *Climate regulation:* life cycle analysis studies show no net-effect of N addition, but forests and grasslands can sequester more C per kg N added up to an optimal level. Above this level there is net loss of C. More uncertainty remains for other ecosystems than forests, such as peatland, tropical systems, and savannas. The role of fires and the temporal scale need to be addressed in order to determine if the net C sequestered remains there for a long time period.
- *Water quality and quantity:* much discussion remains on quality in relation to human health and the currently used limit of 1 mg N/l. It is a limit for human health, fresh water issues (algae blooms, acidification) and estuary food/fish production.
- *Air Quality Regulation:* Air quality is affected by primary emissions of particulates and toxic substances and through dispersion the (clean) atmosphere service is affected. Changes in air quality (NO_x, O_3, particulate matter) then occur through atmospheric chemistry (including aerosol and cloud interactions) and ecosystem interactions (e.g. the uptake and interception of air pollution by vegetation).

- *Cultural aspects:* Nitrogen can be an important concern for recreation (fisheries, heathland) for maintaining 'healthy species and cultural landscapes', which are impacted when biodiversity decreases.
- *Food and fiber:* pollination, forage; soil productivity and fertility.

When considering the effects of N on ecosystem services, it is important to distinguish between different types of ecosystems/species, and protection against N impacts should include other aspects related to N, in addition to biodiversity (Achermann and Bobbink 2003; Bobbink et al. 2010). The Working Group considered the following priorities of ecosystem services in relation to N: biodiversity, air quality/atmosphere, ecosystem changes, NO_3 leaching, climate regulation, and cultural impacts. These are the services for which the best evidence is available in the literature. There is a conflicting interest between greenhouse gas ecosystem services and biodiversity protection. It appears that there is an optimum level of N tolerance for greenhouse gas effects, below which the net greenhouse gas sink is increased with increasing N inputs, while above this level there is an increasing net loss of greenhouse gas (in CO_2 equivalents). For biodiversity, there is no optimum level, and biodiversity is affected negatively with increasing N inputs. The optimum level for different ecosystems might serve as an indicator and/or tolerance level for N.

Long-range transport of N makes fertilization 'uncontrolled'. Nitrogen deposition as the result of long-range transport should be regulated on a large scale, making regulation of NO_x sources a "no-regrets" policy option. Fertilization for ecosystem services (e.g., carbon), other than long-range transport, should be done without losses of other services such as biodiversity loss. Fertilization of forests is done now for wood production, but not in forests for C sequestration. Well-managed forests can accomplish both goals (wood production and C sequestration).

Land use planning, especially in developing countries, is an option for preserving ecosystem services. Land use is a very important issue, especially for tropical regions. In tropical regions, N deposition impacts biodiversity very differently than temperate regions. As a result, the Southern Hemisphere has many different issues relating to N inputs and impacts than in the Northern Hemisphere.

Policy or further development would require the inclusion of end points and an economic analysis of the benefits. The Working Group developed a conceptual framework for determining the causal links between N and ecosystem services (see Fig. 51.1). The next steps for refining this conceptual framework are to explore directional relationships (e.g., adding pluses and minuses), working towards the ultimate goal of developing quantitative relationships.

The Working Group identified important ecosystem services other than biodiversity, most of which were impacted by N inputs. There is strong evidence for cause-effect relationships for most important ecosystem services, such as human health and air quality, N deposition and biodiversity, etc. It must be emphasized that, even though N deposition is important, some biomes have other aspects of the N cycle that must be addressed first. Furthermore, other nutrients, such as phosphorus, should be considered together with N.

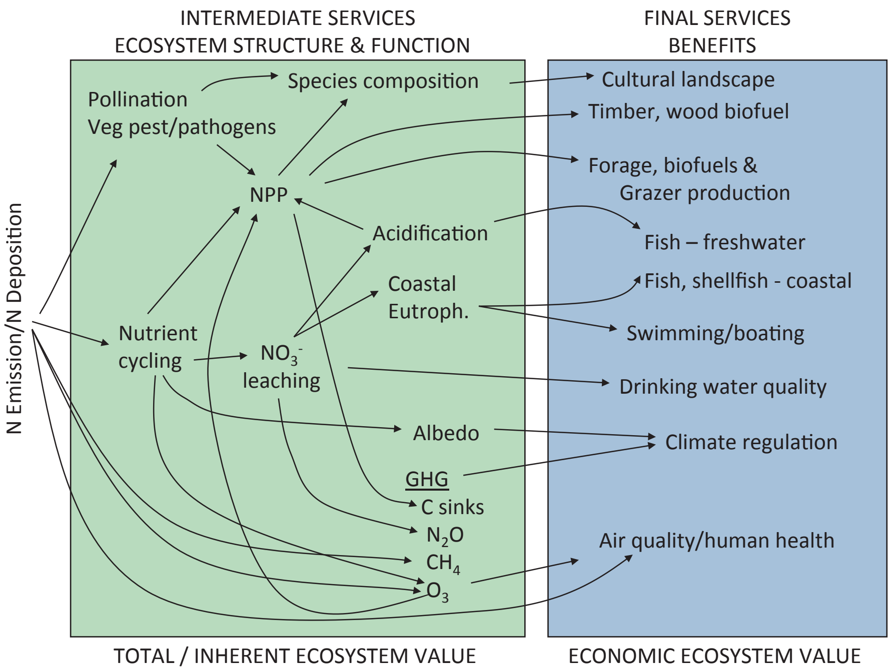

Fig. 51.1 Effect of nitrogen on ecosystem services (after C.L. Goodale and Bridget Emmett)

51.2.2 Recommendations

The Working Group made the following recommendations:

- Ecosystem services should be taken into account in the Conventions in addition to biodiversity and critical loads.
- The current available knowledge is based on research in a limited area of the world. Increased efforts in tropical regions, savannas, peatlands, and other biomes are necessary.
- Nitrogen deposition should be better quantified, including organic-N, as understanding inputs is an important factor in establishing cause-effect relationships.
- The critical loads approach should be made more robust in relation to N, O_3 and climate. The critical load concept must be adapted to include climate change and changes in greenhouse gas balances of ecosystems.
- The ‘blue-box’ eNd points (Fig. 51.1) should be translated to provide effects indicators related to N-deposition in addition to the eutrophic level. Furthermore, the relationships of Fig. 51.1 should be quantified for different ecosystem types.
- Policy and management in relation to ecosystem services are covered by more than one government ministry or agency; it would strengthen the message about

N effects if the issue is well communicated and coordinated (e.g. Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem services).
- The costs of decreases in ecosystem services need to be emphasized and quantified. An important area for further work and progress involves valuation of ecosystem services and inclusion of services and valuation in policy decisions.

