Raia-Silva Massad
Benjamin Loubet *Editors*

Review and Integration of Biosphere-Atmosphere Modelling of Reactive Trace Gases and Volatile Aerosols

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Editors
Raia-Silva Massad
INRA, AgroParisTech, UMR1402
ECOSYS
Thiverval-Grignon
France

Benjamin Loubet
INRA, AgroParisTech, UMR1402
ECOSYS
Thiverval-Grignon
France

Éditions Quæ, R10, 78026 Versailles cedex, France

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Abstract

A full understanding of land-atmosphere exchange processes is a key to properly assess the air pollution and climate change impacts on humans and ecosystems as well as the link between climate change and air quality. Biogenic trace gas emissions used in air quality models are simplified and mostly based on the emission factors that are constitutively unable to integrate the impacts of climate change. Similarly, deposition of tropospheric pollutants in air quality models is simplified, and the effects of land-use changes on emissions and depositions are currently not well defined. We should therefore aim at better quantifying the contribution of terrestrial surfaces to atmospheric pollution and the global greenhouse gas balance.

There is, however, at present no coherent model framework that can encompass the wide range of processes and their interactions that proceed in or near the canopy, and to a large extent govern the carbon and nitrogen land–atmosphere exchanges. In particular, this is true for those processes that operate on short timescales and involve reactive gases and aerosol particles. There is a need to identify major mechanisms and factors affecting the exchange of trace gases and volatile aerosols between the biosphere and the atmosphere and to improve methodologies currently used in accounting for emissions and deposition in landscape- and global-scale models. Moreover, a change in paradigm is needed to consider bidirectional exchanges rather than emission and deposition separately.

Experts in biosphere–atmosphere exchange of trace gases and aerosols came together in Paris in September 2012 in order to integrate the most recent advances made in the field into a common modelling framework adapted for local-, regional- and global-scale models. The international workshop was jointly organized by the EU-COST 804 action, the EU-FP7 ‘Eclaire’ Integrated Project and the INRA and AgroParistech French research institutions. This book reports the major outcomes of the workshop in the form of four reviews based on four different compound types: (i) ammonia, (ii) ozone and nitrous oxides, (iii) volatile organic compounds and (iv) aerosols and acid gases given in the first part. The second part provides four synthesis chapters by compound type on recent research results, key challenges and shortcomings. The third part comprises four synthesis chapters on recent advances and key challenges on the components of a common modelling framework: (i) stomatal exchange and ecosystem functioning, (ii) surface and in-canopy chemistry, (iii) within-canopy turbulence and (iv) soil and litter emissions. The final section consists of a conclusion which proposes a common conceptual modelling framework for reactive trace gases and volatile aerosols exchange in chemical transport model.

Acknowledgments

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We are thankful to the Institut National de Recherche Agronomique, Agronomy and Environment department as well as the AgroParitech for funding and hosting the Workshop.

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Introduction

R.-S. Massad and B. Loubet

The earth system consists of a large number of interacting components. The atmosphere for example is not only controlled by chemical and turbulent processes occurring in situ but also by fluxes of energy and a variety of chemical species between the atmosphere and the biosphere and hydrosphere. Global change is probably going to affect the extent and distribution of these processes. Traditionally the ocean, atmosphere, cryosphere, and biosphere have been considered separately due to strong boundaries between the disciplines. The importance of interactions between the different components is however now firmly recognised.

When considering biosphere—atmosphere exchange of trace gases and volatile aerosols, significant advances have been made in recent years both from an experimental and modelling point of view and on several scales, going from organ to plant to plot and to the landscape level. The current parameterisation of dry deposition of gaseous compounds mostly used in global atmospheric transport models is developed according to the scheme of Wesely (1989). This parameterization was slightly updated by Walmsley and Wesely (1996) but still represents the state of knowledge of the mid 1980s, based on the measurements available at the time. Since then, chemical analysers and measurement techniques have advanced significantly and an increasing number of flux measurements have been made over the past 20 years with large spatial distributions with the development of measurement networks (e.g. FLUXNET, ACCENT). This has resulted not only in identifying major mechanisms and factors affecting the exchange of trace gases and volatile aerosols between the biosphere and

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R.-S. Massad (✉) · B. Loubet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France
e-mail: Raia.Massad@grignon.inra.fr

B. Loubet
e-mail: Benjamin.Loubet@grignon.inra.fr

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the atmosphere, but also to recognize several gaps in the methodologies currently used in accounting for emissions and deposition in landscape and global scale models. For example it is now recognized that several compounds can be released but also taken up by plant stomata. This is well known for ammonia (NH_3) (Schjoerring et al. 1998, 2000; Sutton et al. 1995) but a biological compensation point has also been suggested for nitrogen dioxide (NO_2) and nitric oxide (NO) (Gessler et al. 2000, 2002). Concerning leaf surface deposition, the actual description is based on Henry's constant and reactivity of the chemical species, but there is increasing evidence that this approach tends to underestimate deposition rates (ozone O_3, sulfur dioxide SO_2,…) (Fowler et al. 2009; Massman 2004). Moreover, this deposition rate is affected by chemical interactions both on leaf surfaces and in the canopy airspace (Burkhardt et al. 2009; Flechard et al. 1999). For example, soil emission of NO results in an additional O_3 sink in forest canopies (Dorsey et al. 2004; Duyzer et al. 2004), while co-deposition effects can enhance the deposition rate of NH_3 and SO_2 (Erisman and Wyers 1993; Fowler et al. 2005). Similarly, dry deposition velocities of aerosols are usually calculated by theoretical approaches, most of which are variants and extrapolations of the model developed by Slinn (1982), based on wind tunnel measurements of deposition to grass. Finally, aerosols deposition rates appear to be heavily influenced by atmospheric stability which is not considered in current theoretical predictions.

These interactions are not usually considered in existing modelling routines. While a hierarchy of approaches is possible, a central aim must be to develop numerical models in which the best possible representation of the various processes is included and in which the processes interact systematically. Mechanistic or at least improved empirical descriptions of the underlying processes of these responses need to be included explicitly in surface/atmosphere exchange schemes for global models to be able to respond to changes in climate, chemical composition and vegetation status dynamically.

We can therefore aim at better quantifying the contribution of terrestrial surfaces to atmospheric pollution and the global greenhouse gas balance by developing the relevant components of such a 'top-of-the-range' model to address interactions between atmospheric composition (gas phase and aerosols) and surface emissions and deposition.

Organisation and Structure of the Workshop

Based on these observations a Workshop was held in Paris from the 25th to 27th September 2012 organized and funded by Eclaire FP7 project, COST action ABBA (ES0804), INRA-Ecosys and AgroParistech.

The workshop was structured around three main parts as shown in Fig. 1.

The first part was aimed at reviewing exchange processes and modelling schemes, parameterisations and datasets according to four sets of compounds chosen to be self-consistent: NH_3, NO_x/O_3, Volatile Organic Compounds (VOC) and Aerosols and acid gases. It was organized in a plenary session where background documents were presented followed by four parallel sessions for discussions.

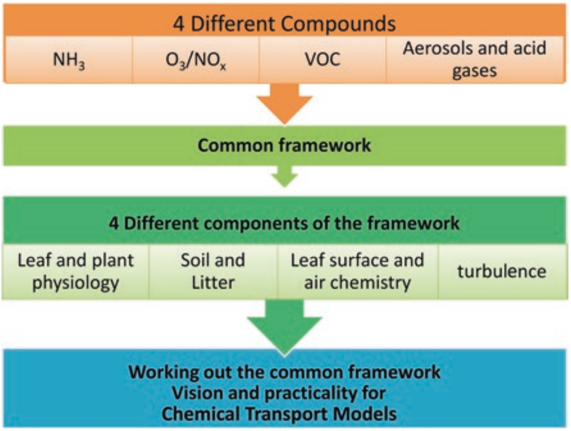

Fig. 1 Structure and organization of the Paris-2012 workshop

The second part consisted of a plenary session where the European Surface Exchange (ESX) model structure was presented followed by discussions on a common conceptual framework to model soil-vegetation-atmosphere exchange of reactive trace gases and aerosols accounting for in-canopy transfer and chemical interactions.

Part three was aimed at integration among different compounds by discussing in parallel sessions around the key elements of the agreed common framework. Those elements were the stomatal exchange with a link to plant physiology, soil and litter exchange, leaf surface exchange and a link to in-canopy chemical reactions, and within canopy turbulent exchange.

The number of participants was around 50, from most of European countries, with four participants from North America (3 from USA and 1 from Canada) and one from Africa (Côte d'Ivoire). Master-2 students from AgroParisTech specialised in "biosphere-atmosphere interactions" followed the workshop and produced a synthesis of the discussions for a "non-specialist" audience that was diffused on the web (https://colloque6.inra.fr/cost_eclaire/Reports/Short-synthesis-presentation).

Objectives

The objective of the workshop was to bring together experts in biosphere-atmosphere exchange of trace gases and aerosols in order to integrate their most recent advances into a common modelling framework adapted for local, regional and global scale models. This required identifying key processes to integrate in future model developments, linking different reactive species together through chemical interactions both on surfaces (plant, soil and litter) and within plant canopies, and reviewing existing measurements on dry deposition and deriving parameterisations for surface exchange models.

- The first goal of the workshop was therefore to review existing exchange processes and modelling schemes, parameterisations and datasets for each of the following compounds: O_3, NO_x, NH_3, VOCs, acid gases and aerosols.

- The second goal was to discuss a common conceptual framework for a soil vegetation atmosphere scheme, which includes acid–gas interactions and in-canopy transfer and chemistry for application from the site up to the global scale.
- The third goal was to discuss the key elements of the agreed common framework (surface chemistry and deposition, in-canopy turbulence and chemistry, stomatal uptake and plant physiology, and soil and litter), for each of the compounds of interest.

Document Structure

This document summarizes the outcomes and contributions to this workshop. It has a structure that is similar to the workshop itself and consists of three main parts.

The first part revolves around review papers that summarize the existing literature and knowledge according to each compound type that were prepared before the workshop and is followed by the reports of the parallel working group discussions on each compound. The second part is a compilation of synthesis around a common conceptual framework organized by compound type and the third is a compilation of syntheses organized by model component type.

A general discussion section is included at the end of the document.

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Part I

Review Documents

Four review documents:

- Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange, Chris R. Flechard, Raia. S. Massad, Benjamin Loubet, Erwan Personne, David Simpson, Eiko Nemitz and Mark A. Sutton.

This manuscript made a very comprehensive review on NH_3 exchange processes and modelling from leaf to global scale. It pointed towards a new paradigm for modelling NH_3 exchange bi-directionally in atmospheric transport and chemistry models, with three layers (soil, plant and atmosphere), including a soil/litter emission potential and a stomatal emission potential both related to the nitrogen status of the ecosystem. The paper also pointed towards the need for "dynamic" agricultural emission "inventories", which would depend on environmental conditions ("NH_3 emissions would be larger in a warm year"). Finally the document recognised the need for a pollution and climate dependent cuticular deposition of NH_3 (NH_3 deposition depends on surface humidity and on the presence of other compounds like acids), and identified the links with ecosystem and surface chemistry models.

- Review on modelling atmosphere-biosphere exchange of Ozone and Nitrogen oxides, Laurens Ganzeveld, Christof Ammann and Benjamin Loubet.

This manuscript made a concise synthesis on NO–NO_2–O_3 exchanges between the atmosphere and terrestrial ecosystems. The manuscript described the main processes involved in these exchanges: turbulent transfer, homogeneous chemical reactions and absorption-adsorption processes at the leaf and the soil surface. The paper pointed towards the need to physically characterise and possibly parameterise O_3 non-stomatal exchange (interaction at the leaf and soil surface, interaction with humidity, soil and leaf surface chemical composition). The uncertainties in NO_2 deposition was also pointed out, and especially the drivers and parameterisation of NO_2 compensation point and potential non-stomatal exchange. Potential interactions of O_3 and NO_x with very reactive VOC were also identified as a gap in current knowledge. The paper finally acknowledged the need for an explicit chemistry and transport model of O_3 and NO_x within the canopy and for a precise modelling of environmental drivers (turbulence, radiation, surface temperature and humidity, stomatal conductance). The lack of high quality consistent datasets on the range of existing ecosystems was also pointed out.

- Bidirectional exchange of volatile organic compounds, Alex Guenther.

This manuscript recalled the number of VOCs and therefore the complexity of modelling VOCs biosphere-atmosphere exchange. To overcome this complexity, a new classification scheme is proposed for VOCs into three major categories based on their surface-exchange behaviour: (1) the reduced VOCs (RVOC), which are mainly emitted by ecosystems and not produced in the atmosphere; (2) the atmospheric oxidation products (AOVOC) which are secondary VOCs produced by oxidation of RVOC in the atmosphere (these include in particular methyl vinyl ketone, MVK, and methacrolein, MAC), and are mainly deposited. However contradictory data show MVK and MAC emissions by stressed plants. The final category (3) is the bidirectional VOCs (BDVOC), for which emission and deposition processes are of similar importance. These include acetaldehyde, formaldehyde, acetic acid and formic acid. The exchange of BDVOC may be represented by compensation points approaches.

- Surface/atmosphere exchange of atmospheric acids and aerosols, including the effect and model treatment of chemical interactions, Eiko Nemitz.

This manuscript makes a review of existing knowledge and models of acid gases (HNO_3, HCl, HONO, SO_2, and organics) and volatile aerosol exchanges. The manuscript points toward the lack of quality data on acid gases depositions and also on some compounds concentrations like hydrochloric acid (HCl) and organics which are not modelled in most current CTM and for which sources are lacking. The manuscript details the volatilisation/condensation process involved in volatile aerosols exchange at the surface and points towards the need to take into account this knowledge to re-analyse aerosol exchange measurements. The mechanism of aerosol evaporation while it is deposited may indeed lead to the miss-interpretation of observed fine aerosol emissions. The manuscript shows the complexity of the volatile aerosol deposition and its interaction with acid gases and ammonia. The issue of developing simplified parameterisations is asked.

Advances in Understanding, Models and Parameterizations of Biosphere-Atmosphere Ammonia Exchange

C.R. Flechard, R.-S. Massad, B. Loubet, E. Personne, D. Simpson, J.O. Bash, E.J. Cooter, E. Nemitz and M.A. Sutton

Introduction

Ammonia in the Environment

Ammonia (NH_3) emission from the biosphere to the atmosphere is one of the many unintended consequences of reactive nitrogen (N_r) creation from inert dinitrogen gas (N_2) through symbiotic biological nitrogen fixation (BNF) and the

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C.R. Flechard (✉)
INRA, Agrocampus Ouest, UMR1069 Sol Agro-hydrosysteme Spatialisation,
35042 Rennes, France
e-mail: chris.flechard@rennes.inra.fr

R.-S. Massad · B. Loubet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

E. Personne
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

D. Simpson
EMEP MSC-W, Norwegian Meteorological Institute, Oslo, Norway

D. Simpson
Department Earth and Space Sciences, Chalmers University of Technology,
Gothenburg, Sweden

J.O. Bash · E.J. Cooter
National Exposure Research Laboratory, Office of Research and Development,
US Environmental Protection Agency, Research Triangle Park, NC 27711, USA

E. Nemitz · M.A. Sutton
Center for Ecology and Hydrology (CEH) Edinburgh, Penicuik, UK

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Haber-Bosch process, and of the agricultural usage of the fixed N_r for crop and meat production (Sutton et al. 2011). Conversely, NH_3 emission is also one of the main precursors of the nitrogen cascade (Galloway et al. 2003), whereby the N atom of the NH_3 molecule may potentially participate in a number of environmental impacts through a series of pathways and chemical and (micro-)biological transformations in the biosphere. As airborne NH_3 is transported downwind from sources, chemically processed in the atmosphere, and dry- and wet-deposited to the Earth's surface, it may be converted in air, vegetation, soils and water successively to NH_4^+, NH_3^-, NO, N_2O, many organic N forms, threatening in terms of air quality, water quality, soil quality, the greenhouse gas balance, ecosystems and biodiversity—5 key threats identified by Sutton et al. (2011).

Quantitatively, NH_3 is currently believed to account for approximately half of all global biospheric, anthropogenic and natural atmospheric N_r emissions, with N_r defined and inventoried as the sum of NH_3–N and oxidized nitrogen NO_x–N. Global estimates of NH_3 and NO_x emissions provided by the Emissions Database for Global Atmospheric Research (EDGAR 2011) were 40.6 and 37.2 Tg N year^{-1} for the year 2008, respectively. Agricultural NH_3 emissions dominate and are of the order of 27–38 Tg NH_3–N year^{-1} (Beusen et al. 2008). Uncertainties in global NH_3 emissions are large, possibly up to 30–40 %, as shown by the variability in other published global figures (e.g. calculated estimates of 75 (50–128), by Schlesinger and Hartley 1992; 45 Tg NH_3–N year^{-1} by Dentener and Crutzen 1994; 54 Tg NH_3–N year^{-1} by Bouwman et al. 1997; 43 Tg NH_3–N year^{-1} by van Aardenne et al. 2001). By comparison, the global biological and industrial N_2 fixation is of the order of 140 Tg N year^{-1} (Galloway et al. 2003), of which NH_3 emissions represent a loss of approximately one-third. The environmental impacts of NH_3 are expected to become more pronounced in many regions of the world where increases in NH_3 emissions are expected to occur during the 21st century, as a result of agricultural intensification and the manifold effects of climatic change on N cycling.