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Chapter 52
Workshop on Nitrogen Deposition, Critical Loads and Biodiversity: Scientific Synthesis and Summary for Policy Makers

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Abstract It is clear that nitrogen (N) deposition impacts on the biodiversity and ecosystem services provided by natural and semi-natural ecosystems have been experienced in Europe, North America and Asia over the last 50 years. Impacts are also estimated to increase in line with increasing rates of N deposition in coming decades across the globe, especially in Asia. To improve the assessment of impacts progress is required in the following key areas: the extent of monitoring networks and the measurement of dry and organic deposition; the modelling of N deposition

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in areas with complex topography; the assessment of impacts on fauna generally and impacts on flora in areas outside the relatively well studied temperate ecosystems; the application of critical load (CL) and level approaches outside of Europe; and the linkage between impacts on biodiversity and important ecosystem services. New indicators are required, in addition to N deposition and critical loads, to demonstrate the wider impacts and to help integrate the biodiversity, air pollution and climate change policy communities.

Keywords Biodiversity • Critical loads • Ecosystem services • Nitrogen deposition • Policy

52.1 Introduction

The International Expert Workshop on Nitrogen Deposition, Critical Loads and Biodiversity was held on 16–18th November, 2009 in Edinburgh, UK. The workshop was organized by the International Nitrogen Initiative (INI) in collaboration with the Long-range Transboundary Air Pollution (LRTAP) Convention and the Convention on Biological Diversity (CBD), and included participation of 140 experts from thirty countries representing most continents and regions of the world. This chapter describes the purpose of the Expert Workshop and summarizes the main conclusions and recommendations both for the scientific community and in support of the needs articulated by the LRTAP Conventions and the CBD.

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52.1.1 Background and Problem Statement

Increases in nitrogen (N) deposition in broad areas of Europe, North America, and parts of Asia over the last 50 years have resulted in losses of plant diversity, shifts in plant community composition, alteration of food webs and changes in ecosystem services. Global scale modelling, using current N emission scenarios, indicates that most regions around the globe will have increased rates of atmospheric N deposition over the next decades, causing concern about significant impacts on global biodiversity. Increased N emissions also have impacts on human health (e.g. as precursors of $PM_{2.5}$ and ozone) and adversely affect crop yields through increased ozone concentrations.

In some parts of the world, such as Europe and Canada, international concern over these impacts has prompted development of an effects threshold approach for assessing the impacts of N deposition, known as the "critical loads" approach. This has provided a valuable tool to assess present and future risks of adverse effects of N deposition. Critical load (CL) exceedance for N was used as an indicator by the Streamlining European 2010 Biodiversity Indicators (SEBI 2010) for assessing, reporting on and communicating achievement of the 2010 target to halt biodiversity loss under the CBD. However, it has been unclear if critical loads and their exceedance could be adopted usefully for global application under the CBD.

In addition to Europe and North America, N deposition is above or approaching critical loads in parts of Asia, Africa and Latin America. However, insufficient studies exist on the effects of N deposition in these regions to provide a basis for a rigorous application of the CLs approach. Other shortcomings in several areas currently hamper adoption of the critical thresholds approach and assessment of N impacts in general:

- Significant uncertainty in total deposition estimates around the globe, particularly for dry deposition;
- Uncertainty about the relationship between biodiversity loss and N dynamics and the translation into CLs;
- Uncertainty in the global transferability of critical level values for ammonia and nitrogen oxides concentrations;
- Need for more field-based evidence for biodiversity effects, where plant studies are often lacking in many regions and studies on animals and other groups are even scarcer;
- More persuasive indicators of biodiversity loss in areas that have exceeded critical N loads are required on a global scale;
- Further development of tools/indicators for N induced biodiversity loss should ideally take account of impacts of N addition on valuable ecosystem services, such as carbon (C) sequestration and regulating services related to soil and water quality, in interaction with climate change.

52.1.2 Workshop Format and Organization

The Workshop considered five key topic areas in plenary and breakout sessions. Overarching themes included the exchange of information between different regions and disciplines, and how measurements and approaches for assessing N deposition and biodiversity loss can be harmonized at a global scale. Key topic areas, serving as the focus for plenary and working group sessions included:

- Progress in monitoring and modelling estimates of N deposition at local, regional and global scales;
- Factors affecting N deposition impacts on terrestrial and aquatic ecosystem biodiversity;
- Development of the CLs concept and its application to different regions of the world;
- Importance of N deposition effects on ecosystem services and interactions with other pollutants (e.g., ozone) and climate change;
- Implications of current knowledge of N deposition and its impacts pertaining to policy, management and capacity building needs.

The following sections outline the main conclusions and recommendations of the Workshop according to these different themes, based on the papers and Working Group discussions reported in the previous chapters. In addition to this volume, selected papers were further developed for inclusion in a Special Issue Section of the journal *Environmental Pollution* (See Appendix 1 to this volume).

52.2 Progress in Monitoring and Modelling Estimates of Nitrogen Deposition at Local, Regional and Global Scales

Reactive nitrogen (N_r) compounds play a central role in the chemistry of the atmosphere, as well as in the functioning of marine, freshwater and terrestrial ecosystems. There is ample evidence that increasing human activities seriously disturb the natural N cycle. Reactive nitrogen enters the environment through a number of processes related to fertilization, waste discharge, and atmospheric emissions, transport and deposition. The Workshop discussed progress and issues pertinent to measurement and modelling of dry and wet deposition of N_r, which are the final removal processes from the atmosphere, at the local, regional and global scales. The present status and developments of networks and techniques for measuring deposition of N_r were reviewed, including recent developments in the modelling of emissions and deposition.

52.2.1 Nitrogen Deposition Monitoring

Wet deposition refers to the removal of gases and aerosols by scavenging in clouds (uptake in cloud droplets/ice crystals, formation and sedimentation of rain) and precipitation scavenging (falling rain droplets and frozen hydrometeors interacting with particles and gases). Since the 1970s, many international, national, and sub-national monitoring networks have been operated.

Over the last decade, the number of wet deposition monitoring sites has generally increased in Asia, Eastern Europe and the United States. Unfortunately, large areas of the world still have few if any wet deposition measurements, including South America, Africa, Australia, Oceania, western/northern Canada, the oceans, and the polar regions.

Dry deposition involves all removal processes of gases and aerosols at the earth's surface. This form of deposition is not measured directly by large-scale monitoring networks because such monitoring requires sophisticated instrumentation and flux measurement methods. Instead, networks measure ambient gas and particle concentrations and combine these data with model estimates of the associated dry deposition removal rates, an approach referred to as the 'inferential technique'. Only a few major networks currently make regionally-representative routine inferential estimates of dry deposition fluxes, for example, the United States Clean Air Status and Trends Network (CASTNET), the Canadian Air and Precipitation Monitoring Network (CAPMoN), and the United Kingdom Acidifying and Eutrophicating Pollutants network (UKEAP). An inferential model is currently under development for Africa through the International Global Atmospheric Chemistry/Deposition of Biogeochemically Important Trace Species (IGAC/DEBITS) program.

For total deposition, no monitoring programs, including the extensive Canadian and US networks, measure all of the major oxidized and reduced nitrogen species needed to estimate the total atmospheric loading of N. The Canadian and US networks, for example, measure particle-NO_3^-, particle-NH_4^+, and gaseous HNO_3, but not NO, NO_2, PAN, NH_3 or organo-nitrates—some of which are important contributors to dry deposition. The dry deposition fluxes (and wet + dry deposition fluxes) of N estimated by these two networks are thought to be quite conservative. Measurements in the UKEAP network and from the NitroEurope 'inferential network', including NH_3, NH_4^+, HNO_3, NO_3^-, highlight that NH_3 is generally the largest single term in dry deposition to semi-natural and forest ecosystems.

The observations reported at the Workshop showed the following general patterns:

- The highest levels of total N deposition occur in China and India with the lowest values in Africa.
- Preliminary estimates of wet deposition show a range of 4 to 7 kg N ha^{-1} $year^{-1}$ in eastern North America, 5 to >7 kg N ha^{-1} $year^{-1}$ in Europe, while sites in East Asia experience wet deposition between 2 and 60 kg N ha^{-1} $year^{-1}$. In Africa the observed total deposition (dry plus wet) is between 7 and 10 kg N ha^{-1} $year^{-1}$.

- The NO_x and NH_3 emissions have been increasing dramatically in Asia since the 1980s, and this increased N deposition is of great concern both on a regional and global level. NO_x emissions have on the other hand decreased in North America and Europe.
- Organic N deposition is not routinely measured in all regions and the quality of available measurements is doubtful; however, the organic N contribution as a fraction may be high in many areas and as an absolute term in high emission areas (i.e. in parts of China).

52.2.2 Nitrogen Deposition Modelling

Many models are available to describe air pollution chemistry and transport. These models range from describing near-point source dispersion to global transport processes; the choice of model depends on the issue and the availability of input data. Because many processes are parameterized in models, the models can only provide a limited representation of reality. Global models are increasingly used for providing maps of reduced and oxidized inorganic N. Resolution of global models range from $1° \times 1°$ to $4° \times 5°$ lat-long, and is expected to improve to $0.5° \times 0.5°$ in the coming years. The spatial domain and resolution of regional models has been steadily improving. In the US and Europe, the typical resolution of continental models has decreased from 36-km to 12-km grid sizes. However, 12-km is still too coarse, as there is a high degree of deposition variability within a grid in complex terrain that is important to CLs modelling. Even in flat terrain, dry deposition depends on land cover type, requiring that methods be developed to account for this ecosystem variability rather than use a single number per grid. Efforts are being made to make dry deposition land-use specific within different models.

52.2.3 Key Recent Developments

Attempts are underway to bring together datasets on wet and dry deposition on the global scale, and international programs (e.g., IGBP and WMO) endorse these attempts. Deposition data availability in Asia is rapidly improving due to the operation of the EANET network and many national networks, and efforts to establish consolidated measurement capacity in Africa are encouraging.

Models are continuously improving. Global models are achieving finer resolution, and regional models are expanding their model domain, as well as improving resolution. Nevertheless, errors in emission inventories and in the meteorological model predictions are still a significant issue for modelling of N deposition and critical loads. In many areas of the work, the uncertainty in spatially resolved emissions inventories dominates the overall uncertainties in model outputs. More detailed emission inventories are being compiled in many areas of the world, either by combining national level detailed inventories, or high resolution bottom-up inventories.

Improvements of the physics in meteorological models are still needed. Regional models in the USA have been used successfully to establish top-down constraints on NH_3 emissions and estimate the seasonality of the NH_3 emissions. With the top-down estimates, the model simulations of the gas-particle partitioning of the inorganic species are significantly improved.

Models are increasingly using the possibility to ingest large sets of observations, a process called data assimilation which was adapted from the numerical weather prediction community. Important information on trends can be obtained from satellite information. The first satellite-based NH_3 measurements were reported recently, but the current infrared satellite instruments remain extremely uncertain in their absolute estimates especially for regions with low thermal contrast, small ammonia concentration and for near ground level concentrations. The recent achievement highlights the opportunity and need for improving satellite observations in future instruments.

52.2.4 Monitoring and Modelling Nitrogen Deposition: Conclusions and Recommendations

The workshop reached the following conclusions regarding the present status of N deposition monitoring and modelling throughout the world:

- High confidence exists for inorganic N wet deposition estimates in the US, eastern Canada, Europe and parts of East Asia. By contrast, long-term wet or dry N deposition information in large parts of Asia, South America, parts of Africa, Australia/Oceania, and oceans and coastal areas is generally lacking.
- Dry deposition can be estimated through a set of tools involving inferential modelling and direct flux measurements, but the tools are not widely applied:
  - The uncertainty level is much higher in dry deposition estimates than in wet deposition;
  - The accuracy of measurements in the best case is on the order of ± 30 % but in the less studied regions, such as the tropics, the accuracy may be ± 50 %.
- Presently, robust estimates of total N deposition are available only for inorganic N, while estimates for organic N are largely missing.
- Models are a necessary complement to measurements as they provide evidence of source attribution and chemistry and transport pathways:
  - Models can help fill gaps in areas where monitoring is limited (chemically and geographically);
  - The confidence level in model outputs increases with accurate emissions data and available monitoring data for validation.