Within the European Union (EU-27), total NH_3 and NO_x emission estimates are also of the same order, at 3.0 and 2.8 Tg N year^{-1}, respectively (European Environment Agency 2012; Sutton et al. 2011), contributing around 7.5 % of global emissions. Although EU-27 NH_3 emissions declined by 28 % from 1990 to 2010, the share of NH_3 in total European N_r emissions increased from 44 % to reach the current level of 51 %, because NO_x emissions almost halved (−47 %) over the same 20 year period (European Environment Agency 2012), due to very significant NO_x emission abatements in the transport, industry and energy sectors. A range of NH_3 emission projections in Europe tend to indicate either a small increase, or possibly a slow linear decline of the order of ~25 % by the year 2100, while NO_x emissions are projected to decline exponentially by ~75 % over the same time horizon (Winiwarter et al. 2011).

As oxidised N_r eventually takes a backseat to reduced N_r emissions in Europe and N. America, the degree to which NH_3 will control atmospheric chemistry and N deposition to sensitive ecosystems is set to increase over the next few decades. In addition, because NH_3 emissions largely originate in agriculture and are predominantly the result of biological processes (with the notable exception of biomass burning and forest fires—e.g. R'Honi et al. 2013), they are much more weather/climate sensitive than are NO_x emissions, which are dominated by industrial, domestic and traffic combustion processes. With global temperatures expected to rise by a few K, and based on thermodynamic considerations (a volatilisation Q_{10} of 3–4), agricultural NH_3 emissions could increase substantially over the 21st century, although water availability is also a critical factor, favouring mineralisation of organic N sources while suppressing NH_3 emissions by allowing dilution and infiltration (Sutton et al. 2013). The net impact of rising temperatures and altered spatial/seasonal precipitation patterns on regional and global NH_3 budgets is as yet uncertain, with the uncertainty being compounded by land-use and land-cover changes and evolving agricultural practices (e.g. fertilization rates, spreading techniques, grazing density). Such an assessment will require the development of fully mechanistic, climate-dependent models for the quantification of surface/atmosphere NH_3 exchange under global environmental change (Sutton et al. 2013).

Requirements for Different Ammonia Exchange Models

Predicting global-change-induced alterations of NH_3 emissions and dry deposition is just one out of a range of environmental issues and ecological applications requiring biosphere/atmosphere NH_3 exchange modelling, along with e.g. local N deposition impacts assessments (Hertel et al. 2011; Theobald et al. 2004, 2009; Sutton et al. 1998b; Loubet et al. 2009a), air quality studies (Pinder et al. 2007; Wu et al. 2008), and transboundary air pollution flux estimation (Simpson et al. 2012; Berge et al. 1999). Models of surface/atmosphere NH_3 exchange have been both developed and applied for a number of purposes and at a large range of spatial scales ranging from the leaf or plant (Massad et al. 2010a), the canopy or ecosystem (Sutton et al. 1998a; Nemitz et al. 2001a; Riedo et al. 2002; Personne et al. 2009), the landscape (Loubet et al. 2009a; Hertel et al. 2006), to the national/regional level (van Pul et al. 2009; Bash et al. 2013) and to the globe (Dentener and Crutzen 1994).

The objectives of the modelling depend on the spatial and temporal scales at which models are ultimately applied. At the field/ecosystem scale, surface exchange models often come as an aid to the interpretation of measured flux data and to further process understanding (e.g. Sutton et al. 1995b; Flechard et al. 1999; Nemitz et al. 2000b; Spindler et al. 2001; Neirynck and Ceulemans 2008; Burkhardt et al. 2009), as the unexplained variability (residuals) points to potential model weaknesses and areas for further improvements. Models may also be used to fill gaps in measured flux time series in order to provide seasonal or annual NH_3 exchange budgets (Flechard et al. 2010). In the absence of measured fluxes, but based on local meteorology and measured ambient concentrations at given sites, inferential modelling provides NH_3 flux estimates for individual ecosystems (Smith et al. 2000; Zimmermann et al. 2006; Walker et al. 2008; Zhang et al. 2009; Flechard et al. 2011). At larger (landscape, regional, global) scales, surface/atmosphere schemes are parameterized for different land uses and embedded within modelling contexts that encompass the whole cycle (from an Earth-Atmosphere-Earth perspective) of emission, dispersion, transport, chemistry and deposition (van Pul et al. 2009; Asman et al. 1998).

The process understanding gained over the years from controlled environment studies and field-scale measurements is eventually formalized into soil-vegetation-atmosphere transfer (SVAT) models, which then feed—in simplified, generalized forms—into landscape-scale models (LSMs), regional or global chemistry and transport models (CTMs), and dynamic global vegetation models (DGVMs).

Ammonia Measurement and Modelling Approaches

The development, parameterization and validation of models over the years has been, to a large extent, underpinned by the ever-increasing availability of NH_3 concentration and/or flux datasets across all scales.

At sub-landscape scales (cuvette, chamber, plot, field), this has stemmed from technological advances in NH_3 flux measurement instrumentation, capable of adequate lower detection limits, continuous online analysis for extended periods of time, selective quantification of gaseous NH_3 from aerosol NH_4^+, together with tolerable troubleshooting and maintenance workloads. In particular, at the field scale, wet denuder systems with automated online detection (Wyers et al. 1993; Blatter et al. 1994; Erisman et al. 2001; Thomas et al. 2009) have helped produce many exchange flux datasets by aerodynamic gradient methods (AGM) or Bowen ratio techniques, both at remote background locations with low (sub-ppb) concentration levels (Flechard and Fowler 1998b; Milford et al. 2001a), and over polluted semi-natural ecosystems and fertilized agricultural systems (Wyers and Erisman 1998; Nemitz et al. 2000a, b; Neirynck and Ceulemans 2008; Sutton et al. 2009b; Flechard et al. 2010; Wolff et al. 2010a; Loubet et al. 2012; Walker et al. 2013). Relaxed eddy accumulation systems have allowed NH_3 flux measurements at one single height (Nemitz et al. 2001b; Meyers et al. 2006; Hensen et al. 2009a). In parallel, a range of new generation, fast-response optical and mass spectrometry instruments have emerged over the last 15 year (see von Bobrutzki et al. 2010, for a review and intercomparison), which have proved suitable for eddy covariance (EC) measurements of large (emission) fluxes such as those occurring after the land spreading of manures (Whitehead et al. 2008; Sintermann et al. 2011). However, many of these instruments have yet to realize their full potential for the smaller exchange fluxes typical of unfertilized background situations (Famulari et al. 2004), not least due to aerosol NH_4^+ interference and to high-frequency damping losses of NH_3 fluctuations from adsorption/desorption within the measurement system, especially air inlet lines and online filters (Ellis et al. 2010; Whitehead et al. 2008).

At landscape/regional/global scales, it is much harder to make flux measurements, and modelled surface/atmosphere exchange cannot easily be directly validated. At the landscape scale, limited use has been made of plume measurements and inverse modelling of strong sources (Hensen et al. 2009b; Flesch et al. 2007; Blackall et al. 2007; Loubet et al. 2009b; Carozzi et al. 2013). However, model evaluation, especially at the regional scale, typically relies on the indirect indicators provided by measured wet deposition of NH_x ($NH_3 + NH_4^+$) and, wherever available, ambient NH_3. Ammonia concentration measurements as part of spatial networks of atmospheric pollution monitoring using low-cost, long-term sampling, are available in few places worldwide (Tang et al. 2009; Adon et al. 2010). Encouragingly, recent developments in satellite-based infrared spectroscopy to map NH_3 concentrations (Clarisse et al. 2009; Shephard et al. 2011; R'Honi et al. 2013) suggest that the monitoring of NH_3 from space will help validate large-scale atmospheric models and refine current modelled estimates of regional and global NH_3 emissions.

Advances in instrumentation, flux measurements and process understanding since the early 1980s have allowed the atmospheric pollution modelling community to move from a unidirectional paradigm for NH_3 (fixed discrete point sources *versus* diffuse dry deposition everywhere else), to a dynamic bi-directional view, in which sources and sinks alternate in space and time depending on weather, pollution climate and agricultural management (Sutton et al. 2013). The major mechanisms and controls of NH_3 exchange have been identified at the substrate, plant, and ecosystem scales, even if there remain substantial gaps in knowledge, but the methodologies and models currently used to estimate emissions and deposition at landscape and regional scales have not all reached comparable levels of complexity. This is only partly due to computational limits (CPU time), as the very detailed processes operating at very short timescales might become prohibitive when run over regional and multi-annual scales. More likely, however, it is often a consequence of the lack of fine resolution, detailed input data required to run the schemes, compounded by the difficulty of turning largely heterogeneous measurement (flux) datasets into a generalised, unified and self-consistent modelling theory.

Scope of the Review

The state of the art of NH_3 surface/atmosphere exchange (measurement and modelling) has been examined in a number of reviews, e.g. Sutton et al. (1993c, 1995b, 2007, 2013), Asman et al. (1998), Nemitz et al. (2001a), Hertel et al. (2006, 2012), Loubet et al. (2009a), van Pul et al. (2009), Fowler et al. (2009), Wu et al. (2009), Massad et al. (2010b), Zhang et al. (2010). The present contribution seeks to bring together the most recent advances in measurements, understanding and modelling of surface/atmosphere NH_3 exchange over the vegetated land area, including the application of fertilizers, manures and slurry to farmland. Note that although NH_3

emissions from farmstead livestock housing and manure storage facilities represent around 20 % (and biomass burning an additional 15 %) of total emissions globally (EDGAR 2011), these will not be considered specifically. Similarly, sea/air exchange is not treated here, even though marine NH_3 emissions can be substantial, e.g. 30 Gg NH_3–N year^{-1} over the EMEP grid area (Barrett 1998).

The present paper focuses on bi-directional NH_3 exchange over vegetation and soils in both (semi)-natural vegetation and agricultural systems, as well as uni-directional exchange (emission) fluxes from land-applied mineral N fertilizers and manures. A brief overview is first given of the meteorological, thermodynamic, chemical and biological processes controlling NH_3 emission and uptake at the substrate, plant and ecosystem levels. Existing models of surface exchange are examined at the different scales from the leaf to the globe, with an emphasis on the development of canopy-scale models and their implementation at larger scales (landscape, regional). Although the conceptualization of a model and its parameterization (the calibration of its parameters based on observations) are quite different things, in the surface exchange literature the two terms have sometimes been used interchangeably. The ultimate objective of this work is to integrate current knowledge into a common modelling framework adapted for local, regional and global scale models, and to examine the degree to which measurement and input data are available, or missing, in order to parameterize, and ultimately run, surface/atmosphere exchange models at the different scales.

Processes Controlling NH_3 Emission and Uptake in the Soil/Plant/Atmosphere Continuum

Thermodynamic and Chemical Controls

At the level of each potential NH_3 source or sink in the soil/vegetation system (apoplast, leaf cuticle, surface water films, leaf litter, soil solution, fertilizer pellets, applied manure), the gaseous NH_3 concentration ($NH_{3,g}$) in equilibrium with dissolved [$NH_{3,aq}$] and [NH_4^+] is governed by Henry's law (K_h) and the NH_3 protonation constant (K_a) (Seinfeld and Pandis, 2006; see Montes et al. 2009, for a review of K_a and K_h parameterizations, and Fig. 1a, b). In the context of the atmospheric exchange through stomata with the leaf apoplast, this equilibrium concentration has been called the compensation point, here denoted χ_{cp}; the net gaseous NH_3 flux to or from the air surrounding the substrate then depends on the concentration difference χ_{cp}–χ_a, where x_a is the ambient NH_3 concentration (Farquhar et al. 1980). This differential between surface and air concentrations can be applied for many substrates: if the concentration gradient is zero then there is no net exchange flux; if $\chi_{cp} > \chi_a$ then NH_3 emission from the substrate occurs, while with $\chi_{cp} < \chi_a$ there is a net uptake by the substrate. By convention, a positive flux denotes NH_3 emission, negative indicates deposition or uptake.

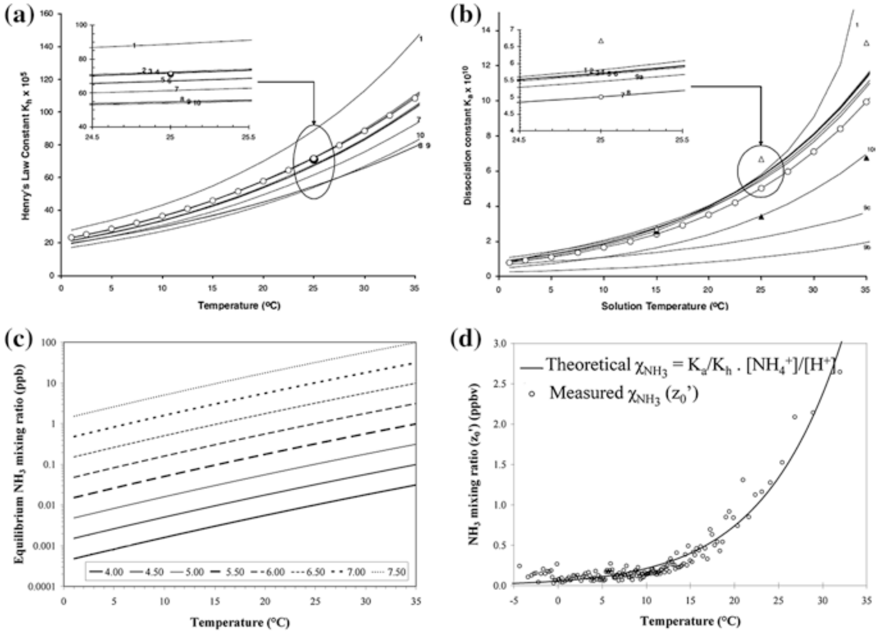

Fig. 1 Thermodynamic controls of the air/solution NH_3/NH_4^+ partitioning. **a** and **b** compilation by Montes et al. (2009) of published values, parameterizations and temperature dependencies of Henry's law coefficients (K_h) and dissociation constants (K_a); the curve numbers refer to specific experiments cited in Montes et al. (2009), for solutions ranging from pure water to slurries and high activity solutions; **c** theoretical equilibrium air NH_3 concentration of a 100 μM NH_4^+ solution as a function of temperature and showing the effect of pH in the range 4–7.5, calculated according to Sutton et al. (1994); **d** fitting of a theoretical thermodynamic curve to micrometeorologically measured surface NH_3 (Z_0') concentrations over Scottish peatland, resulting in a best fit for the $[NH_4^+]/[H^+]$ ratio (Γ) of 132 for the moorland ecosystem (Flechard and Fowler 1998b)

Temperature Effects and the R Ratio ($[NH_4^+]/[H^+]$)

Thermodynamics dictate that any warming of the substrate, at constant substrate pH, theoretically results in a displacement of dissolved NH_3 to the gas phase, promoting NH_3 emission or at least opposing uptake by the substrate from the air. The relationship of x_{cp} to temperature is exponential (Seinfeld and Pandis 2006), with a warming of 45 K roughly translating into a doubling of the compensation point (Fig. 1c) for a given $[NH_4^+]/[H^+]$ ratio in the liquid phase (Flechard and Fowler 2008). The $[NH_4^+]/[H^+]$ ratio is henceforth termed Γ and characterises the NH_3 emission potential, normalised for temperature. Measured values of Γ have been shown to be vastly variable (up to 5 orders of magnitude difference) between various parts of plant canopies, e.g. leaf surface water, soil, litter, bulk leaf tissue and the apoplast, e.g. in grassland (Sutton et al. 2009b; Burkhardt et al. 2009) and in maize (Walker et al. 2013), but the different χ_{cp} values all respond in the same way to temporal temperature changes as long as Γ is constant.

In practice, it is clear that ecosystem N and NH_4^+ pools are ever changing and that Γ values may undergo diurnal, seasonal and annual cycles in response to weather, phenology, senescence, etc., such that the theoretical temperature response with respect to NH_3 fluxes is not necessarily verified in the long term. Modelling approaches based on the temperature response of a Γ emission potential should therefore theoretically also deal with temporal Γ dynamics in the various parts of an ecosystem.

In the atmosphere, the reversible equilibrium of the gas/aerosol NH_3/HNO_3/NH_4NO_3 triad is also temperature (and relative humidity, RH) sensitive (Mozurkewich 1993), with likewise a displacement of aerosol-phase NH_4^+ and NO^- towards gaseous NH_3 and HNO_3 in warmer (and drier) conditions. Depending on the relative mixing ratios of NH_3, HNO_3 and NH_4NO_3, and on temperature and RH in the air column within and just above vegetation, gas/particle inter- conversion may alter the net NH_3 flux, as exchange velocities for gas-phase NH_3 and aerosol-phase NH_4^+ are different (Brost et al. 1988; Nemitz et al. 2004; see Section "Vertical Distribution of Sources and Sinks Withinand Above Ecosystems").

Surface/Substrate PH and Acid/Base Ratio

Substrate pH is also a major chemical control of NH_3 fluxes; for a constant $[NH_4^+]$ in solution the compensation point increases by a factor of 3.2 for every additional 0.5 pH unit, and by 10 for every pH unit (Fig. 1). Thus the wide range of pH values, and their temporal variations, typically encountered in plants and on other environmental surfaces, clearly show the importance of using accurate values in models of both emission from fertilizers and background bi-directional exchange. Apoplastic pH typically varies in the range 5–7 (Farquhar et al. 1980; Schjoerring et al. 1998; Hill et al. 2002; Massad et al. 2008), and a range of stress factors can induce temporal variations (Felle and Hanstein 2002). The pH of the apoplast can increase by a few tenths of a unit in drought-stressed plants (Sharp and Davies 2009), while both NH_3 and CO_2 can also alkalinize the apoplast (Hanstein and Felle 1999; Felle and Hanstein 2002). In grassland, Loubet et al. (2002) reported a sharp rise in apoplastic pH (from ~6.5 to ~7.5) as grazing animals were introduced to the pasture. Leaf age can be a factor; in perennial *Luzula sylvatica,* young leaves were found to have much higher apoplastic pH than old leaves, leading to 4 to 10-fold higher NH_3 compensation points (Hill et al. 2002).

On external leaf surfaces, the pH of rain and dew is typically acidic, in the range 3.5–6 (Burkhardt et al. 2009; Flechard et al. 1999), but alkaline conditions may also occur in plant surface wetness, resulting from the presence of soil particles (Sutton et al. 1993a; Walker et al. 2013). Also, instantaneous or chronic exposure to elevated NH_3 levels is likely to raise surface pH and affect the magnitude of the surface exchange flux (Wu et al. 2009).

Jones et al. (2007) showed that the non-stomatal resistance (R_{ns}) of moorland plants to the uptake of atmospheric NH_3 increased linearly with ambient NH_3 concentration in the range 0–100 $\mu g\ m^{-3}$. This indicates that at high ambient NH_3

levels, the non-stomatal dry deposition process is self-limiting as the cuticle and other canopy surfaces may become NH_3-saturated and a high pH strongly suppresses the effective NH_3 solubility. Such situations occur typically in the vicinity of point sources such as animal production facilities (Loubet et al. 2009a), where ambient concentrations decrease exponentially with distance, from typically >100 $\mu g\ m^{-3}$ within the nearest 50 m of animal buildings and manure storage areas down to less than 10 $\mu g\ m^{-3}$ within a kilometer (Walker et al. 2008).

The concurrent dry and wet deposition of acidic atmospheric gases and aerosols contributes to the regulation of plant surface pH, and much depends on the prevailing pollution climate, the occurrence and duration of surface wetness, and the relative abundancies of NH_3 (the major atmospheric base) and of atmospheric acids (Erisman and Wyers 1993; Flechard et al. 1999). Thus plant surface (cuticle, wetness) pH is the main (if implicit) underlying mechanism that accounts for some parameterizations for non-stomatal resistance to NH_3 deposition, developed in a range of publications (Erisman et al. 1994; Nemitz et al. 2001a; Massad et al. 2010b; Wichink-Kruit et al. 2010), and based on the atmospheric molar ratios of NH_3 to SO_2 or NH_3 to total acids (SO_2, HNO_3, HCl), as proxies of surface alkalinity/acidity.

For field applied manures, the pH of cattle and pig slurries is typically in the range 7.5–8, but values down to 6.3 and up to 9.0 have been reported (Sintermann et al. 2012). This, combined with the natural variability of soil pH across agricultural landscapes in which manures are applied to land, contributes to the large variability in fluxes and NH_3 emission factors (EF) (Genermont and Cellier 1997; Segaard et al. 2002; Sommer et al. 2003; Sintermann et al. 2012). It should be noted that farmers typically monitor and manage soil pH to insure it is in an optimal range for the crop being produced and models should take this into account when estimating NH_3 fluxes for agricultural crops.

Meteorological Controls

Weather affects ecosystem/atmosphere NH_3 exchange directly through the physical effects of wind speed, turbulence, global radiation, atmospheric stability and water (rainfall, dewfall, snowfall, evapotranspiration). The enhancement by wind speed and surface friction of NH_3 volatilisation rates after slurry spreading or inorganic fertilizer application is well documented, with the effect being quantified by the aerodynamic resistance (R_a) to heat and trace gas transfer (Genermont and Cellier 1997; Segaard et al. 2002; Sommer et al. 2003). After slurry spreading, the radiative heating of the surface drives the evaporation of water from deposited manure and possibly the formation of a crust, which adds an additional surface resistance (R_c) to the aerodynamic (R_a) and the laminar boundary layer (R_b) resistances to emission (Sommer et al. 2003).

Unstable atmospheric conditions favour convective mixing and NH_3 volatilisation, although they tend to co-occur with warm days with strong evaporation and high vapour pressure deficit (VPD), during which a slurry crust may form. Rainfall at the time of spreading tends to suppress NH_3 emission by diluting thick slurry and facilitating infiltration into the soil, where NH_4^+ ions adsorb to sites of cation exchange; however, after a dry period rainfall may dissolve the dry slurry crust and solubilise NH_4^+, which then becomes available for volatilisation. Similarly, short-lived NH_3 emission pulses may be triggered by rainfall after dry weather spells, for example in agricultural soils amended with mineral fertilizer and up to several weeks following fertilization (Walker et al. 2013), or in natural alkaline soils in arid environments, such as, e.g. the Mojave Desert (McCalley and Sparks 2008).

The same meteorological drivers similarly impact patterns of background and bi-directional exchange. Large wind speeds and unstable conditions reduce R_a and thus tend to increase emissions from the canopy (upward fluxes) as well as dry deposition (downward fluxes). However, large wind speeds also increase NH_3 dispersion (Loubet et al. 2009a) and thus tend to reduce ambient NH_3 concentration levels close to point sources (Flechard and Fowler 1998a), such that, although the exchange velocity is higher (higher turbulence, lower R_a), the dry deposition flux may not be greater (Flechard and Fowler 1998b).

Leaf Surface Wetness

The control by rainfall and dewfall is more straightforward, with leaf-surface water generally acting as a more efficient sink for highly water-soluble NH_3 than does a dry cuticle, and water droplets also physically blocking stomatal apertures (Zhang et al. 2003), all favouring dry deposition and limiting emission by the ecosystem. Water droplets, and also thin water films formed by deliquescent particles on leaf surfaces (Burkhardt and Eiden 1994), are often acidic and increase the affinity and sink potential of the canopy for atmospheric NH_3 (Flechard and Fowler 1998b), as well as for NH_3 emitted by the underlying soil and leaf litter (Nemitz et al. 2000a). Burkhardt and Eiden (1994) also describe a “wick” effect of microscopic water films, by which the migration of NH_4^+ ions between the apoplast and the external cuticle, along stomatal guard cell walls, is controlled by pH and NH_4^+ concentration gradients. Similarly, Sutton et al. (1995a) describe transcuticular fluxes of NH_4^+ between apoplast and leaf surface. Contrary to direct gaseous NH_3 transfer through stomates, such liquid-phase mediated transfers are controlled by the presence of free water and are controlled by relative humidity and/or the hygroscopicity of particles at the surface, but they do contribute to the net canopy-scale NH_3 flux.

The succession of wet and dry meteorological phases, such as nocturnal/diurnal cycles of dew formation and evaporation, and brief showers followed by sunny spells, may lead to alternating patterns of NH_3 uptake and re-emission from plant leaf surfaces. Cases of NH_3 desorption from cuticles following leaf surface water evaporation have been reported (Sutton et al. 1995c, 1998a; Flechard et al. 1999; Neirynck and Ceulemans 2008), demonstrating the reversibility of the non-stomatal uptake process. Further, recent NH_3 flux measurements over maize, coupled with surface water pH observations and controlled experiments, suggest that wet leaf surfaces may actually occasionally provide a less efficient sink for NH_3 than dry cuticles, as a result of trans-cuticular base cation leaching and the presence of alkaline soil particles, both raising the pH of surface wetness (Walker et al. 2013).

All the processes described above are dependent on prevailing meteorological conditions, with surface wetness being controlled by the ratio of rainfall to evapotranspiration (driven by atmospheric VPD, wind speed and net radiation), while soil particle emission (erosion) is governed by wind speed, soil dryness, as well as agricultural activities, e.g. tillage. Air, vegetation and soil temperatures control a host of plant physiological (Section "Plant Physiological Controls"), soil and microbiological processes (Section "Soil and Microbial Processes"). Plant growth and root NH_4^+ intake, microbial activity, ammonification (microbiological NH_4^+ fixation from N_2), nitrification (microbiological oxidation of NH_4^+ into NO^-), soil respiration (mineralisation of soil organic matter) and leaf litter decay, all generally increase with temperature (given adequate water and nutrient supply) and regulate the dynamics of ecosystem NH_4^+ pools and NH_3 exchange fluxes.

Plant Physiological Controls

Vegetation may be a net source or a net sink for NH_3, depending on the nitrogen status of plants and thus (indirectly) on the influx of nitrogen into the ecosystem, whether by fertilization of through atmospheric deposition (Massad et al. 2010b), providing a negative feedback where long-term NH_3 deposition tends toward ecosystem saturation (Sutton et al. 1993c). The present section focuses on the physiological parameters controlling the NH_x status of the apoplast of green leaves (defined as the intercellular space where water and solutes can move freely), stems and inflorescences, and to some extent of senescing attached leaves.

The Stomatal Compensation Point

Meyer (1973) was the first to recognize that NH_3 is present (as $NH_{3,aq}$ and NH_4^+) in intercellular fluids on the cell walls of the mesophyll cells of leaves (the apoplast), so that a compensation point air concentration of NH_3 exists. This was later shown in measurements by Lemon and Van Houtte (1980) and most famously by Farquhar et al. (1980). Prior studies using dynamic chamber measurements had typically shown consistent uptake by plant leaves and a direct control by stomatal conductance (e.g. Hutchinson et al. 1972), but the NH_3 concentrations applied to the chamber inlet were often much greater than typical ambient levels encountered in the field (0.1–10 $\mu g\ m^{-3}$), and above the stomatal compensation point (χ_s), precluding emissions from the apoplast. Since then, many controlled environment studies have shown linear relationships between ambient NH_3 (χ_a) concentration and the NH_3 flux, with a bi-directional exchange switching from an emission at low χ_a levels to an uptake at higher χ_a levels, the switch occurring at χ_s (Sutton et al. 1995b; Husted et al. 1996; Schjoerring et al. 1998; Hill et al. 2001).

The stomatal compensation point is the equilibrium NH_3 concentration associated with the $[NH_x]$ concentration in the apoplast, which results from the balance in healthy leaves of several production and consumption processes. These include: NH_4^+ import via the xylem; active (unidirectional) NH_4^+ transport into leaf cell cytoplasm and vacuole; passive (bi-directional) NH_3 transport between apoplast and cells; NH_4^+ assimilation within the cytoplasm into amino acids via the glutamine synthetase/glutamate synthetase (GS/GOGAT) cycle; and NH_4^+ generation by, e.g. photorespiration, nitrate reduction, protein turnover and lignin biosynthesis (Joy 1988; Schjoerring et al. 1998, 2002; Massad et al. 2008, 2010a). The experimental inhibition of GS by methionine sulfoximine in barley in the laboratory (Schjoerring et al. 1998), or the use of barley mutants with a reduced GS activity (Mattsson and Schjoerring 1996), both lead to NH_4^+ accumulation in the apoplast and dramatic increases in stomatal NH_3 emissions, demonstrating the critical role of GS (and GOGAT) in avoiding $NH_4{}^+$ accumulation in leaf tissues and regulating NH_3 emission.

Apoplastic PH

It is worth noting that, as the stomatal compensation point is not simply a function of $[NH_4^+]$ in the apoplast, but rather a direct function of the $[NH_4^+]/[H^+]$ ratio (or Γ) in the apoplast (Γ_s) (Section "Thermodynamic and Chemical Controls"), χ_s increases exponentially with pH. Any internal physiological regulation of apoplastic $[H^+]$ that does not have a commensurate effect on $[NH_4^+]$ therefore systematically affects χ_s and the stomatal NH_3 flux. Unlike intracellular pH, which must be maintained within a narrow range (7.2–7.5) to allow all plant metabolic functions to proceed, apoplastic pH is rather variable due to a fairly low passive buffer capacity (Felle and Hanstein 2002). The necessary regulation of intracellular pH is responsible for proton transfers across the cytoplasmic membrane, leading to apoplastic pH changes (Massad et al. 2008). In addition, plant responses to environmental stress factors such as drought have also been shown to affect apoplastic pH (Felle and Hanstein 2002; Sharp and Davies 2009), as do variations in ambient soluble trace gas (NH_3, CO_2) concentrations (Hanstein and Felle 1999). Thus small fluctuations in membrane transport, gas exchange (stomatal conductance) and intercellular mass exchange impact apoplastic pH (Felle and Hanstein 2002). Apoplastic pH is also believed to be influenced by N nutrition (Raven 1988), even if the effect is unclear (Massad et al. 2008). Plant species relying on NO^- nutrition and assumed to assimilate NO^- in the shoots tend to have higher apoplastic pH, while vegetation relying on mixed N sources (NH_4^+, NO^-, organic N) and more likely to favour root assimilation tend to exhibit lower apoplastic pH values (Hoffmann et al. 1992).

Plant Nitrogen Nutrition

Plant nitrogen uptake and status, development stage and species all affect Γ_s, resulting in diurnal and seasonal fluctuations at the ecosystem scale (Schjoerring et al. 1998; Massad et al. 2008, 2010b). The form of inorganic nitrogen (either NH_4^+ or NO^-) being taken up by roots has been shown to impact stomatal NH_3 emission significantly, with emissions from NH_4^+-fed barley being a factor 10 higher than those from NO^--fed plants, consistent with higher leaf tissue $[NH_4^+]$ and higher xylem NH_4^+ concentration, given equivalent N contents of the nutrient solution (Mattsson and Schjoerring 1996).

Such effects of N form may have consequences for spatial distributions of Γ_s values across landscapes, since well-aerated agricultural soils are generally NH_3^--rich and NH_4^+-poor, while in permanent grasslands, heathlands and mature forests the opposite situation prevails (Schjoerring et al. 1998). Even though it is often assumed that all NH_4^+ is assimilated in the roots prior to transport to the shoots as amino acids, some studies have shown that at least a fraction of NH_4^+ might be transported prior to assimilation (Massad et al. 2008). By contrast, upon absorption by roots, NH_3^- can either be reduced to NH_4^+ in root cells, stored in root cell vacuoles, exported via the xylem to the leaves or expelled to the outside of the root. Thus the NH_4^+ abundance in xylem and in the apoplast of leaves depends both on the soil $[NH_4^+]/[NH_3^-]$ ratio and on the balance of root assimilation, transport and storage in roots. Further, although Γ_s generally increases with increasing N supply (Mattsson and Schjoerring 1996), and preferentially with NH_4^+ supply to the roots for several plant species, the relationship between the amount of N absorbed by the roots and the compensation point is not straightforward because of a possible masking effect due to apoplastic pH change (Mattsson and Schjoerring 2002; Massad et al. 2008).

High concentrations of N and NH_4^+ in bulk leaf tissues are expected to result in high Γ_s values (Schjoerring et al. 1998). Mattson et al. (2009a) measured apoplastic pH and NH_4^+ concentrations of the eight most abundant graminae species of a fertilized grass sward in N. Germany, using the apoplas- tic extraction by vaccuum infiltration technique (Husted and Schjoerring 1995). This direct method for the determination of Γ_s is based on the measurement of the leaf apoplastic NH_4^+ concentration and pH by means of extraction with successive infiltration and centrifugation of leaf segments (Husted and Schjoerring 1995). The measured apoplastic NH_4^+ concentrations differed by almost one order of magnitude between species, while apoplastic pH values also varied from 6.0 to 6.9. The resulting Γ_s values ranged from about 30 to over 700 and correlated very strongly (linearly) to bulk leaf $[NH_4^+]$, with the consequence that three out of eight grass species with the highest stomatal compensation points could behave as NH_3 sources, while the remaining five species were consistent sinks throughout the 3 week measurement campaign. Such variations in stomatal NH_3 emission potentials among species within the same habitat demonstrate the challenge of modelling the exchange at the ecosystem scale.

Massad et al. (2010b) compiled 60 published values of Γ_s for non-managed (non-fertilized) ecosystem types including forests, heathlands and moorlands (average 502, range 3–5604), and 96 published Γ_s values for managed systems including croplands, and fertilized and/or grazed grasslands (average 782, range 16–5233). In addition to data obtained using the vaccuum infiltration technique, the data included estimates by cuvette-based controlled experiments and by field-scale micrometeorological flux measurements. Massad et al. (2010b) concluded that the key driver of Γ_s appears to be the total N input to the ecosystem (whether by fertilization, atmospheric deposition, or both), and that Γ_s values were positively and exponentially related to bulk tissue $[NH_4^+]$. Fertilized agricultural ecosystems generally show higher Γ_s values than semi-natural vegetation, although very large Γ_s values were also reported for example over polluted forest sites in the Netherlands and Belgium, which have been subjected to high nitrogen deposition loads for decades (Neirynck and Ceulemans 2008; Wyers and Erisman 1998).

Temporal Variations

The apoplastic Γ_s ratio undergoes temporal variations on seasonal (Fig. 2) and diurnal timescales. Seasonal variations are expected to occur since the assimilation, transport and turnover of nitrogen change dramatically with plant developmental stage, and the seasonal NH_3 exchange pattern may vary for different types of vegetation depending on which processes dominate the actual N utilization (Schjoerring et al. 1998).