Based on these conclusions, the Workshop recommended the following actions regarding N deposition monitoring, modelling and capacity building.

52.2.4.1 Monitoring

- The number of regional-scale, long-term monitoring sites for routine measurement should be increased to allow global coverage for trend assessment.
- The number of N species routinely measured should be increased in order to close the atmospheric N budget, most notably organic N (wet and dry), NH_3, HNO_3 and NO_2.
- Measurements must be improved to allow necessary validation and improvement of model parameterization, including:
  - Dry deposition flux of gaseous and particulate N species;
  - Higher temporal resolution data, especially to capture diurnal variations;
  - Higher spatial resolution to cover areas not covered by the model;
  - Data quality information.

52.2.4.2 Modelling

- The resolution and meteorological parameterization of chemical transport models needs to be improved to avoid problems in characterizing precipitation amounts, especially in situations with complex orography.
- New emission data sets should be quality-assured in future modelling.
- NO_x emissions from lightning and ships should be addressed in the models as these are important sources for some regions.
- Meteorology-driven modules should be applied in order to obtain accurate spatial and temporal emission estimates, especially for ammonia.

52.2.4.3 Capacity-Building

- Increased effort should be given to capacity-building for measuring and modelling wet and dry deposition in the developing world.
- All measurement networks should participate in quality assurance programs, such as administered by the WMO.
- Increased efforts should be given to promote interaction and involvement in regional networks.

52.3 Factors Affecting Nitrogen Deposition Impacts on Biodiversity

Emissions of ammonia (NH_3) and nitrogen oxides (NO_x) strongly increased in the second half of the 20th century. Because of short- and long-range transport of these nitrogenous compounds, atmospheric N deposition has clearly increased in many natural and semi-natural ecosystems across the world. Areas with high atmospheric

N deposition include central and western Europe, eastern USA and, since the 1990s, Eastern Asia. Various "mechanisms" lead to change in plant and animal species composition and number after N enrichment due to increased N deposition. The Workshop considered those mechanisms, as well as the factors that affect the influence of N deposition impacts on biodiversity.

52.3.1 Impacts on Biodiversity

A highly complex series of events occurs when N inputs increase in a region with originally low background N deposition rates. While many ecological processes interact and operate at different temporal and spatial scales, the main impact "categories" on vegetation can be identified, including:

- direct foliar impacts;
- eutrophication;
- acidification;
- negative effects of reduced N compounds such as NH_3; and
- increased susceptibility to secondary stress and disturbance factors (e.g., drought, frost, pathogens, herbivores).

Until recently, research on the impacts of N deposition has mainly focused on plants/vegetation and abiotic processes. Research on the effects of increased N inputs on faunal diversity in semi-natural and natural ecosystems is largely lacking. However, there is a clear impact on fauna, as N deposition affects the production and quality of food and environmental conditions, including micro-climate, vegetation structure, and heterogeneity of the landscape needed by animal species to complete their life-cycles.

52.3.2 Factors Affecting the Diverse Impacts of Nitrogen

The severity of atmospheric N deposition impacts on flora and fauna depends on a complex number of factors, of which the most important are:

- duration and total amount of the N inputs;
- chemical and physical form of the airborne N input;
- intrinsic sensitivity to changes in N availability of the plant and animal species present;
- abiotic conditions; and
- past and present land use or management.

Important conditions include buffering capacity of soils and waters (acid neutralizing capacity; alkalinity), original soil nutrient availability (N and phosphorus (P)), and soil factors which influence decomposition, nitrification, N immobilization and denitrification rates. As a consequence, high variations in sensitivity to atmospheric N deposition have been observed between different ecosystems across the globe.

52.3.3 Nitrogen Deposition Impacts on Biodiversity: Conclusions and Recommendations

Overall, the Workshop concluded that some systems are more vulnerable than others, some systems have been more severely affected than others, and severely impacted systems may be permanently altered and unable to return to their original state in the foreseeable future. Specific conclusions were also reached regarding regional and global impacts on biodiversity, as well as potential indicators of these impacts:

- There is a spectrum of responses to N deposition, for example, rates of loss in biodiversity are greatest at the lowest and initial stages of N deposition increase;
- Changes in species composition are related to the relative amounts of N, C and P in the plant soil system;
- Enhanced N inputs have implications for both the freshwater C cycle and global C cycle;
- Nitrogen deposition is having a negative effect on European and North American biodiversity, with growing evidence for impacts in other parts of the globe e.g. Asia. However, much more is known about impacts to flora than to fauna;
- While very little is known about tropical ecosystem responses, tropical ecosystems are major biodiversity hotspots and are increasingly recipients of very high N deposition rates;
- Nitrogen deposition dramatically alters forest fungi and mycorrhyzal relations with plants; the rapid response of forest fungi and arthropods makes them good indicators of change which should receive more attention;
- Nitrogen deposition increases sensitivity to climate change and other stresses;
- Climate change, air pollution, and land use must be addressed as integrated problems;
- Predictive tools (models) that address ecosystem scale processes are necessary to address complex drivers and responses;
- Criteria can be identified for projecting sensitivity of terrestrial and aquatic ecosystems to N deposition:
  - Nutrient poor conditions (flora adapted to low nutrients and low to moderate buffering capacity);
  - Highly weathered soils (high Ca/Al ratio in soil);
  - Sensitive sites typically have a high proportion of N-fixers, potential for increases in ruderal species, insectivorous plants, high bryophyte cover (often sites with communities of high conservation significance); seasonally dry communities.

Research recommendations that follow from the scientific evidence to date are to:

- Expand empirical information about, and theoretical underpinnings of, ecosystem and food web responses to increasing N deposition. Identify which changes are important and potentially irreversible. Investigate responses to the reduction of N deposition, to assess whether recovery can occur.