In two barley *(Hordeum vulgare)* cultivars grown in hydroponics, Husted et al. (1996) showed a marked decrease in the NH_3 stomatal compensation point in the period from tillering to anthesis, followed by an increase during senescence. In a fertilized ryegrass *(Lolium perenne)* pasture, van Hove et al. (2002) found that mean spring and summer apoplastic $[NH_4^+]$ were a factor 2–3 lower than in autumn and winter, but no distinct trend for apoplastic pH. Similarly, in a beech *(Fagus sylvatica)* forest, Wang et al. (2011) measured a gradual decrease of Γ_s from leaf expansion (June) ($\Gamma_s > 150$) until the mid-season (August) ($\Gamma_s < 100$), followed by an increase during late season and approaching senescence ($\Gamma_s > 170$). Consequently, during the two (early season and late season) Γ_s peaks, the leaves could act as an NH_3 source, while during the mid-season stomatal uptake prevailed. The authors concluded that a low glutamine synthetase activity in young, emerging beech leaves as well as in senescent leaves and hence, a low capacity for NH_4^+ assimilation, resulted in increased concentrations of tissue and apoplastic NH_4^+. Cellular breakdown during senescence and the associated catabolism of proteins, amino acids and chlorophyll liberates large amounts of NH_4^+, which is no longer assimilated and raises the NH_3 emission potential of plants, even before leaves drop to the litter on the ground surface (Mattsson and Schjoerring 2003). Age-related differences in the NH_3 compensation point of

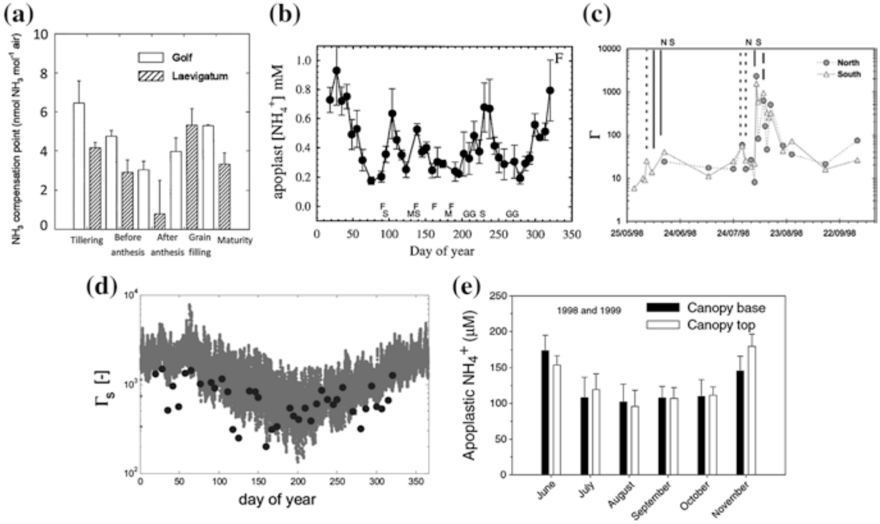

Fig. 2 Seasonal variations of: **a** stomatal compensation point in *Hordeum vulgare* (Husted et al. 1996); **b** apoplastic [NH_4^+] in fertilized and grazed *Lolium perenne* grassland (van Hove et al. 2002); **c** apoplastic Γ_s in fertilized and grazed *Lolium perenne* grassland in two adjacent fields (North and South) (Loubet et al. 2002); **d** apoplastic Γ_s in *Lolium perenne*/*Poa trivialis* grassland (Wichink-Kruit et al. 2010); and **e** apoplastic [NH_4^+] in *Fagus sylvatica* (Wang et al. 2011). In **b,** *F* and *S* indicate application of artificial fertilizer (calcium nitrate) and slurry, respectively; *M* mowing and *G* grazing by cows. In **c,** *vertical lines* indicate management events: *dotted lines* cut; *bold line* fertilization; *bold dashed lines* grazing. The Γ symbol represents the ratio [NH_4^+]/[H^+]

Luzula sylvatica were also found to be considerable (Hill et al. 2002), with both apoplastic pH and NH_4^+ concentrations increasing during leaf expansion and declining prior to senescence.

Diurnal patterns of Γ_s are generally less systematic than seasonal ones, even if there can be a large degree of hour-to-hour variability (Sutton et al. 2000; Herrmann et al. 2009; Flechard et al. 2010). Although diurnal cyles of NH_3 exchange fluxes have been observed in e.g. *Brassica napus* (Husted et al. 2000), *Hordeum vulgare* (Schjoerring et al. 1993) and tropical grassland (Trebs et al. 2006), with highest NH_3 emission rates typically occurring during the daytime and low rates at night, much of the observed diurnal variability in fluxes may be attributed to the temperature effect rather than to Γ_s (Sutton et al. 2000; Personne et al. 2009). Reported diurnal variations in apoplastic NH_4^+ and H^+ concentrations often do not follow any particular trend (Husted et al. 2000; vanHove et al. 2002), even if some observations in a mixed graminae sward did tend to indicate higher Γ_s values during the day than at night (Herrmann et al. 2009), especially after the grass was cut and fertilized.

Fertilization Effects on the Apoplastic Emission Potential

Agricultural management (fertilization, animal grazing, grass cutting) is another source of temporal variability for Γ_s. A number of studies have shown that, in managed agricultural systems, field fertilizer application results in a Γ_s peak during the days following the application and usually a return to the pre-fertilization value within one to two weeks. Mattsson and Schjoerring (2002) demonstrate that leaf apoplastic NH_4^+ is a highly dynamic pool, closely reflecting changes in the external (e.g. root) N supply. In fertilized *Lolium perenne* grassland, Loubet et al. (2002) measured an increase in both apoplastic $[NH_4^+]$ and Γ_s by up to two orders of magnitude immediately following the application of ammonium nitrate fertilizer, but the effect was short-lived, lasting only two weeks (Fig. 2). Mattsson et al. (2009b) also observed a sharp (factor 10) increase in the apoplastic NH_4^+ concentration of newly emerging leaves after cutting and fertilization of mixed grassland, whereby the NH_3 compensation point peaked the day after the fertilizer was applied and thereafter decreased over the following 10 days until reaching the same level as before fertilization. Smaller increases in Γ_s associated with grass cuts and grazing have also been reported (Milford et al. 2001b; van Hove et al. 2002; Loubet et al. 2002; Wang and Schjoerring 2012).

Stomatal Conductance

Another major physiological control of NH_3 exchange fluxes at the leaf and plant level is the regulation of stomatal opening and conductance, through which the gaseous exchange between the sub-stomatal cavity and the atmosphere is mediated. Stomatal conductance (G_s) has long been known to be controlled by global radiation (R_g) or photosynthetically active radiation (PAR), air temperature (T_a), vapour pressure deficit (VPD), and soil water content (SWC) (Jarvis et al. 1976; Emberson et al. 2000a, b). Heat and drought stress cause stomata to close during the daytime, reducing G_s, evapotranspiration, CO_2 assimilation and the stomata/atmosphere transfer of trace gases including NH_3. For example, NH_3 flux measurements over soybean during dry summer conditions showed much suppressed stomatal exchange fluxes, and the bulk of the exchange dominated by non-stomatal fluxes, due to limited soil water availability and drought affecting stomatal opening during the afternoon (Walker et al. 2006). Those authors pondered whether their results were representative of soybean within their study area, but it should be stressed that such measurements are extremely valuable to characterize NH_3 exchange in dry conditions and regions of the world, since a large majority of existing field NH_3 flux datasets are representative of reasonably well-watered conditions in temperate climates.

Further, research over the past 20–30 year has shown the impact of rising CO_2 (Ainsworth and Rogers 2007) and O_3 (Wittig et al. 2007) concentrations on stomatal conductance, with expected reductions of G_s of the order of −20 to −30 % for elevated CO_2 and −10 to −20 % for elevated O_3. Within the context of global change, such impacts on G_s should be accounted for when considering present and future scenarios of NH_3 exchange.

Soil and Microbial Processes

Many processes within the soil profile and on the soil surface lead to an NH_4^+ pool being present and available for exchange with the air column above the ground. Within the topsoil and particularly the root zone of any land ecosystem, the NH_4^+ pool is depleted by root absorption, by nitrification, by microbial immobilization, and by emission to the atmosphere; it is replenished by atmospheric deposition, by symbiotic N_2 fixation (BNF) and ammonification, by microbial turnover, by mineralization of soil organic matter (SOM) and of N-containing root exudates, and by the decay of leaf litter on the ground surface. Adsorption and binding to negatively charged clay mineral and organic colloids represent a transient pool, while dilution and infiltration through the deeper soil layers decrease the emission potential. In addition, in fertilized agricultural systems, the large and sporadic inputs of mineral and organic forms of N lead to sudden increases in available N and particularly NH_4^+, often well in excess of the instantaneous plant and microbial demand. In keeping with the Γ_s terminology adopted for the apoplastic $[NH_4^+]/[H^+]$ ratio, corresponding terms may be defined for the topsoil layer (Γ_{soil}), for the leaf litter (Γ_{litter}), or collectively a ground layer term (Γ_g). Figure 3 illustrates how typical values measured for Γ_{soil} and Γ_{litter} far outweigh (by 2–3 orders of magnitude) Γ_s values in fertilized cut grassland, especially during the days following the application of fertilizer.

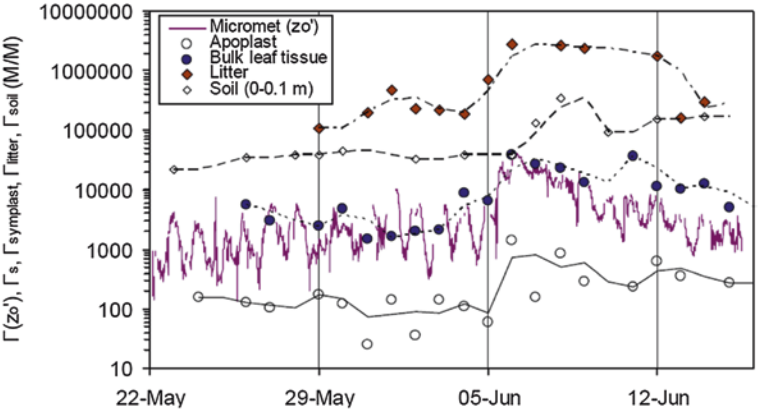

Fig. 3 Time course of estimated Γ values (ratio of $[NH_4^+]/[H^+]$) in different compartments of a mixed grassland ecosystem (from Sutton et al. 2009b). The grass was cut on 29 May and lifted for silage on 31 May. Fertilizer (100 kg Nha^{-1} as calcium ammonium nitrate) was applied on 5 June

Soil Background Emission Potential

Ammonium and ammonia are naturally present in soils as a product of microbial turnover and soil organic matter mineralisation, while fertilization (mineral and organic) as well as grazing in grasslands both supply large quantities of reduced N to agricultural soils. However, soil NH_4^+ is depleted by root uptake during the growing season, and by nitrification in well-aerated soils, while the soil NH_3 emission potential (Γ_{soil}) also largely depends on soil pH. One of the earliest studies on this effect made regional scale estimates of ammonia emission from soils based on mineralization rates, although at that time field verification of the modelled fluxes were missing (Dawson 1977).

In a more recent study over grassland, David et al. (2009) also identified the underlying soil as a strong potential source, but only after the grass was cut and for a short period of time (~1 day), and even then the soil potential emission was a factor of 3 lower than that of the leaf litter. However, few publications have ever shown soil below vegetation to be an ammonia source, be it below a grassland canopy in summer (Sutton et al. 1993b), under barley (Schjoerring et al. 1993), or oilseed rape (Nemitz et al. 2000a).

Neftel et al. (1998) actually suggested that soil must be a sink for NH_3 in a triticale field, since their semi-permeable membrane setup for direct measurements of NH_3 concentration in the soil showed consistently low ($<0.1\ \mu g\ m^{-3}$) concentrations. This was despite large measured $[NH_4^+]$ values in soil KCl extracts, which, accounting for the soil pH of 6.5, should have resulted in soil pore space NH_3 concentrations 2 orders of magnitude higher than those measured. They concluded from this discrepancy that the largest part of the estimated ammonium content in the soil was not in the liquid phase, but was instead adsorbed to solid soil particles, and thus not available for gas exchange with open porosity and the atmosphere. Similarly, Nemitz et al. (2000a) measured much lower NH_3 concentrations at a depth of -0.1 m within the soil than just above the leaf litter of oilseed rape, ruling out the possibility that the underlying soil may have been an NH_3 source in that study, and pointing to the importance of substantial NH_3 gradients at the air-soil-litter interface. There are altogether few reports of soil emission potentials for vegetated canopies in the literature that clearly distinguish the soil emission potential and flux from those associated with the leaf litter or the whole canopy (see Massad et al. 2010b for a review).

Soil Emissions After Fertilizer and Manure Application

Ammonia emission from the soil layer is most important after fertilization, especially if the fertilizer is urea-based or organic manure (Genermont et al. 1998; Segaard et al. 2002; Meyers et al. 2006; Sintermann et al. 2012). At the European scale, the land-spreading of organic manures is believed to contribute around 30–40 % of total NH_3 emissions (Sintermann et al. 2012, and references therein). Values of Γ_{soil} typically increase by one or several orders of magnitude after slurry spreading (Flechard et al. 2010). Although Fig. 3 indicates that Γ_{litter} was a factor of 10 higher than Γ_{soil} in the grassland system in Sutton et al. (2009b), even after fertilization, this study dealt with mineral fertilizer, and the situation is quite different for organic manures. A dominant mechanism of NH_3 loss to the atmosphere is the hydrolysis of urea and/or uric acid present in large quantities in animal wastes i.e. urine, slurries and farm yard manures, by the urease enzyme present in the excreted faeces and also in the soil. This leads to large concentrations of dissolved NH_x and thus a high pH, promoting NH_3 volatilisation from the liquid phase. Urea hydrolysis also produces dissolved inorganic carbon, and the subsequent volatilisation of CO_2 increases pH, while NH_3 volatilisation decreases pH and is in principle self-limiting.

Apart from meteorological effects (Section "Meteorological Controls"), the most important processes controlling NH_3 volatilisation are the ion production and buffering processes controlling the pH of the slurry/soil liquid, the solid chemistry that determines precipitation of NH_4^+ to slurry dry matter, the physical processes controlling the movement of slurry liquid into and within the soil, the interaction of slurry liquid with soil cation exchange capacity (CEC) (Sommer et al. 2003; Genermont and Cellier 1997). Note that the method of field application (splash plate, trailing hose, trailing shoe, soil injection) is also expected to make a difference, with "low emission" application techniques being promoted in a number of countries to abate field losses (Sintermann et al. 2012; Carozzi et al. 2013).

Soil pH is expected to be a critical parameter controlling the magnitude of the percentage loss of volatilised NH_3 to the total NH_x content of land-spread slurry, with emissions being effectively suppressed ($<5\ \%$ loss) at soil pH 5 and potentially reaching over 50 % at pH 7 (Genermont and Cellier 1997; Loubet et al. 2009a). However, in practice there remain questions regarding the extent to which soil pH influences NH_3 losses from surface applied fertilizer and manures, as incomplete mixing may typically occur. Thus when and where soil pH affects the flux is a very complex question.

Soil microbial nitrification of the applied manure or fertilizer NH_4^+ depletes the NH_x pool and thus may potentially limit the NH_3 emission potential in the days following field spreading. Whether nitrification significantly reduces NH_3 emission factors depends on nitrification rates, which have been shown to be extremely variable. For example Felber et al. (2012) measured very fast conversion of applied NH_4^+ from cattle slurry to NO^- in top soil (0–10 cm) of grassland, with most of the NH_4^+ being nitrified within 2 days. By contrast, Laubach et al. (2012) found that nitrification proceeded more slowly in grassland fertilized with cattle urine, as soil $[NH_4^+]$ only decreased by half over a week, although here soil $[NH_4^+]$ was roughly a factor of 50 higher than in the study by Felber et al. (2012). Such variability highlights the need to give nitrification proper consideration in models of NH_3 volatilisation.

Emissions from synthetic fertilizers depend on the form of inorganic N applied but are typically smaller per unit added N than from manures. Emission from urea-based compounds are larger than from ammonium nitrate fertilizers, which do not raise soil solution pH. The use of urease inhibitors has been shown to reduce and delay NH_3 volatilisation from urea in a number of field trials, including in a fertilized maize field, in which Walker et al. (2013) detected two distinct emission pulses spread over one month.

Despite extensive trials with a large literature over the last 25 year and good fundamental understanding of NH_3 losses from field-applied manures and fertilizers (e.g. Segaard et al. 2002, and the Ammonia Loss from Field-applied Animal Manure (ALFAM) database), there remain substantial uncertainties in field-scale NH_3 fluxes and the associated emission factors (EF). Sintermann et al. (2012) compiled and reviewed over 350 EF measurements published between 1991 and 2011 and raised questions about the representativeness, and possible overestimation, of NH_3 fluxes measured in medium-sized (20 m diameter) plots by mass balance methods such as the integrated horizontal flux (IHF) approach. The authors point out that emerging NH_3 volatilisation flux measurements at the field (>1 ha) scale over the last 5–10 year generally indicate much lower (~factor 2) NH_3 losses, typically below 30 % of slurry NH_x content, than did many medium-sized plot measurements carried out in the early 1990s (typically 50–80 % losses), with serious implications for local and regional scale NH_3 budgets. A recent re-assessment by Neftel et al. (2013) of EF measurements made in Switzerland in the early 1990s, using the z_{inst} (simplified IHF) method (Wilson et al. 1982), hinted that these early EF values may have been significantly overestimated due to a combination of at least three factors, all leading to a systematic overestimation: over-speeding of the cup anemometers near the ground, cross-interference of plots located at distances of 70 m, and inadequate values of the z_{inst} scaling factor. Such careful reanalyses of historical EF datasets from other countries might provide clues for the apparent discrepancies, or inconsistencies, reported in Sintermann et al. (2012).

Emission Potential of the Leaf Litter and Influence of Plant and Ecosystem N Cycling

Apart from fertilizer-induced NH_3 volatilisation, significant emissions may also occur from soil in barren land and in senescent plant canopies where leaf litter on the soil surface contributes to emissions (Sutton et al. 2009b; Massad et al. 2010b). Ammonia emissions from the leaf litter, even if understood in principle, remain very uncertain due to the limited number of studies (e.g. Denmead et al. 1976; Harper et al. 1987; Nemitz et al. 2000a; Mattsson and Schjoerring 2003; David et al. 2009; Wang and Schjoerring 2012). The literature generally indicates very large Γ_{litter} values but their temporal dynamics are poorly understood. By contrast to mineralization rates of plant litter incorporated into soils (e.g. Nicolardot et al. 1995), little is known about processes within detached leaves lying on the ground surface. Schjoerring et al. (1998) argued that NH_4^+ production by mineralization and liberation in the leaf tissue are coupled to degradation of chlorophyll and of soluble proteins in detached senescent leaves; this is by contrast to senescing leaves that are still attached to the plant, which still have a relatively efficient N remobilisation and are able to avoid accumulation of correspondingly high NH_4^+ levels by transfer to other parts of the plant.

For the ground leaf litter, it has been assumed that $[NH_4^+]$ is controlled by the litter water content, by mineralization and nitrification rates as well as the amount of $[NH_4^+]$ released to the atmosphere as NH_3 (Nemitz et al. 2000a). The NH_3 emission potential of the leaf litter (Γ_{litter}) is first and foremost dependent on the initial bulk N content of senescent leaves as they become detached from the plant; N-rich leaves are obviously more likely than N-poor leaves to liberate large amounts of NH_4^+ via mineralisation on the ground. The nitrogen content of plant residues is controlled by contrasting processes in perennial woody species and in annual or biennial non-woody plants, as detailed hereafter.

Role of Translocation on the Leaf Litter Nitrogen Content of Trees

In trees, the litter N content is controlled by the ratio of ecosystem-internal N cycling (litter production, mineralisation, root uptake) to tree internal N cycling (assimilation, translocation, storage). These processes ensure that large amounts of N remain available to the plant and are moderately protected against immobilisation in stable soil organic compounds or losses via leaching and gaseous emission (Wang et al. 2013). The N status of attached senescing leaves is controlled by the degree to which N is retranslocated from such leaves into the rest of the tree before leaf fall. The re-translocation is directed either into woody roots and/or the trunks in deciduous species, or from previous years leaves into the youngest age class needles in conifers. The resulting reduction in foliar N content may be expressed as the fraction of N re-translocation relative to the initial N content in the green leaves.

Comparing three European forests subject to contrasting atmospheric N deposition loads, Wang et al. (2013) found that this N re-translocation efficiency was lowest in a Douglas fir stand (37 %) subject to very large (45 kg N ha^{-1} $year^{-1}$) N deposition, compared to a temperate beech forest (70 %) and a boreal pine stand (62 %) exposed to much lower N deposition (ca. 20 and 5 kg Nha–1 $year^{-1}$, respectively). The boreal pine site thus returned the lowest amount of N via foliage litter to the soil, while the temperate Douglas fir stand returned the highest amount of litter N to the ground. The authors concluded that forests activate very different mechanisms to reduce N losses in foliage litter production: (i) increased N re-translocation efficiency, (ii) increased leaf longevity, (iii) decreased foliage N content and and (iv) decreased foliage mass. Despite the lowest leaf longevity and highest leaf N contents, the beech canopy reduced the N losses via leaf litter production by having very efficient N re-translocation prior to leaf fall.

Nitrogen Content in Leaf Litter and Other Residues in Crops and Grassland

Nitrogen re-allocation from ageing leaves to younger leaves, to growing seeds and to storage for the next growing season may also occur in annual and biennial non-woody plants, such as many agricultural crops, and in perennial grasslands (Wang and Schjoerring 2012). However, in many cases all the non-harvested above-ground biomass eventually returns to soil, either as litterfall during the growing season, or after harvest. Thus the soil layer is the ultimate resting place for the non-harvested stem and foliar N, both from bottom- canopy senescent leaves dropping to litter during the growing season, as well as litterfall following complete senescence or harvest. In a ryegrass *(Lolium perenne)* grassland, Wang and Schjoerring (2012) found that green photosynthesizing leaves generally had the largest total N concentration, followed by stems and inflorescences. By contrast, the lowest total N content occurred in senescent leaves, indicative of N re-allocation. The situation was reversed for the bulk Γ ratio (total leaf tissue $[NH_4^+]/[H^+]$), with green leaves and stems generally showing substantially lower Γ values than senescent leaves and litter. Thus, although remobilization had reduced total N concentrations in senescent leaves and litter, mineralization of organic N compounds still lead to much higher bulk $[NH_4^+]$ values than in green leaves.

Many studies have observed large NH_3 concentrations near the ground surface and litter in closed canopies (e.g. Denmead et al. 1976; Nemitz et al. 2000a), resulting from the production and accumulation of NH_4^+ by mineralisation of litter organic compounds. In mixed grassland, David et al. (2009) defined the litter as the sum of both senescing attached leaves and dead/decomposing detached leaves. By means of dynamic chamber measurements (cuvette), they found that emissions from the litter were the largest source in the canopy and that emissions were higher from wet than from dry litter. They also found that peak NH_3 emissions from litter leaves occurred both after a step decrease and a step increase of air relative humidity, due to a change in either increased evaporation or increased mineralization. This was consistent with the findings within an oilseed rape canopy by Nemitz et al. (2000a), who demonstrated with a simple dynamic litter model that shrinking liquid pools within the leaf litter lead to more concentrated NH_4^+ pools and increased emissions. Here, measurements of within- canopy vertical NH_3 concentration profiles, from a depth of −0.1 m in the soil up to the top of the oilseed rape canopy (1.4 m), showed mean in-soil and top-canopy concentrations of the same order (1–2 $\mu g\ m^{-3}$), but much higher concentrations (~9 $\mu g\ m^{-3}$) just above the leaf litter. This information, coupled with the inverse Lagrangian modelling technique (ILT) (Raupach 1989) to determine the vertical distribution of NH_3 concentration, sources and sinks within the canopy, demonstrated the existence of a large emission potential within decomposing litter leaves on the soil surface, which was consistent with previous studies (e.g. Denmead et al. 1976). However, in order to simulate diurnal variations of the measured NH_3 concentration at the surface of the leaf litter (χ_{litter}), Nemitz et al. (2000a) needed to adopt a dynamic approach for Γ_{litter}. By contrast, using a constant Γ_{litter} resulted in an overestimation of χ_{litter} at the start and an underestimation of χ_{litter} towards the end of the modelled period. This reflected the dynamics of the litter NH_4^+ pool, which could be shown in a simple dynamic model to be controlled by (a) mineralization and nitrification rates according to Dawson (1977) and (b) the response of the leaf water content to relative humidity (RH), as proposed by van Hove and Adema (1996).

Vertical Distribution of Sources and Sinks Within and Above Ecosystems

The magnitude and direction (or sign) of the net vegetation/atmosphere NH_3 flux are controlled by the difference between the ambient NH_3 concentration (χ_a) and the canopy compensation point, denoted χ_c and introduced by Sutton et al. (1995b). The x_c modelling concept (further developed in Section "Ammonia Exchange Models and Parameterizationsfrom the Leaf to the Globe: State-of-the-Art") reflects the fact that both NH_3 emission and deposition may co-occur at different levels within a canopy or plant-soil system, with for example emissions by a leaf litter on the soil surface and by sunlit stomates in the upper part of the canopy, concurrent with deposition to wet non-stomatal leaf surfaces and also possibly uptake by cooler, shaded stomates in the lower part of the canopy (Sutton et al. 1995a; Nemitz et al. 2000a, b, 2001a; Personne et al. 2009). Given this multi-layered vertical distribution of sources and sinks and internal canopy cycling of NH_3, χ_c defines the net bulk, canopy-scale potential for emission or deposition when set against the atmospheric NH_3 concentration x_a occurring overhead.

Micrometeorological NH_3 flux measurements made above ecosystems provide estimates of the net exchange between the whole soil/litter/canopy system (including the within-canopy air space) and the free atmosphere. Such ecosystem-scale measurements by themselves do not provide the sink and source contributions of the different canopy components (soil, litter, stomates, green leaves, senescing leaves, stems, inflorescences, non-stomatal (cuticular) surfaces, etc.) to the net exchange. Measurements using dynamic chamber may be used to isolate certain terms, such as individual leaves, soil or litter, but other terms such as the partitioning between stomatal and non-stomatal fluxes (Sutton et al. 1995a), or the air column sink/source term from gas-particle interconversion (GPIC) (Brost et al. 1988; Nemitz et al. 1996), can only be apprehended by using models. The ability to model the different canopy component flux terms quantitatively is crucial to determine the net canopy-scale flux (for e.g. regional-scale modelling), but it also provides insights into the NH_3 canopy cycling and reveals potential feedbacks between total N inputs and the net NH_3 flux (Sutton et al. 1995a).

The NH_3 exchange literature shows many examples of vertical stratification of sources and sinks within soil-plants systems, and of widely varying NH_3 emission potentials for canopy components. This is exemplified by the different Γ ratios (Fig. 3) in grassland, ranging over 4–5 orders of magnitude (Sutton et al. 2009b), and by a similar picture in maize (Walker et al. 2013), which also included a Γ term for leaf surface wetness (dew, guttation).

Within-Canopy Vertical NH_3 Concentration Profiles

The vertical distribution of—and relationships between—the various NH_3 sources and sinks are influenced by canopy structure, leaf area index (LAI) and leaf area density profile, which control within-canopy turbulence as well as vertical profiles of wind speed, NH_3, temperature and RH. Ammonia profiles within cereal canopies have often shown the largest concentration at mid-canopy, at the height of the greatest leaf density (e.g. Meixner et al. 1996), which was consistent with the widely held assumption that, above cereal crops, NH_3 emissions mostly originate from stomata (e.g. Farquhar et al. 1980). By contrast, in canopies of grass-clover pasture as well as soybeans, oilseed rape and quackgrass, within-canopy profiles showed the highest concentrations at ground level (Denmead et al. 1976; Lemon and van Houtte 1980; Sutton et al. 1993b; Nemitz et al. 2000a, 2009a; Bash et al. 2010), which is generally attributed to leaf litter decomposition and NH_3 emission from the soil. In the light of the latter studies, and especially given the much larger emission potentials associated with the soil and leaf litter than with the apoplast (Fig. 3), the role of stomatal emissions as a major control of the net canopy-scale flux must be re-examined.

Although the apoplast may, under certain circumstances, act as an NH_3 source, this very much depends on the vertical position of leaves, which is correlated with their age, temperature, and their proximity to the free atmosphere or to the soil/litter layer.

Recapture of Soil/Litter-Emitted NH_3 by the Overlying Canopy

For agricultural crops during the growing season, soil emissions might be expected to be largely recaptured by the overlying canopy, either by stomatal absorption or by surface wetness uptake (Nemitz et al. 2000a; Meyers et al. 2006). In practice, the fraction of NH_3 estimated to be recaptured is very variable between studies.

The ability of plant canopies to recapture substantial amounts of NH_3 released from fertilizer or plant residues at the ground is an important issue in agricultural air quality that is still a matter of debate (Denmead et al. 2008). For example, management options to reduce NH_3 volatilization losses from urea include to delay its field application (Denmead et al. 2008), or to use urease inhibitors (Walker et al. 2013). In the second of these, it is envisaged that a developed canopy would attenuate canopy wind speeds, leading to lower transport rates in the canopy air space, increased NH_3 concentrations, and greater uptake by the canopy foliage (Denmead et al. 2008).

By combining vertical in-canopy NH_3 profile measurements with ILT modelling, Nemitz et al. (2000a) calculated that all NH_3 emitted from the ground level was recaptured within the lowest half of an oilseed rape canopy, except during windy nighttime conditions, and that the net ecosystem daytime emission (measured by the flux gradient technique above the canopy) originated from the top half of the canopy. The N loss from the plant's top leaves and siliques (seed cases) to the atmosphere as gaseous NH_3 was more than balanced by the lower leaves uptake from NH_3 emitted by decomposing leaf litter. Similarly, in a fully developed grassland canopy (before cutting), Nemitz et al. (2009a) measured in-canopy profiles of NH_3, which again were consistent with a large ground-level source, presumably from senescent plant parts, which was entirely recaptured by the overlying canopy. This ground-level source was believed to be responsible for the sustained NH_3 emissions observed after grass cutting, as indicated by independent bioassay and chamber measurements (David et al. 2009). The GRassland AMmonia Interactions Across Europe (GRAMINAE) grassland experiment, summarised by Sutton et al. (2009a, b), demonstrated that overall, net above-canopy fluxes were mostly determined by stomatal and cuticular uptake before the cut, by leaf litter emissions after the cut, and by fertilizer and litter emissions after fertilization.

A range of other experiments in crops have shown only partial canopy recapture of soil emissions. In maize, Bash et al. (2010) calculated, using an analytical first-order closure inverse source/sink model, that the fraction of soil-emitted NH_3 that was recaptured by the overlying canopy was 73 % for fertilizer applied to the soil surface (see also Walker et al. 2013). In another maize canopy, over which dairy waste effluent was spread, Harper et al. (2000) found that 17 % of the soil NH_3 emission was recaptured by the canopy during one ILT modelling run in mid-afternoon. However, overall only 21 % of the net emissions came from the soil, while 79 % came from the foliage. This occurred because the fertilizer was sprayed from above the canopy, so that much of the NH_3 was emitted from leaf surfaces even before the fertilizer hit the ground. This shows that the fertilizer application method alters the soil-canopy source and sink relationship and should be accounted for in CTMs as a way to more accurately simulate the impact of agricultural management practices on fertilizer NH_3 emissions.

In a sugarcane crop, Denmead et al. (2008) estimated that the percentage of canopy recapture of NH_3 volatilized from urea fertilizer applied to the ground was of the order of 20 % for a LAI of 2, but they indicated that this fraction would increase with LAI, and that the efficiency of NH_3 recapture would be different in denser canopies or crops with different canopy structure. By extension, in dry climates, and for young and/or sparse or recently cut vegetation (grassland), the soil source strength potential is likely to be more fully expressed (as net emission to the atmosphere), since the canopy recapture fraction is likely to be small. In such systems, if the soil layer r ratio is large, then the net canopy-scale flux is likely to be largely independent of stomatal and leaf surface exchange if LAI is small (Nemitz et al. 2001a).

Gas-Particle Interconversion (GPIC) Within and Above the Canopy

Air column chemistry within and above the canopy, and particularly the reversible thermodynamic equilibria of the NH_3–HNO_3–NH_4NO_3 and NH_3–HCl–NH_4Cl gas-aerosol triads, is known to affect NH_3 surface-atmosphere exchange rates

(Brost et al. 1988). There are three ways in which gas- particle conversion and aerosol evaporation affect NH_3 fluxes and local N_r budgets (Nemitz et al. 2009b):

1. Vertical flux divergence and error in flux measurement. The presence of additional sources or sinks in the air below the flux measurement height means that the measured flux differs from the true surface exchange. Thus, fluxes measured by micrometeorological techniques that operate at a single measurement height (z_m), such as EC and relaxed eddy accumulation (REA), may need to be corrected for this effect. While these single height approaches still derive the correct local flux at the measurement height, the situation is more complex for gradient flux measurements. In that case, the vertical NH_3 gradient is modified by the chemistry, so that the aerodynamic gradient technique (AGM) may need to be modified to derive the correct NH_3 flux, including the chemical production or depletion term within the canopy space in addition to foliar exchange (Nemitz et al. 2004; van Oss et al. 1988).
2. Error in inferential estimates and deposition modelling. Deposition and emission are often derived from the air concentration in an inferential approach, using resistance models of a range of complexity. This approach does not usually consider chemical conversion within the resistance analogue (Kramm and Dlugi 1994). In addition, changes in the gas/particle partitioning modify air concentrations compared with the simulation of an atmospheric transport model that ignores chemical reactions. For example, the NH_3 air concentration is lowered by transfer to the particle phase, further stimulating stomatal emission, which is governed by the difference between stomatal compensation point and atmospheric concentration. A multi-layer modelling framework that simulates the coupled exchange, transport and chemistry inside the canopy is needed to resolve this effect (Nemitz et al. 2012; Ellis et al. 2011).
3. Modification of the local N_r budget. Gas-to-particle conversion usually occurs in situations of strong NH_3 emission. In this case a fraction of the emitted NH_3 is converted into slowly depositing NH_4NO_3 aerosol, "increasing" the potential for local N deposition and lowering the air concentration of NH_3 near the surface, thus stimulating further emissions from NH_3 compensation points. At the same time, fast depositing HNO_3 is converted into slowly depositing NH_4NO_3 aerosol, "decreasing" net N deposition. Similarly, NH_4NO_3 evaporation may occur near the surface, due to elevated canopy temperatures and reduced concentration of NH_3 and HNO_3 (driven by deposition), usually over semi- natural vegetation, which provides an efficient sink for NH_3. This process converts slowly depositing aerosol NH_4NO_3 into fast depositing HNO_3 and NH_3 gas, thus increasing total N deposition.The net effect of gas-to- particle conversion on the local N budget will depend on the relative magnitudes and exchange rates of the different compounds involved.

The potential degree of vertical flux divergence depends on the comparative chemical timescales for the evaporation or formation of NH_4NO_3 and NH_4Cl and the timescales for turbulent transport, which are different within and above the canopy; it also depends on the relative mixing ratios of NH_3 compared with the other chemically interactive species (gaseous HNO_3 and HCl and aerosol-phase NH_4^+, NO^- and Cl^-). Thus Nemitz et al. (2000c), for example, found ample evidence that there was the potential for NH_4Cl formation (i.e. an NH_3 sink) within an oilseed rape canopy in S. Scotland, where the in-canopy turbulence was low and residence times long. By contrast, above the canopy they predicted that there was potential for NH_4Cl evaporation (i.e. an NH_3 source). The small aerosol concentrations measured at their site resulted in chemical timescales for the evaporation or formation of NH_4NO_3 and NH_4Cl that were much longer than those for diffusive transport above the canopy. This meant that gas-particle interactions were unlikely to have affected above-canopy flux-gradient measurements of NH_3, and indicated that the aerodynamic gradient method is applicable to NH_3 flux measurements in environments with low particle concentrations (relative to NH_3) without the need to correct for the effects of GPIC. However, the relative effect of these interactions on the fluxes of HNO_3 and NH_4NO_3 may be considerable (cf. Nemitz et al. 2012). During the GRAMINAE Braunschweig experiment, gas-particle interactions were also believed to have had a minor effect on measured ammonia fluxes, though the relative effect on calculated aerosol deposition rates was significant (Sutton et al. 2009b; Nemitz et al. 2009b).