- Conduct assessments of the distribution, ecology, conservation status, threats, and risk of extinction for species of different taxonomic groups, especially faunal and freshwater species and many terrestrial invertebrates, in order to make meaningful comparisons and models of the relationship between species composition in ecosystems, N deposition, and resultant compositional change of the species diversity over time.
- Complete an assessment of understudied regions of the world, such as the tropics and developing regions of Asia. It should be considered: which ecosystems, communities, and organisms are vulnerable to atmospheric N deposition; what are the current deposition amounts and trends; and what are the risks posed by future N deposition amounts to natural areas and their species.
- Quantify the connections between N deposition effects on biodiversity and subsequent change in ecosystem services.
- Develop and apply more modelling capability related to N deposition effects on ecosystems/biodiversity, particularly for aquatic systems, non-temperate forest or alpine ecosystems.

Based upon the scientific evidence to date, policy implications are to:

- Protect highly vulnerable ecosystems that are still unaffected by N deposition impacts;
- Where current or future N deposition overlaps with potentially sensitive areas of high biodiversity conservation value (in terms of numbers of endemics-ecoregions etc), conduct inventories of species and implement monitoring of changes over time;
- Consider N deposition effects in conjunction with other human-caused drivers of climate change and land and water use;
- Build on existing knowledge to define connections between biodiversity and ecosystem services;
- There are different pathways by which N deposition affects biodiversity, which policy making should consider including:
  - Competitive advantage of some species over others;
  - Enhancement of invasive species over natives (which in some places can alter disturbance cycles such as fire return frequency);
  - Nutrient imbalance propagated up the food chain;
  - Acidification through loss of acid neutralizing capacity or base cations.

Overall, the workshop recommended that:

- the CBD continue to recognize that excessive N affects biodiversity;
- the LRTAP Convention continues to recognize that loss of biodiversity is an important adverse effect of N transport and deposition;
- a combined approach to the problem by both Conventions might be a productive means to address the impacts of N deposition on biodiversity.

52.4 Development of the Critical Loads Concept and Current and Potential Applications to Different Regions of the World

In some regions, including the EU and North America, the CL approach is used to quantify the extent of acidification and eutrophication impacts of N deposition on ecosystems. When atmospheric deposition of reactive N is below CLs, it is assumed not to cause adverse effects to plant species diversity. However, because ecological endpoints may differ regionally, the global usefulness of the critical loads concept must be carefully examined, especially with respect to regionally specific ecosystem services. The Workshop considered whether the critical load of N is a relevant, necessary and sufficient indicator to address adverse effects of reactive N on biodiversity in different regions of the world.

Critical loads for acidification have been computed and mapped in Asia, including critical loads for sulphur (S), N and acidity in China. On a global scale, the Stockholm Environment Institute (SEI) has assessed the sensitivity of soils to acid deposition and other studies have derived and mapped CLs of acidity and nutrient N for terrestrial ecosystems. Critical loads of nutrient N have been mostly used in semi-natural areas in Europe to protect biodiversity, but may merit application elsewhere. The relative importance of receptors, biodiversity-endpoints and N deposition varies among regions in the world. This has implications for the use of critical loads to support policies in the field of air pollution and biodiversity.

52.4.1 Current and Potential Application of Critical Loads Under CLRTAP and CBD

Critical loads are used under the LRTAP Convention to assess impacts of emission abatements on the environment in relation to both acidification and eutrophication. Furthermore, critical levels and health guidelines are important threshold indicators to protect human health and the environment. Reductions of the exceedance of critical loads and levels has been an explicit policy target in establishing effect-based LRTAP Convention protocols, including the protocol to abate acidification, eutrophication and ground level ozone (Gothenburg 1999), as well as the National Emission Ceilings Directive (NECD) for the European Union countries in 2001. Despite this progress, many ecosystems in Europe are still in exceedance of their CLs and levels.

The CBD formulated a target to be reached by 2010 “to achieve a significant reduction of the current rate of biodiversity loss at the global, regional and the national level as a contribution to poverty alleviation and to benefit all life on earth”, which has subsequently not been met. The CBD developed a number of indicators to assess progress toward meeting its 2010 target, including the ‘change in abundance of selected species’ and ‘nitrogen deposition,’ although reference to a critical load for N was not mentioned. In addition to the 2010 target of CBD, the European Commission developed its Biodiversity Conservation Strategy (ECBS), which was adopted in 1998. In support of the ECBS, the European Environment Agency developed indicators to monitor the progress towards the CBD 2010 target in a project entitled "Streamlining European 2010 Biodiversity Indicators" (SEBI 2010). For this effort, 26 indicators were proposed, including exceedance of the CL of N.

While biodiversity is an endpoint common to both the LRTAP Convention and the CBD, the development and use of critical loads is operational only under the LRTAP Convention. Other indicators related to excess ambient concentrations of reactive N, such as critical levels of ammonia and ozone, are included under the LRTAP Convention, but not used under either CBD or SEBI 2010. Conversely, indicators relevant to expressing the risk to biodiversity have been included in the set of indicators of both CBD and SEBI 2010, but do not feature in the effect-based work of the LRTAP Convention.

52.4.2 Critical Loads Concept and Application: Conclusions and Recommendations

Overall, the Workshop reached several general conclusions:

- The CL approach is a useful tool for assessing the ability of ecosystems to 'tolerate' reactive N inputs;
- There is still room for improvement in the formulation of the approach, but when used carefully, it can be a useful exploratory tool even if few data are available (e.g., soil N characteristics, deposition amounts);
- Optimal use of CLs requires expert knowledge of ecosystem structure and function to provide reference states in order to determine if deposition amounts exceed safe levels.

The Workshop reached specific conclusions and recommendations regarding the state of the knowledge and next steps in answer to the following questions:

- Can simplified approaches for estimating CLs be developed for new regions?
- How can existing CL approaches be improved?
- Can we separate out $NH_3$from NO_x in relation to CLs?
- Is there a need to develop freshwater CLs?
- How can the CL approach support the goals and work of the CBD?