In more polluted environments, the impact of GPIC on NH_3 exchange can be significant. Over heathland in warm conditions in the Netherlands, Nemitz et al. (2004) established that there was near-surface evaporation of volatile NH_4^+ (i.e. an apparent NH_3 source) during the aerosol de-position process, which led to a substantial overestimation of the NH_3 flux (by the gradient method) of $+20$ ng m^{-2} s^{-1} during the day. They concluded that NH_4^+ evaporation may lead to a significant underestimation of NH_3 deposition to semi-natural vegetation during daytime by current measurements and models, in which such processes are not explicitly accounted for. This is particularly true if flux measurements are carried out in areas where large aerosol concentrations lead to short chemical timescales and where large concentration of volatile NH_4NO_3 or (less likely) NH_4Cl are present. These conditions are fulfilled above semi-natural vegetation in the vicinity of high NH_3 emission densities, common in the Netherlands and other areas with high livestock densities.

Model simulations by van Oss et al. (1988) successfully simulated observations of NH_3^--aerosol deposition faster than permitted by turbulence above the Dutch forest Speulderbos. They showed that NH_3 emission fluxes obtained at Speulderbos may not originate from the foliage but could at least partly be explained by the evaporation of NH_4NO_3 close to or within the canopy. However, evaporation of NH_4NO_3 from leaf surfaces may have a similar effect. The complex topic of air column chemistry and gas-particle interconversion and its relevance to NH_3 exchange is addressed more fully by Nemitz et al. (2012).

The stratification and interactions of processes controlling surface/atmosphere NH_3 exchange reviewed in this section are illustrated in Fig. 4, which was originally drawn to summarise the scientific objectives and tasks within the GRAMINAE Braunschweig experiment (Sutton et al. 2009a). This project focused on processes in fertilized and cut grassland, but Fig. 4 can essentially serve as a

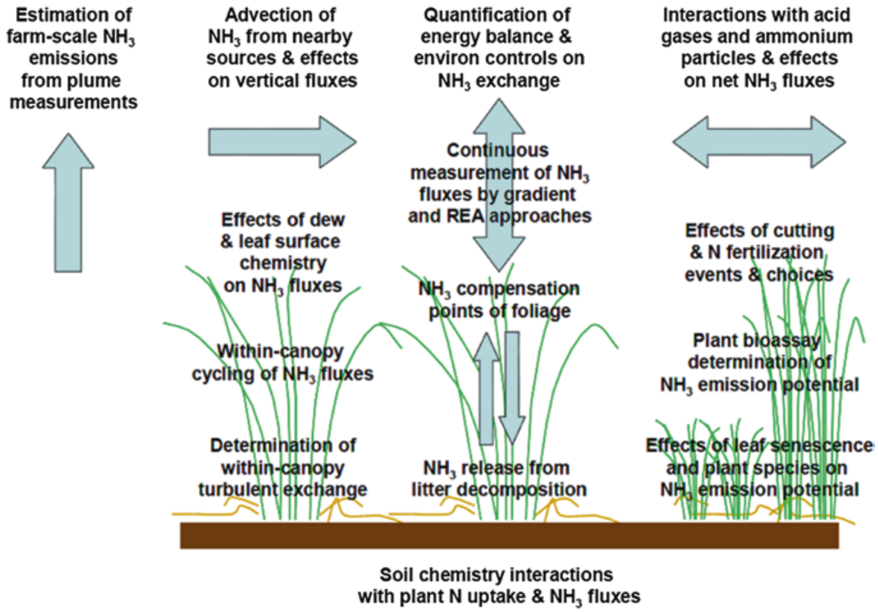

Fig. 4 Overview of processes controlling surface/atmosphere NH_3 exchange in the soil-vegetation-atmosphere continuum, summarising the scientific objectives of the GRAMINAE integrated experiment (from Sutton et al. 2009a), but relevant for NH_3 exchange studies in any ecosystem

blueprint for any integrated project aiming at a full understanding of component-scale and canopy-scale NH_3 fluxes in other vegetation types (for semi-natural ecosystems, the management and fertilization issues can simply be ignored). The figure illustrates intuitively that NH_x pools exist, expand or shrink over time, and interact at all levels of the ecosystem: soil (agregates, cation exchange sites, water-filled porosity, open porosity); soil surface, fertilizer residues and litter; plant (xylem, phloem, apoplast, cytoplasm, vacuole, organelles); plant surfaces (water films, cuticle, deliquescent aerosols); and even in the air space within and above the canopy. Surface/exchange models should therefore, in theory, seek to simulate the temporal as well as the vertical variability in these pools, in order to simulate the dynamics of canopy-scale fluxes.

Ammonia Exchange Models and Parameterizations from the Leaf to the Globe: State-of-the-Art

A large number of models have been developed to simulate NH_3 exchange fluxes for the different ecosystem components or processes (soil, litter, leaf, plant, heterogeneous-phase chemistry), either separately or integrated into canopy-scale 1-dimensional (1-D) soil-vegetation-atmosphere (SVAT) frameworks.

Landscape-scale, regional-scale and global-scale models are 2-D or 3-D, and they typically include simplified versions of canopy-scale models to simulate the 1-D surface exchange as part of the wider modelling context of emission, dispersion, transport, chemistry and deposition. The level of complexity of 1-D NH_3 exchange models depends on the different purposes and temporal scales as well as spatial scales, at which they are put to use. Modelling approaches range from the fully empirical to the primarily mechanistic. This section provides an overview of existing models, and their current parameterizations, ranging from the component (or substrate) scale to the global scale. The review is by no means exhaustive, but instead focuses on state-of-the-art models, and those models which represent potential options for implementation into integrated canopy, or larger scale, models. At each level, the model's scope, advances, challenges, and degree of validation are discussed. Model names are highlighted in bold characters on first mention, and a summary of models is provided in Table 1.

Table 1 A selection of soil, plant, ecosystem, atmosphere models, dealing with NH_3 emission, dry deposition, bi-directional exchange, dispersion, chemistry, transport, from the process scale to the global scale

Full model name	Acronym/short name	Reference
Process-based soil, manure, fertilizer, or agro/ecosystem emission		
AGRIN	AGRIN	Beuning et al. (2008)
Ammonia Loss from Field-applied Animal Manure	ALFAM	Sogaard et al. (2002)
Crop Environment REsource Synthesis	CERES	Godwin et al. (1984)
Crop environment REsource synthesis—EGC (INRA)	CERES-EGC	Gabrielle et al. (1995)
DeNitrification DeComposition	DNDC	Li et al. (1992), Li (2000)
Environmental Policy Integrated Climate	EPIC	Williams et al. (2008)
Generation of emissions from Uric Acid Nitrogen Outputs	GUANO	Blackall et al. (2007), Riddick (2012)
Volt'Air	Volt'Air	Genermont and Cellier (1997)
Leaf/plant-scale stomatal exchange		
Multi-Layer BioChemical	MLBC	Wu et al. (2003)
Pasture Simulation	PaSim	Riedo et al. (1998, 2002)
STomatal AMmonia compensation Point	STAMP	Massad et al. (2010a)
Canopy/ecosystem-scale dry deposition/exchange		
DEPosition of Acidifying Compounds	DEPAC	Erisman et al. (1994)
DEPosition of Acidifying Compounds v.3.11	DEPAC 3.11	Wichink-Kruit et al. (2010), Van Zanten et al. (2010)
Dynamic pollutant Exchange with Water films on vegetation Surfaces	DEWS	Flechard et al. (1999)
Multi-Layer Model	MLM	Meyers et al. (1998)

(continued)

Table 1 (continued)

Full model name	Acronym/short name	Reference
PLant ATmosphere INteraction	PLATIN	Grunhage and Haenel (1997, 2008)
SPRUCE forest DEPosition	SPRUCEDEP	Zimmermann et al. (2006)
SURFace ATMosphere NH_3	SURFATM-NH3	Personne et al. (2009)
Landscape-scale dispersion and deposition		
American Meteorological Society/ Environmental Protection Agency Regulatory Model	AERMOD	Perry et al. (2004)
Atmospheric Dispersion Modelling System	ADMS	Carruthers et al. (1999)
DDR	DDR	Asman et al. (1989)
DEPO1	DEPO1	Asman (1998)
Flux Interpretation by Dispersion and Exchange over Short range	FIDES-2D	Loubet et al. (2001)
Local Atmospheric Dispersion and Deposition	LADD	Hill (1998)
MOdel of Dispersion and Deposition of Ammonia over the Short-range	MODDAAS-2D	Loubet et al. (2006)
Operational Priority Substances (Pro 4.1)	OPS-Pro 4.1	van Jaarsveld (2004)
Operational Priority Substances (Short Term)	OPS-st	van Jaarsveld (2004), van Pul et al. (2008)
Operationelle Meteorologiske Luftkvalitetsmodeller DEPosition	OML-DEP	Olesen et al. (2007); Sommer et al. (2009)
TREND/OPS	TREND/OPS	Asman and van Jaarsveld (1992)
Regional-scale chemical transport models		
A Unified Regional Air-quality Modelling System	AURAMS	Zhang et al. (2003)
CHIMERE	CHIMERE	Vautard et al. (2001)
Community Multiscale Air Quality	CMAQ	Byun and Schere (2006)
Danish Ammonia MOdelling System	DAMOS	Geels et al. (2012)
European Monitoring and Evaluation Programme	EMEP	Simpson et al. (2012)
Fine Resolution AMmonia Exchange	FRAME	Singles et al. (1998)
LOng Term Ozone Simulation EURopean Operational Smog	LOTOS-EUROS	Wichink-Kruit et al. (2012)
Multi-scale Atmospheric Transport and CHemistry	MATCH	Klein et al. (2002)
Global-scale chemical transport models		
Goddard Earth Observing System Chemical transport model	GEOS-Chem	Bey et al. (2001), Wang et al. (1998)
MOdel of the Global UNiversal Tracer transport In The Atmosphere	MOGUNTIA	Dentener and Crutzen (1994)
Tracer Model version 5	TM5	Huijnen et al. (2010)
UK Met. Office Global Three-Dimensional Lagrangian Model	STOCHEM	Collins et al. (1997), Bouwman et al. (2002)

Process/Component Scale Models: Soil, Manure, Fertilizer, Leaf Litter, Leaf, Cuticle, Air Column Chemistry

Ammonia Emissions from Slurry and Fertilizer Applied to Soils (Γ_{soil} Emission Potential)

Various modelling concepts have been developed to account for the physico-chemical processes controlling NH_3 emission from mineral or organic manures upon field application to bare soil, and to simulate the peak emissions and diurnal trends of NH_3 emissions following slurry application (e.g. Van der Molen 1990; Sommer et al. 2003; Montes et al. 2009). Genermont and Cellier (1997) developed a mechanistic model (Volt'Air) that simulates the controls by soil, meteorology and slurry characteristics on NH_3 volatilisation from field-applied slurry, accounting for the transfers and equilibria in the topsoil and between the soil and the atmosphere. The model included energy balance and advection submodels, which made it suitable for field scale applications using simple meteorological data. Sensitivity analysis showed that soil pH has a large influence on volatilization. The model is also sensitive to soil adsorption capacity and some hydraulic characteristics (saturation water conductivity, water content at field capacity) (Garcia et al. 2011). Volt'Air has also been extended to simulate emissions by mineral fertilizers (Laguel-Hamaoui 2012).

The process-based AGRIN model, developed by Beuning et al. (2008), combined model theory of soil biological processes such as SOM decomposition, nitrification and denitrification (DNDC, Li et al. 1992; Li 2000), with Volt'Air-type models of NH_3 volatilization (Genermont and Cellier 1997; Van der Molen et al. 1990). New processes were also introduced to improve model performance, such as a separate slurry layer. In such models a key challenge is to simulate the pH of the emitting layer, which may be rather different from, or independent of, the background pH value for the underlying topsoil, e.g. in cases where infiltration is limited. Also, for implementation in CTMs, regional soil pH maps need to account for the effects of liming practices.

Empirical/statistical regression approaches for slurry emissions include the Ammonia Loss from Field-applied Animal Manure (ALFAM) model (Segaard et al. 2002), whereby volatilisation is described mathematically by a Michaelis-Menten-type equation, with the loss rates as the response variable, and soil water content, air temperature, wind speed, slurry type, dry matter content of slurry, total ammoniacal nitrogen content of slurry (TAN $= [NH_x] = [NH_3] + [NH_4^+]$), application method and rate, mode of slurry incorporation and measuring technique are the explanatory variables. Similarly, using regression analysis, Menzi et al. (1998) used the results of field and wind tunnel experiments to derive a simple empirical model to estimate ammonia emissions after the application of liquid cattle manure on grassland. Their model takes into account the mean saturation deficit of the air, the TAN content of the manure and the application rate. Lim et al. (2007) proposed an artificial neural network (ANN) approach for predicting ammonia emission from field-applied manure, which combined principal component analysis (PCA)-based preprocessing and weight partitioning method (WPM)-based post-processing. Their so-called PWA (standing for PCA-WPM-ANN) approach is expected to account for the complex nonlinear effects between the NH_3 emission variables such as soil and manure states, climate and agronomic factors.

For soils amended with commercial fertilizers, such as anhydrous NH_3, urea, ammonium nitrate, or mixtures of these forms, soil NH_3 emission is modelled in the Community Multiscale Air Quality (CMAQ) model (Foley et al. 2010) by a simplified version of the US Department of Agriculture's Environmental Policy Integrated Climate (EPIC) model (Williams et al. 2008; Cooter et al. 2010), which includes simulation of nitrification through a combination of a first-order kinetic rate equation (Reddy et al. 1979) and elements of the Crop Environment REsource Synthesis (CERES) crop model (Godwin et al. 1984). The rate of N transformation is computed as a function of soil pH, temperature, and soil moisture effects on nitrification and subsequent volatilization. In EPIC, volatilization is simply a fixed fraction of nitrification, while the CMAQ-EPIC coupling application makes use of the bi-directional flux paradigm to characterize the emission. One basic hypothesis of the simplified EPIC processes included in CMAQ is that characterization of the nitrification process alone will adequately simulate the concentration of NH_4^+ and H^+ in agricultural soils. The upper 15–45 cm of the soil layer reflects the impact of specific tillage practices on biogeochemical process rates. The EPIC/CMAQ method requires knowledge of physical properties of the ambient soil profile, meteorology, and regional crop management practices and uses a crop growth model to estimate tillage and fertilizer application timing and amount. This information is provided to CMAQ by a full EPIC management simulation. The EPIC model also can perform detailed dynamic slurry or solid form manure simulations, but this information is not yet implemented in the current coupling with CMAQ. For NH_3 transfer to the surface, the EPIC/CMAQ model formally develops and evaluates refinements to the Nemitz et al. (2001a) model for NH_3 flux over a managed agricultural soil, that includes a soil resistance term (see Section "Canopy/Ecosystem Scale Models"). A similar approach was also developed using the Volt'Air NH_3 emission module and the CERES-EGC crop growth model (Gabrielle et al. 1995; Theobald et al. 2005).

Although strictly speaking not pertaining to the manure or fertilizer categories, NH_3 emissions from seabird excreta (guano) on the ground of land-based colonies present similarities and their study and modelling proves relevant in this context. Agricultural sources of NH_3 are complicated by different management practices across the globe, whereas seabird emissions represent a model system for studying climate dependence (Riddick et al. 2012). Seabird colonies are the largest point sources of ammonia globally (up to ~6 Gg NH_3 colony^{-1} year^{-1}, on average; Blackall et al. 2007). Riddick et al. (2012) present an NH_3 emission mid estimate with an overall uncertainty range of 270 [97–442] Gg NH_3 per year for seabird colonies globally. In the Generation of emissions from Uric Acid Nitrogen Outputs (GUANO) model (Blackall et al. 2007; Riddick 2012), the emission of NH_3 from seabird excreted N is described in four steps: (i) Excretion of nitrogen rich guano, in the form of uric acid based on a seabird energetics model (Wilson et al. 2004);

(ii) conversion of uric acid total ammoniacal nitrogen (TAN), with a climate- and surface pH-dependent rate; (iii) TAN partition between NH_4^+ and NH_3 on the surface; and (iv) NH_3 volatilization to the atmosphere, controlled by the wind speed, aerodynamic resistance (R_a and R_b) and the fraction of NH_3 re-absorbed by the substrate and re-captured by any overlying vegetation.

The review by Sintermann et al. (2012) of published NH_3 emission factors for field applied slurry showed that (i) very substantial differences between EF estimates from field-scale (both AGM and EC) measurements and the ALFAM and Menzi et al. (1998) simple empirical models, for Swiss datasets (e.g. Spirig et al. 2010; Sintermann et al. 2011), with estimates TAN losses in the range 5–30 % by measurements versus 20–70 % by these two models; and (ii) that EF estimates by measurements depended on the spatial scale at which they were carried out (chamber, small or medium plot, field), suggesting strong potential methodological biases. This provides a very clear indication that the current level of validation for models of NH_3 volatilisation from field applied manures is rather poor. The authors concluded that new series of measurements are urgently needed in order to (i) provide systematic comparisons of measurements from medium-scale plots and field-scale measurements under identical conditions, and using a range of different measurement techniques, and (ii) pursue the characterisation of NH_3 EFs in terms of the influence of slurry composition and application method, soil properties and meteorology. Such future experiments should ideally cover the detailed temporal dynamics (hourly or better over the full course of emission) to help understand the environmental interactions, and must report on the parameters required to perform a plausibility check and to apply and develop process-oriented models.