52.4.2.1 Simplified Approaches for Estimating Critical Loads in New Regions

Conclusion First approximations can be useful even if they are coarse. Workshop discussions clarified that certain types of systems are most likely to be affected by excess N, such as nutrient poor communities, highly weathered soils, and seasonally dry sites. Identification of sensitive systems using simplified approaches could target areas where development of empirical data is needed to improve modelling.

Recommendation Countries not currently using a CL approach should be encouraged to develop it, firstly by using overlay maps for assessing mass balance parameters (e.g., soil, land cover, deposition) in order to assess which regions might be sensitive to N deposition. Simplified approaches may be most useful for countries in regions (e.g., South America, Africa, Asia) where insufficient information is available in order to initiate engagement in an assessment process.

52.4.2.2 How Can Existing Critical Load Approaches Be Improved?

Conclusion It is important to increase the certainty of CL calculations by focusing on empirical data needs, particularly for understudied ecosystems (e.g., tropical, Mediterranean, high elevation environments).

Recommendations Improve modelling approaches (e.g. the steady state mass balance approach used under the LRTAP Convention), particularly the estimation of required parameters such as soil nitrate leaching and denitrification. Improvement of dynamic models for predicting plant community changes and continued work on existing models to determine CL values is also required.

52.4.2.3 Can We Separate Out NH_3 from NO_x in Relation to Critical Loads?

Conclusion Currently, the state-of-the-art does not allow separate consideration of the two N species. The view was expressed by soil chemists that the nitrification of NH_3 to NO_xoccurs very rapidly in most soils and that the effects could not easily be separated. Exceptions might occur under wet, anoxic conditions, but these would be important at local scales, rather than regionally. By contrast, it is has been shown that oxidized versus reduced N, and dry versus wet deposition had given different effects in a limited number of experimental studies, including on epiphytic lichens species composition.

Recommendation This topic provoked significant debate among Workshop participants, but no final position was reached due to the relative paucity of knowledge in this area. Workshop participants recommended that substantial efforts should be made to improve knowledge in this area.

52.4.2.4 Is There a Need to Develop Freshwater Critical Loads?

Conclusion Understanding in this area could be improved, and areas of concern include high elevation areas, northern ecosystems, and estuarine/coastal areas.

Recommendation Efforts should be made to improve knowledge on this topic, and the approach must include both N and P as drivers.

52.4.2.5 How Can the Critical Load Approach Support the Goals and Work of the CBD?

Conclusion Air pollution is one of many threats to plant and animal communities, along with other issues such as climate change and land-use. Though the stressors are intertwined, CL analysis provides a tool which can help sort out the contribution of air pollutants to community disturbance.

Recommendation Biodiversity reference goals should be defined (i.e., what state is desired?) for the CL approach to be most useful. Ecosystem specialists should be consulted to determine what future states are "desirable" in order to determine what N pollution pressure is "tolerable" (i.e., the critical load) to achieve the desired state.

52.5 Impacts of Nitrogen Deposition on Ecosystem Services in Interaction with Other Nutrients, air Pollutants and Climate Change

Ecosystems provide a full suite of services that are vital to human health and livelihood. The Millennium Ecosystem Assessment (MEA 2005) distinguished four categories of ecosystem services: provisioning, regulating, supporting and cultural. Provisioning services involve the role of ecosystems in supplying products such as food, fibre, wood/fuel, and fresh water. Regulating services refer to the regulation of climate, water quantity (e.g., ground water recharge, occurrence of floods), water quality and diseases, and are related to the impact of ecosystems on greenhouse gas exchange and buffering and filtering capacity of the soil affecting water and element fluxes. Supporting services relate to the capacity of natural and semi-natural ecosystems to regulate essential ecological processes and life support systems through bio-geochemical cycles. Cultural services relate to the role that ecosystems play in recreation and tourism, aesthetic and educational considerations, and changes to ecosystems of cultural significance such as the loss of iconic species.

52.5.1 Relationships Between Nitrogen Deposition and Impacts on Ecosystem Services with Other Nutrients, Air Pollutants and Climate Change

There are many ways in which N deposition may affect ecosystem services. Examples include impacts on:

- Diversity of plant species through impacts on habitat for wild plants, affecting biological diversity and related products (provisioning service);
- Production of crops and forests (provisioning service of timber/wood fuel) and carbon sequestration (climate regulating service);

- Production of non-CO_2 greenhouse gases (methane, N_2O, ozone) and plant albedo (climate regulating services);
- Water quantity by affecting water uptake and thereby ground water recharge and runoff to surface waters (provisioning service of fresh water and water regulating service);
- Water/soil quality by its impact on acidity (pH) and on soil accumulation and leaching of N, aluminium and metals to ground water and surface water (regulating service, i.e. clean soil and water);
- Soil biodiversity and thereby nutrient cycling and primary production (supporting service).

52.5.2 Nitrogen Deposition and Ecosystem Services: Conclusions and Recommendations

The Workshop reviewed the present state of the knowledge on N deposition in relation to impacts on ecosystem services, as well as potential interactions with additional stressors, such as climate change and other pollutants. The Workshop agreed on the following general conclusions:

- Organic N is an overlooked N input that can range from 20 % (land-based) to 40 % (oceans) of total N input and is important for ecosystem functioning;
- Nitrogen budgets in ecosystems are essential to determine the cycling and effects of N in the system;
- Reducing uncertainty in N deposition estimates is key to untangling different threats to ecosystem services (e.g., climate, land use, GHGs).
- Tropospheric ozone pollution (of which NO_x is a precursor) often has a negative impact on net primary productivity and the net interaction between N deposition and tropospheric ozone is unclear;
- Nitrogen deposition inhibits methane uptake and increases N_2O emission (especially through nitrate inputs) in forests;
- Nitrogen deposition increases the C sink in forests, but 5–10 % of this effect tends to be counteracted by altered N_2O and methane fluxes with the atmosphere.

The Workshop reached specific conclusions and recommendations regarding the state of the knowledge and next steps in answer to the following questions:

- What are the most important ecosystem services affected by N deposition?
- On which services should the most attention be focused?
- What is the linkage between plant species diversity changes, as the main indicator for critical N loads, on faunal species diversity and biodiversity-based products, such as impacts on edible wild plants, medicinal plants?
- Is there a linkage between biodiversity changes and ecosystem services or are most effects due to other more direct pathways?
- What other indicators in addition (or related) to effects on biodiversity can be used to assess CLs?

- How do other factors, such as climate, ozone, other inputs (CO_2, P), affect ecosystem services?
- Should other factors be taken into account in CL assessments or are the critical limits for other effects less stringent than those for biodiversity (e.g., nitrate leaching occurs after the biodiversity limits are exceeded)?
- Do we need to take regional differences into account and, if so, at what scale?

52.5.2.1 Conclusions Regarding Ecosystems Services

There is strong evidence for cause-effect relationships between N deposition and ecosystem service impacts for most important ecosystem services. The workshop identified important ecosystem services that are affected by N deposition, in addition to biodiversity impacts. Focusing on semi-natural areas, participants identified several ecosystem service categories and relationships:

- *Climate regulation*—Life cycle analysis studies show no net-effect of N addition. However, forests and grasslands can sequester more C per kg N added up to an optimal level, with a loss of C occurring above the optimal level. More uncertain is the net effect of N inputs on peatland, tropical systems and savannas, and the role of fires. The temporal scale must be addressed.
- *Water quality and quantity*—The group identified water quality impacts in relation to human health, with consideration of the 1 mg N/l limit for human health impacts, as well as impacts on fresh water ecosystem issues (e.g., algae blooms, acidification) and impacts on estuarine systems (e.g., food/fish production).
- *Atmospheric (= 'ecosystem') service*—Nitrogen emissions and atmospheric concentrations affect important atmospheric services, such as aerosols and air quality (NO_x, O_3, particulate matter).
- *Cultural aspects*—Nitrogen inputs can have important impacts that affect recreation (fisheries, heathland), and is very important for 'healthy species and cultural landscapes,' which are impacted when biodiversity decreases.
- *Food and fibre*—Nitrogen inputs impact pollination, forage; soil productivity and fertility.
- In general, the most limiting services in relation to N deposition are: biodiversity; air quality/atmosphere; ecosystem changes; nitrate leaching; climate regulation; and cultural services.

The Workshop reached additional conclusions pertaining to impacts of N deposition on biodiversity and more generally:

- It is important to distinguish between different types of ecosystems/species, and the protection against N inputs should (apart from biodiversity) include other aspects related to the effects of N deposition;
- There is a potential conflict between GHG ecosystem services and biodiversity protection, and this is an important policy issue that should be considered;

- Long-range transport of N makes fertilization ‘uncontrolled.’ Fertilization for ecosystem services (carbon) should be done without losses. Land-use planning, especially in developing countries, is an option for preserving ecosystem services;
- Consideration should be give to whether an appropriate indicator is the optimum-N level or the N-tolerance level.

52.5.2.2 Recommendations Regarding Ecosystem Services

The Workshop recommended the following:

- Ecosystem services should be considered by both CBD and the LRTAP Convention in addition to biodiversity and CLs;
- Current knowledge on ecosystem services and N deposition is based on research in a limited area of the world. There should be increased research effort in various biomes, such as tropical regions, savannas, and peatlands;
- Nitrogen deposition should be better quantified, including organic-N, which is an important factor in cause-effect relationships;
- The CLs should be made more robust in relation to N, ozone, and climate;
- Efforts are needed to translate final ecosystem service benefits into effect indicators related to N-deposition, in addition to the eutrophic level;
- Ecosystem services are the responsibility of several authorities. A well communicated and coordinated effort is necessary to make the ecosystem services approach useful and viable in a policy and management context (e.g., Intergovernmental Platform on Biodiversity and Ecosystem Services, which was established in 2010).

52.6 Conclusions for Policy and International Conventions: Links Between Air Pollution and Biodiversity

The following main conclusions for policy development have been reported to the Executive Body of the Convention on Long-range Transboundary Air Pollution (UNECE 2009) and made available to the secretariat of the Convention on Biological Diversity (CBD).

Nitrogen deposition is currently one of the major drivers for detrimental effects on biological diversity. Total N deposition exceeding the critical loads, which represent long-term tolerance of ecosystems against pollutant load, and the deposition itself have been defined as risk indicators. These indicators are already in use by the CBD and LRTAP Conventions. They are based on sound scientific knowledge on the empirical and modelled impacts on sensitive receptors.

The exceedance of CLs of N and the total N deposition have been linked to observed changes in the flora and fauna of aquatic and terrestrial ecosystems. Nitrogen critical loads have been successfully used in policy support in Europe and are being developed for North America. However, comprehensive experience in applying them at the global level is still lacking. Further practical indicators, developed by various research and policy processes, are needed to describe the negative impacts of N on biodiversity. They may link to generic receptors, such as to forests and sensitive coastal areas, or be targeted, such as on endangered species or conservation areas.

In addition to N deposition, also other air pollutants and changes in climatic conditions and land use affect biodiversity simultaneously. Therefore, links to related work within the climate change community[1] would further enhance the necessary understanding of the interlinkages of the problem. This could also help to assess impacts in the long-term timeframe, e.g. 2100 and further. Currently, the LRTAP Convention and tentatively the Convention on Biological Diversity emphasize the main target year 2020, but also have considered visionary, aspirational targets for 2050. Such time scales would help in discussing the desired status of biodiversity, as historical conditions may not be achievable.

Increased collaboration at the technical level between the three scientific communities on air pollution, biodiversity and climate change brings considerable benefits for scientific work supporting policy discussions. Specified bodies of the LRTAP Convention[2] and the Convention on Biological Diversity[3] could exchange data and methodologies, e.g. at joint technical meetings. Such work should make the best use of existing networks on monitoring, modelling and policy support, and propose further work to fill the main gaps in the knowledge.

As a first step, the experts recommended:

a. The LRTAP Convention Executive Body invites the Bureau of the Working Group on Effects, the Bureau of the EMEP Steering Body and the Co-Chairs of the Task Force on Reactive Nitrogen, in consultation with the secretariat, to explore possibilities for collaboration with appropriate technical bodies under the Convention on Biological Diversity, and report to the Executive Body at its session in 2010;
b. The secretariat to the Convention on Biological Diversity explores possibilities for collaboration between its appropriate bodies and those under the LRTAP Convention.