Litter Emissions (Γ_{litter} Emission Potential)

The model developed by Nemitz et al. (2000a) to simulate the dynamics of the litter NH_3 emission potential, based on measurements of $[NH_4^+]/[H^+]$ ratio in bulk tissue extracts and on mineralization and nitrification rates, is one of very few available methods at present and appears to be relatively easy to implement. A more detailed mechanistic treatment is provided by EPICv.0509 (see Appendix A in Cooter et al. 2012; Williams et al. 2008), in which soil organic C and N are split into three compartments: microbial biomass, slow humus and passive humus, and organic residues added to the soil surface or belowground are split into metabolic and structural litter compartments as a function of C and N content. Following the CENTURY (Parton et al. 1994) approach, EPIC includes linear partition coefficients and soil water content to calculate movement as modified by sorption, which are used to move organic materials from surface litter to subsurface layers; temperature and water controls affecting transformation rates are calculated internally in EPIC; the surface litter fraction in EPIC has a slow compartment in addition to metabolic and structural litter components; while lignin concentration is simulated as an empirical sigmoidal function of plant age.

Although the NH_3 emission potential of the litter (Γ_{litter}) is very high, especially in fertilized agricultural systems (Fig. 3), this component has been very much understudied compared with, say, apoplastic Γ_s. Within the European Union-funded collaborative project ECLAIRE ("Effects of Climate Change on Air Pollution and Response Strategies for European Ecosystems"; http://www.eclaire-fp7.eu), work is on-going to characterise NH_3 emission potentials in a range of litter samples from selected ECLAIRE monitoring sites across Europe. The incubation of litter samples in a two- factorial design of different soil moistures (20–80 % water-filled pore space) and temperatures (5–20 °C) should provide a better understanding of litter emission dynamics.

Leaf/Plant-Scale Stomatal Exchange (R_s Emission Potential)

Substantial progress has been achieved over the last 10 years in modelling the cell and plant physiological mechanisms that determine the apoplastic Γ_s ratio and its temporal variations. In particular, the Pasture Simulation (PaSim) ecosystem model for the simulation of dry matter production and C, N, H_2O and energy fluxes (Riedo et al. 1998), accounts for the effects of nitrification, denitrification and grazing, and was extended by Riedo et al. (2002) to couple NH_3 exchange with ecosystem functioning. For this purpose, the above-ground plant substrate N pool in previous versions of PaSim was sub-divided into apoplastic and symplastic components. The apoplastic substrate N pool was linked to the stomatal NH_3 exchange, while soil ammoniacal N (NH_x) was partitioned between the soil surface and several soil layers, with the soil surface NH_3 exchange being driven by the NH_4^+ content in a soil surface layer (set at 0–3 mm depth). This was the first attempt by any model to account for plant N nutrition and development stage in predicting r_s. One significant drawback identified by the authors was that PaSim did not consider the form of N taken up by the roots (reduced or oxidised), which may be significant since plants absorbing NH_4^+ have higher NH_3 emissions compared with plants absorbing NO^- (see Section "Plant Physiological Controls"). Riedo et al. (2002) offered this as an explanation for the lack of late summer emissions in their simulations, in contrast to observed fluxes in a Scottish pasture.

Another significant development is the stomatal ammonia compensation point (STAMP) leaf-scale model for C3 plants by Massad et al. (2010a), in which Γ_s is likewise related to plant N and C metabolism. Here, five compartments are considered explicitly: xylem, cytoplasm, apoplasm, vacuole and sub-stomatal cavity, while the main processes accounted for are (i) transport of NH_4^+, NH_3 and NO^- between the five compartments; (ii) NH_4^+ production through photorespiration and NO^- reduction; (iii) NH_4^+ assimilation by the GS/GOGAT cycle; (iv) chemical and thermodynamic equilibriums in all the compartments; and (v) and stomatal transfer of NH_3 (Fig. 5). In contrast to PaSim, STAMP accounts for either NH_4^+-based nutrition, NO^--based nutrition, or a combination of both. However, STAMP only represents a leaf (single-layer canopy) in a vegetative stage of growth, in which apoplast and cytoplasm are relatively uncoupled with respect to NH_x; STAMP

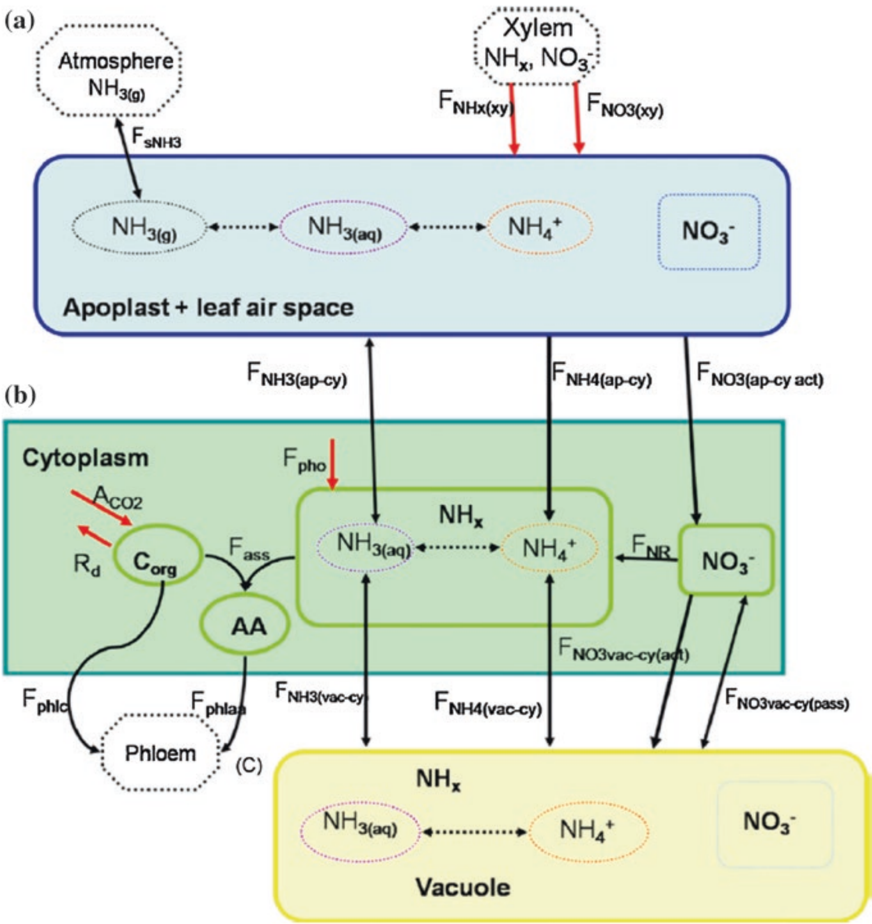

Fig. 5 Components and flow diagram of the STAMP (stomatal ammonia compensation point) model by Massad et al. (2010a). *Oneway arrows* represent active transport, *two-way arrows* represent passive diffusion, *dotted arrows* represent equilibria and *red arrows* represent forcing variables

does not account for the effects of senescence on NH_3 metabolism, restricting model applicability in the case of plants having senescent leaves and in multilayered canopies. STAMP was validated against measured χ_S values and both apoplastic and intra-cellular NH_x concentrations, using flux chamber measurements with 7–9 oilseed rape plants at 5 weeks of age (Massad et al. 2009). The model has yet to be scaled up to the crop canopy level, integrating soil and plant processes, which will also require the model to be thoroughly tested against field data.

Unlike PaSim and STAMP, the stomatal compensation point model integrated by Wu et al. (2009) in the MultiLayer BioChemical (MLBC) dry deposition model of Wu et al. (2003) is not driven by ecosystem, plant and leaf biochemistry and metabolism, but it does explore from a theoretical viewpoint the issue of potential feedbacks between emission, deposition and leaf temperature on the dynamics of apoplastic Γ_s. Simulations show that modeled apoplastic [NH_4^+] and [H^+] display significant diurnal variation when the buffer effect of the underlying metabolic processes generating or consuming NH_4^+ are ignored, and that the model predictive capability for canopy-scale exchange fluxes over fertilized soybean (measurements by Walker et al. 2006) is slightly improved by incorporating the feedback of NH_3 flux on apoplastic [NH_4^+] (vs. a constant Γ_s approach). Ignoring entirely the apoplastic buffer effects associated with xylem supply and cytoplasmic exchange appears to be an unrealistic oversimplification, but the dynamic stomatal compensation point MLBC runs by Wu et al. (2009) do raise the issue of the significance for modelling of diurnal Γ_s variations, which have been observed elsewhere (e.g. Herrmann et al. 2009), albeit of a smaller magnitude.

Leaf Surface Aqueous Chemistry (Γ_d Emission Potential)

Water droplets resting on leaf surfaces have long been known to act as sinks for soluble atmospheric trace gases including SO_2 (Brimblecombe 1978; Fowler and Unsworth 1979) and NH_3 (Sutton et al. 1992). Although leaf wetness is usually assumed to increase surface affinity (i.e. reduce surface resistance) for NH_3 uptake, Sutton et al. (1995c, 1998a) recognized that exchange with leaf surface water could be reversible and they developed the first capacitance-based model to simulate NH_3 desorption from the drying out cuticle of a wheat canopy. One underlying assumption was that part of the previously deposited NH_3 was not fixed by reaction to form low vapour pressure salts (e.g. $(NH_4)_2SO_4$) and thus may be released back to the atmosphere upon evaporation of surface wetness, with this leading to an increase in [NH_4^+] in the leaf surface water pool, and the associated values termed T_d and x_d. The water film thickness (M_{H_2O}), which scaled by LAI determines the bulk canopy leaf surface water storage ($M^c_{H_2O}$), was estimated on the basis of relative humidity at the surface (Sutton et al. 1998a; van Hove et al. 1989; Burkhardt and Eiden 1994). The treatment of leaf surface wetness as a dynamic pool of NH_4^+, with periods of pool contraction (evaporation) followed by periods of expansion (dewfall, rainfall), meant that the bi-directional cuticular NH_3 flux (into or out of the adsorption capacitor C_d) was dependent on previous fluxes (hysteresis). The charging resistance (R_d) was calculated as R_d (s m^{-1}) = 5000/C_d, equivalent to an 83 min time constant, and the NH_3 surface reaction rate (K_r) and surface solution pH (needed to calculate Γ_d) were both prescribed.

The Sutton et al. (1998) C_d/R_d simple dynamic approach was subsequently adopted by Neirynck and Ceulemans (2008) for Scots Pine forest; here, however, water film thickness was calculated as a function of the normalized output of a leaf wetness sensor (LW), while parameterizations of both K_r and surface pH were obtained by optimizing the model results to minimize bias and maximize the R^2 between observed and modelled fluxes.

A significant development of the capacitance model was provided by Flechard et al. (1999), here termed DEWS (Dynamic pollutant Exchange with Water films on vegetation Surfaces), originally developed in moorland vegetation. This model has since been applied for managed grassland to the Braunschweig flux dataset (Burkhardt et al. 2009). By contrast to the Sutton et al. (1998a) and Neirynck and Ceulemans (2008) implementations of the C_d/R_d model, in which leaf surface solution pH was prescribed or statistically optimized, the dynamic chemistry model of Flechard et al. (1999) simulated solution chemistry, pH and F_d mechanistically, where Henry and dissociation equilibria were forcedby measured ambient concentrations of the trace gases NH_3, SO_2, CO_2, HNO_2, HNO_3 and HCl. The oxidation of SO_2 to SO_4^- by O_3, O_2 and H_2O_2 and the exchange of base cations and NH_4^+ between the leaf surface and plant interior were also accounted for. The cuticular adsorption resistance (R_d) was parameterized as an exponential function of the ionic strength of the solution. Activity coefficients were included in the numerical calculations of the equilibrium pH and solute concentrations for solutions with ionic strengths up to 0.3 M.

Although mechanistically satisfying, and successful in field-scale studies, these dynamic chemistry models to simulate surface-wetness-related NH_3 fluxes are computationally intensive, requiring short time steps (seconds to minutes), and thus they have not been implemented until now in large-scale models such as CTMs. Most models use unidirectional, steady-state cuticular resistance approaches for leaf surface wetness, in which no Γ_d is assumed. Instead, the non-stomatal resistance to deposition, associated with the epifoliar NH_3 sink and termed R_w here (or R_{ext}, or R_{ns}, or R_{cut}, in different models; e.g. Flechard et al. 2011), typically decreases with increasing RH (or increases with VPD), to reflect the larger sink strength of wet surfaces. The effect of pH on NH_3 uptake rates is reflected, in some models or parameterizations, in the dependence of R_w on the atmospheric molar ratio of SO_2/NH_3 or Total Acids/NH_3 (e.g. Erisman et al. 1994; Nemitz et al. 2001a; Massad et al. 2010b; Simpson et al. 2012), or simply on the NH_3 concentration itself (Jones et al. 2007). Figure 6 shows the exponential decay curve fitted to a compilation of published R_w values (at 95 % RH) as a function of the Total Acids/NH_3 ratio, at a range of NH_3 flux measurement sites, for four major ecosystem types (Massad et al. 2010b). Despite a substantial scatter, there is no question that, at sites where the pollution climate is dominated by NH_3, non-stomatal uptake is severely restricted by a high pH and high surface $[NH_4^+]$ (e.g. high Γ_d).

A "hybrid" non-stomatal NH_3 exchange modelling concept, half-way between capacitance ($\Gamma_d > 0$, bi-directional) and resistance ($\Gamma_d = 0$, deposition-only) models, was developed within the DEPosition of Acidifying Compounds (DE-PAC 3.11) model by Wichink-Kruit et al. (2010) and Van Zanten et al. (2010). Their model recognized the existence of a non-zero Γ_d emission potential (which they termed Γ_w), which increased with ambient NH_3 concentration at a given site. However, the parameterization of the external leaf surface pathway was not truly bi-directional, since the equivalent χ_d (or χ_w) was approximately parameterized as a fraction of the ambient air concentration (χ_a), and thus χ_d never exceeded χ_a.

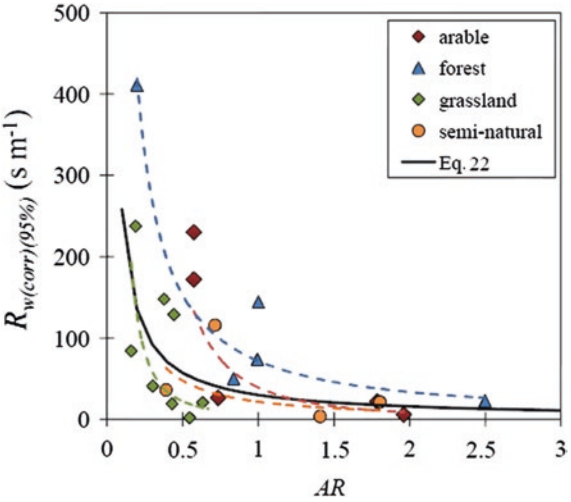

Fig. 6 External leaf surface resistance at 95 % relative humidity ($R_{\mathrm{w(corr)(95\ \%)}}$) as a function of the ratio of total acids/NH (AR = ($2SO_2 + HNO_3- + HCl)/NH_3$) in the atmosphere separated according to ecosystem type. $R_{\mathrm{w(corr)(95\ \%)}}$ was normalised for LAI and temperature. From Massad et al. (2010b)

Nonetheless, the parameterization accounted for saturation effects at high air concentrations, in a similar fashion to e.g. the NH_3-dependent R_w of Jones et al. (2007), with the difference that non-zero values of Γ_d and χ_d were mechanistically more realistic. In making this modification, much of the uncertainty in the dependence of the cuticular exchange on the pollution climate and ecosystem was transferred from R_w to χ_w. While the exact partitioning between the two terms remained uncertain, the hybrid approach had the advantage of accounting, in theory, for the bi-directional and concentration-dependent exchange with the leaf cuticle, while avoiding the requirement for more complex time-dependent dynamic modelling solutions.

Air Column Chemistry

Nemitz (2012) present a comprehensive review of models dealing with acid gases, aerosols and their interactions with NH_3, and thus only a brief overview is given here. Several numerical models have been developed for the implementation of modified gradient techniques to infer the surface flux of NH_3 and chemically reactive species from profile measurements and accounting for GPIC effects on vertical flux divergence (Brost et al. 1988; Kramm and Dlugi 1994; Nemitz et al. 1996; van Oss et al. 1988; Nemitz and Sutton 2004; Ryder 2010). Modelling results showed that reactions could theoretically change NH_3 fluxes by as much as 40 % (Kramm and Dlugi 1994) or even lead to flux reversal (van Oss et al. 1988).

For the chemical source/sink term associated with the NH_3–HNO_3–NH_4NO_3 triad, the kinetics of the chemical inter-conversion can either be described by the use of chemical timescales, reaction rate coefficients, or by using a full model of size-resolved chemistry and microphysics. Brost et al. (1988) were the first to model the effect of the NH_3–HNO_3–NH_4NO_3 equilibrium on surface exchange fluxes of NH_3, and described the reaction as a first-order relaxation towards equilibrium with a characteristic time τ_C. The later model by van Oss et al. (1988) also described the shift towards equilibrium by a relaxation-type equation for the flux divergence. The first-order relaxation approach received criticism from Kramm and Dlugi (1994), who proposed an alternative model, favouring a reaction rate formulation using rate coefficients for condensation (k_1) and evaporation (k_2), and coupled with an inferential resistance model for the estimation of surface exchange fluxes from single-point concentration data. Nemitz (1998) argued that both first-order relaxation and reaction rate approaches were actually equally valid, but there are large uncertainties in the reaction rate coefficients (Kramm and Dlugi 1994) and in chemical timescales (Wexlerand Seinfeld 1990).