[1] The United Nations Framework Convention on Climate Change (UNFCCC) and the Intergovernmental Panel on Climate Change (IPCC).

[2] Representing both the scientific and policy-oriented bodies, for example, the International Cooperative Programme on Modelling and Mapping, the Task Force on Reactive Nitrogen, and the Task Force on Integrated Assessment Modelling.

[3] For example, the Subsidiary Body for the Scientific, Technical and Technological Advice and the planned Intergovernmental Panel Biodiversity and Ecosystem Services.

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Appendix

The following additional papers resulting from the Expert Workshop on "Nitrogen deposition, critical loads and biodiversity" have been included in a Special Issue Section of the journal Environmental Pollution (volume 159 (10), 2211–2299, October 2011):

Goodale, C.L., Dise, N.B., Sutton, M.A. (2011). Special issue on nitrogen deposition, critical loads, and biodiversity. Introduction. *Environmental Pollution 159* (10), 2211–2213.

Cornell, S.E. (2011). Atmospheric nitrogen deposition: Revisiting the question of the importance of the organic component. *Environmental Pollution 159* (10), 2214–2222.

Posch, M., Aherne, J., Hettelingh, J.-P. (2011). Nitrogen critical loads using biodiversity-related critical limits. *Environmental Pollution 159* (10), 2223–2227.

Lu, X., Mo, J., Gilliam, F.S., Yu, G., Zhang, W., Fang, Y., Huang, J. (2011). Effects of experimental nitrogen additions on plant diversity in tropical forests of contrasting disturbance regimes in southern China. *Environmental Pollution 159* (10), 2228–2235.

Jacobson, T.K.B., Bustamante, M.M.da C., Kozovits, A.R. (2011). Diversity of shrub tree layer, leaf litter decomposition and N release in a Brazilian Cerrado under N, P and N plus P additions. *Environmental Pollution 159* (10), 2236–2242.

Stevens, C.J., Duprè, C., Dorland, E., Gaudnik, C., Gowing, D.J.G., Bleeker,A., Diekmann, M., Alard, D., Bobbink, R., Fowler, D., Corcket, E., Mountford, J.O., Vandvik, V., Aarrestad, P.A., Muller, S., Dise, N.B. (2011). The impact of nitrogen deposition on acid grasslands in the Atlantic region of Europe. *Environmental Pollution 159* (10), 2243–2250.

Liu, X., Duan, L., Mo, J., Du, E., Shen, J., Lu, X., Zhang, Y., Zhou, X., He, C., Zhang, F. (2011). Nitrogen deposition and its ecological impact in China: An overview. *Environmental Pollution 159* (10), 2251–2264.

Ochoa-Hueso, R., Allen, E.B., Branquinho, C., Cruz, C., Dias, T., Fenn, M.E., Manrique, E., Pérez-Corona, M. E., Sheppard, L.J. Stock, W.D. (2011). Nitrogen de-

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DOI 10.1007/978-94-007-7939-6,

position effects on Mediterranean-type ecosystems: An ecological assessment. *Environmental Pollution, 159* (10), 2265–2279.

Bleeker, A., Hicks, W.K., Dentener, F., Galloway, J., Erisman, J.W. (2011). N deposition as a threat to the World's protected areas under the Convention on Biological Diversity. *Environmental Pollution 159* (10), 2280–2288.

De Vries, W., Posch, M. (2011). Modelling the impact of nitrogen deposition, climate change and nutrient limitations on tree carbon sequestration in Europe for the period 1900–2050. *Environmental Pollution 159* (10), 2289–2299.

Glossary of Key Terms

Acidification (of soil)
The loss of nutrient bases (calcium, magnesium, potassium) in the soil, through leaching, and their replacement by acidic elements (hydrogen and aluminium). Pollutant nitrogen deposition (e.g. nitrogen oxides and ammonia) enhances the rate of acidification.

Atmospheric Deposition
Removal of suspended material from the atmosphere, this can be classed as either 'wet' or 'dry'. Wet deposition occurs when material is removed from the atmosphere by precipitation. In dry deposition, the material is removed from the atmosphere by contact with a surface.

Biodiversity
Biodiversity is the variability among living organisms, from genes to the biosphere. The value of biodiversity is multi-fold, from preserving the integrity of the biosphere as a whole, to providing food and medicine, to spiritual and aesthetic well-being.

Carbon sequestration
The capture and removal of carbon dioxide from the atmosphere and storing it in an alternative carbon related reservoir, e.g. soil organic matter, charcoal, tree growth.

Critical Level
Concentration or cumulative exposure of atmospheric pollutants above which direct adverse effects on sensitive vegetation may occur according to present knowledge.

Critical Load
A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

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Ecosystem services
The benefits people obtain from ecosystems. These include provisioning services such as food and water; regulating services such as flood and disease control; cultural services such as spiritual, recreational, and cultural benefits; and supporting services such as nutrient cycling that maintain the conditions for life on Earth.

Eutrophication
The enrichment of the nutrient load in ecosystems (terrestrial and aquatic), especially compounds of nitrogen and/or phosphorus. This leads to an undesirable disturbance to the balance of organisms in the ecosystem, affecting terrestrial and aquatic biodiversity and water quality.

Exceedance
The amount of pollution above a 'critical level' or 'critical load', expressed in different ways, such as accumulated area of exceedance.

Leaching
The washing out of soluble ions and compounds by water draining through soil.

Nitrogen cascade
A term used to describe the passage of reactive nitrogen through the environment.

Nutrient Nitrogen Critical Load
Empirical nutrient nitrogen critical loads are based on observed changes in the structure or function of ecosystems as reported in the refereed literature from the results of experimental or field studies, or in a few cases dynamic ecosystem modelling.

Reactive nitrogen
Collectively any chemical form of nitrogen other than di-nitrogen (N_2), the unreactive gas which makes up around 78 % of the atmosphere. Reactive nitrogen (N_r) compounds include ammonia (NH_3), nitric oxide and nitrogen dioxide (NO_x), nitrous oxide (N_2O), nitrate (NO_3^-) and many other chemical forms, and are involved in a wide range of chemical, biological and physical processes.

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