For the calculation of the concentration and flux profiles modified by chemical reactions, additional information linking the flux (F_χ) to atmospheric turbulence is required to solve the vertical flux divergence, i.e. the $\delta F_\chi/\delta z$ differential, which constitutes a so-called closure problem (Nemitz 1998). Second-order closure (SOC) approaches use information from the budget equations of the turbulent fluxes, which include second-moment terms. By contrast, first-order closure (FOC), also called K-closure models, use information provided by the concentrations themselves, implying that K-theory is used for the flux-gradient relationship. SOC tends to be regarded as a reference and should be accurate, but there are difficulties in applying the method to all atmospheric stabilities. By contrast, FOC is much easier to apply in all stabilities, but there are limitations of the applicability of inert K-theory to reactive species. Thus efforts have been made to estimate the magnitude of the error induced by FOC compared with SOC, and to develop modified K-theories and correction procedures (Nemitz 1998).

The effects of ground NH_3 emissions on NH_4NO_3 formation, the extension of existing FOC approaches by the NH_3–HCl–NH_4Cl triad, and the inclusion of vertical gradients of temperature, relative humidity and aerosol composition were innovative aspects developed by Nemitz et al. (1996) and Nemitz (1998). The numerical model presented by Nemitz and Sutton (2004) took the approach further and developed a modified gradient technique, which explicitly calculated the particle size distribution of the NH_4^+ aerosol as a function of height, in addition to the concentration and flux profiles of the bulk aerosol species. From the change of the size distribution with height (z), apparent aerosol deposition velocities could be inferred, which may be compared with values derived from eddy-covariance (EC) measurements, e.g. using optical particle counters. With the knowledge of the size distribution it became also possible to calculate the chemical timescale (τ_C) of the equilibration process (Wexler and Seinfeld 1990) as a function of the size distribution at each height. Ryder (2010) took this approach another major step forward, by modeling the evolution of a mixed, size- distributed aerosol in a fully coupled model treating transport, emission/deposition, chemistry, phase transition and aerosol microphysics in a multi-layer approach, which also resolved chemical interactions within the canopy. All previous approaches were based on single-layer (big-leaf) exchange models.

The advances in GPIC/flux interaction modelling over the last 15 year have therefore been very substantial, but models have not yet been applied on a routine basis at spatial scales larger than the field. Also, despite the increasing availability of multiple gas and aerosol species concentrations and fluxes over a range of ecosystems (e.g. Douglas fir forest, van Oss et al. 1988; oilseed rape, Nemitz et al. 2000b; heathland, Nemitz et al. 2004, Nemitz and Sutton 2004; tropical pasture, Trebs et al. 2004; grassland, Nemitz 1998, Nemitz et al. 2009b, Wolff et al. 2010a, Thomas et al. 2009; spruce forest, Wolff et al. 2010a, b), model results have only rarely been compared with measurements. Significant future model improvements could be anticipated from a systematic processing of all existing datasets and from conducting model sensitivity analyses of the minimum complexity required to reproduce measurements adequately. It should be noted that, in general, the relative effect of GPIC on fluxes of acids and aerosols is larger than that on NH_3 (Nemitz et al. 2012).

Canopy/Ecosystem Scale Models

Canopy-scale models integrate component processes and their interactions within SVAT frameworks, with the objective of predicting the net ecosystem NH_3 flux from the inputs of: (i) ambient NH_3 and other concentrations (χ_a); (ii) meteorology (global and net radiation, temperature, relative humidity or VPD, wind speed, and friction velocity, sensible, latent and ground heat fluxes if available); and (iii) ecosystem characteristics such as LAI, canopy height (h_c). Model concepts range from simple, steady-state, "Big-Leaf" canopy resistance (R_c)/deposition velocity (V_d) approaches, to complex, dynamic, multiple-layer canopy compensation point schemes. Most models are based on the resistance analogy, in which the flux ($F\chi$) between two potentials A and B is equal to the potential difference ($\chi_A-\chi_B$) divided by the resistance ($R_{A,B}$), with the soil-canopy-atmosphere system being represented as a network of potentials connected by resistances in series (for different layers) and in parallel (for different pathways) (e.g. Monteith and Unsworth 1990).

Canopy Resistance (R_c) Models

Canopy resistance/deposition velocity (R_c/V_d) models (e.g. Baldocchi et al. 1987; Wesely 1989; Erisman et al. 1994; see review by Wesely and Hicks 2000) simulate NH_3 dry deposition to the surface, whereby R_c is the total resistance to deposition resulting from component terms such as stomatal (R_s), mesophyll (R_m),

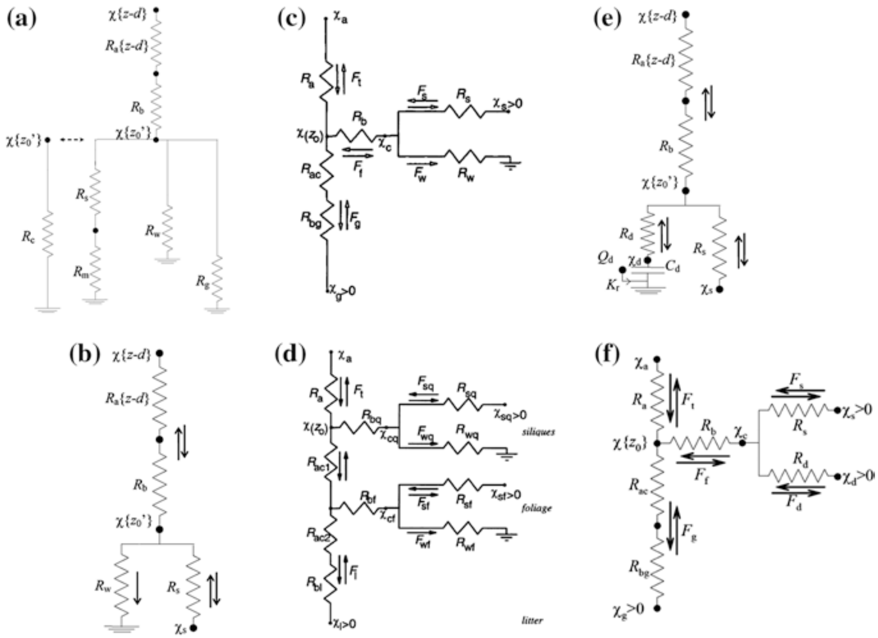

Fig. 7 Typical surface/atmosphere schemes for the modelling of net canopy-scale NH_3 fluxes. **a** Generic example of canopy resistance (R_{c}) model; **b** the 1-layer $\chi_{\mathrm{s}}/R_{\mathrm{w}}$ canopy compensation point model by Sutton et al. (1995b); **c** the 2-layer $\chi_{\mathrm{s}}/\chi_{\mathrm{g}}/R_{\mathrm{w}}$ canopy compensation point model by Nemitz et al. (2001a); **d** the 3-layer (soil, foliage, silique/inflorescence) canopy compensation point model by Nemitz et al. (2000b); **e** the 1-layer $\chi_{\mathrm{s}}/\chi_{\mathrm{d}}/R_{\mathrm{d}}$ capacitance canopy compensation point model by Sutton et al. (1998a); and **f** the 2-layer $\chi_{\mathrm{s}}/\chi_{\mathrm{g}}/\chi_{\mathrm{d}}/R_{\mathrm{d}}$ dynamic chemistry canopy compensation point model by Burkhardt et al. (2009)

non-stomatal/external/cuticular (R_{w} or R_{nS} or R_{ext} or R_{cut}), or soil (R_{Soil} or R_{g}) resistances (Fig. 7a). $R_{\mathrm{c}}/V_{\mathrm{d}}$ models assume a zero NH_3 emission potential in the canopy, and thus the exchange is uni-directional (deposition-only). The deposition velocity is calculated as the inverse sum of R_{c} in series with the aerodynamic (R_{a}) and viscous sub-layer (R_{b}) resistances above the canopy, and the flux F_{x} as the product of NH_3 concentration (χ_{a}) and V_{d}:

$$V_{\mathrm{d}}\{z\} = (R_{\mathrm{a}}\{z\} + R_{\mathrm{b}} + R_{\mathrm{c}})^{-1} \tag{1}$$

$$F_{\chi} = V_{\mathrm{d}}\{z\} \times \chi_{\mathrm{a}}\{z\} \tag{2}$$

where V_{d}, R_{a} and χ_{a} are all expressed at the same reference height (z) above d, the displacement height. The resistances R_{a} and R_{b} are relatively well characterised and readily calculated from micrometeorological measurements (e.g. Monteith and Unsworth 1990; Garland 1977). Stomatal resistance to gaseous transfer is typically derived in the different models using a generic light-response function within a multiplicative algorithm also accounting for Γ, VPD and SWC stress factors (Jarvis 1976; Emberson et al. 2000a, b).

Some models split PAR into its direct and diffuse fractions and compute the sunlit and shaded components of LAI, such that total (or bulk) stomatal resistance is calculated from sunlit and shaded resistances weighted by their respective LAI fractions (Baldocchi et al. 1987). By contrast the much simpler R_s routine by Wesely (1989) only requires global radiation and surface temperature as input, and may be used when land use and vegetation characteristics are not well known.

Canopy resistance models often use a Big-Leaf approach, i.e. they do not distinguish several layers vertically in the canopy, nor do they simulate in-canopy turbulent transfer, and vegetation is thus assumed to behave as one single leaf. Such models can nonetheless include an in-canopy aerodynamic resistance term (R_{ac}) in series with R_{soil} (e.g. Wesely 1989; DEPAC, Erisman et al. 1994; European Monitoring and Evaluation Programme (EMEP), Simpson et al. 2012; A Unified Regional Air-quality Modelling System (AURAMS), Zhang et al. 2003). Most of the existing R_c model variants, alongside specific innovations, actually borrowed model parts and parameterizations from other models, e.g. PLant ATmosphere INteractions (PLATIN, Grunhage and Haenel 1997), drawing on Wesely (1989), Sutton et al. (1995b) and DEPAC; or SPRUCE forest DEPosition (SPRUCEDEP, Zimmermann et al. 2006), drawing on PLATIN, Wesely (1989), DEPAC, EMEP and AURAMS.

In contrast to big leaf R_c models, the MLBC dry deposition model proposed by Wu et al. (2003), based on the Multi-Layer Model (MLM) by Meyers et al. (1998), described gaseous exchange between the soil, plants, and the atmosphere. A biochemical stomatal resistance model based on the Berry-Farquhar approach (Berry and Farquhar 1978) described photosynthesis and respiration and their coupling with stomatal resistance for sunlit and shaded leaves separately. Various aspects of the photosynthetic process in both C3 and C4 plants were considered in the model. The source/sink term S(z) was parameterized using terms to account for fluxes through the stomata of sun-lit and shaded leaves, and for fluxes through the cuticles of the leaves. The canopy was divided into $N = 20$ equally spaced levels, and S(z) was evaluated at each height, and summed with appropriate normalization. Vertical leaf area density LAI(z) was assumed to be described by a beta distribution (Massman 1982), which was chosen for compatibility with the roughness length and displacement height model of Massman (1997). Plant canopy structures were fit by one of six typical vertical profiles.

Canopy Compensation (χ_c) Point Models

The recognition that there is a non-zero NH_3 emission potential (Γ) in most vegetation types, as well as in different parts of the canopy (Section "Processes Controlling NH3 Emission and Uptakein the Soil/Plant/Atmosphere Continuum"), has led to the development of a range of canopy compensation point (χ_c) models, in which the net bi-directional flux to or from the atmosphere is provided generically from the difference between χ_c and

$$\chi_{a} : F_{\chi} = \frac{\chi_{c} - \chi_{a}\{z\}}{R_{a}\{z\} + R_{b}}. \tag{3}$$

For the formulation of χ_{c} itself, various canopy architectures have been put forward. The first χ_{c} model was developed by Sutton et al. (1995b, 1998a) and is often referred to as the “two-leg” χ_{c} model (Fig. 7b), featuring bidirectional exchange with stomata and deposition to non-stomatal surfaces. Here the R_{w} term accounted for all non-stomatal canopy sink terms, including leaf cuticle waxes and water, and allowed both deposition from the atmosphere as well as re-capture of NH_3 emitted by stomata. The canopy compensation point was calculated as (Sutton et al. 1995b):

$$\chi_{c} = \frac{\frac{\chi_{a}\{z\}}{R_{a}\{z\}+R_{b}} + \frac{\chi_{s}}{R_{s}}}{(R_{a}\{z\} + R_{b})^{-1} + R_{s}^{-1} + R_{w}^{-1}} \tag{4}$$

This 1-layer framework has been successfully applied for situations in which the canopy was closed and/or where soil NH_3 emission was negligible. However, where soil or litter NH_3 emission took place and dominated the canopy-scale flux, very large and unrealistic apoplastic Γ_{s} ratios (compared with independent estimates by apoplastic bioassays) were required to simulate the observed net emissions (Milford 2004). The 2-layer model by Nemitz et al. (2001a) was thus the logical extension of the 1-layer χ_{s}/R_{w} model, introducing, in addition to stomatal χ_{s} and non-stomatal R_{w}, a soil + ground surface emission potential (termed χ_{g} in Fig. 7c), mediated by in-canopy R_{ac} and by a further ground surface viscous sublayer term (R_{bg}). This $\chi_{s}/\chi_{g}/R_{w}$ model has been extensively tested and applied in diverse contexts, and was proposed as the optimum compromise between simplicity and accuracy, capable of describing bi-directional NH_3 exchange in atmospheric transport models over a very wide range of vegetation types (Nemitz et al. 2001a; Massad et al. 2010b; Cooter et al. 2010). As with the 1-layer χ_{c} model, the central term in solving the resistance model is χ_{c}, the resolution of which provides (Nemitz et al. 2001a):

$$\begin{aligned}\chi_{c} &= [\chi_{a}(R_{a}R_{b})^{-1} + \chi_{s}\{(R_{a}R_{s})^{-1} + (R_{b}R_{s})^{-1} + (R_{g}R_{s})^{-1}\} + \chi_{g}(R_{b}R_{g})^{-1}] \\ &\quad \times \{(R_{a}R_{b})^{-1} + (R_{a}R_{s})^{-1} + (R_{a}R_{w})^{-1} + (R_{b}R_{g})^{-1} + (R_{g}R_{s})^{-1} \\ &\quad + (R_{b}R_{w})^{-1} + (R_{g}R_{s})^{-1} + (R_{b}R_{w})^{-1}\}^{-1}.\end{aligned} \tag{5}$$

A three-layer model was also developed by Nemitz et al. (2000b), to account for a third potential NH_3 emission/uptake layer in the inflorescences or siliques at the top of an oilseed rape canopy, in addition to foliar and ground exchange. Here, two terms were defined for R_{ac} (R_{ac1} from siliques to foliage, R_{ac2} from foliage to ground), as were two R_{b} terms and two R_{w} terms for the siliques and foliage layers (Fig. 7d). The authors concluded that the leaf stomata were an effective NH_3 sink, whereas the leaf litter dominated nighttime emissions with the silique layer thought to dominate daytime emissions.

As modelled fluxes are highly sensitive to soil and plant surface temperatures (Section "Thermodynamic and Chemical Controls"), an accurate description of in-canopy vertical profiles of temperature is highly desirable, such that each r potential through the profile (Section "Vertical Distribution of Sources and Sinks Withinand Above Ecosystems") is expressed with the proper temperature scaling. Thus the Surface Atmosphere (SURFATM)-NH_3 SVAT model of Personne et al. (2009) coupled an energy budget model (Choudhury and Monteith 1988) with a pollutant exchange model, which was based on the $\chi_s/\chi_g/R_w$ model of Nemitz et al. (2001a), and additionally included a diffusive resistance term from the topsoil layer to the soil surface. In a 3-week simulation for the Braunschweig grassland, Personne et al. (2009) demonstrated that the energy balance model was suitably adapted for modelling the latent and sensible heat fluxes as the grass was cut then fertilized, based on prescribed (measured) values LAI and h_c. The model reproduced the temperatures of leaf and ground surfaces satisfactorily, except for a few days during which the cut grass lay on the ground prior to lifting. The model was later successfully validated against a two-month flux measurement period over a triticale canopy, where is was found that a very small cuticular resistance ($R_w < 1$ s m^{-1} at RH > 75 %, $R_w = 32$ s m^{-1} at RH = 50 %) was required to explain the observed fluxes (Loubet et al. 2012). In a similar fashion to SURFATM-NH_3, in the Wu et al. (2009) NH_3 stomatal compensation point version of the Wu et al. (2003) MLBC model (see above), the scheme was re-parameterized in order to derive leaf temperature from the energy balance at each level (z) in the canopy.

Elsewhere, earlier R_c models have also been modified to include a surface NH_3 compensation point, such as: the surface exchange scheme within AURAMS (Zhang et al. 2003, 2010) with a 2-layer $\chi_s/\chi_g/R_w$ structure; the revision of the DEPAC model (Erisman et al. 1994) into DEPAC3.11 with a 1-layer $\chi_s/\chi_w/R_w$ structure (van Zanten et al. 2010; Wichink-Kruit et al. 2010); a revised χ_s/R_w version of PLATIN (Griinhage and Haenel 2008); or the inclusion of the 2-layer $\chi_s/\chi_g/R_w$ by Nemitz et al. (2001a) into CMAQ for managed agricultural soils (Cooter et al. 2010, 2012; Bash et al. 2013) (see parameterization details below).

A further degree of complexity has been added by leaf surface NHx capacitance approaches, as an alternative to the steady-state, uni-directional R_w pathway in the χ_c models described above (Fig. 7b–d). Dynamic numerical solutions for the variable non-stomatal leaf surface NH_x pool have been grafted onto 1-layer (Fig. 7e; Sutton et al. 1998a; Flechard et al. 1999; Neirynck and Ceulemans 2008) and 2-layer (Fig. 7f; Burkhardt et al. 2009) χ_c models. For individual sites, such models tend to improve the overall model predictive capability only marginally, compared with steady state R_w-based χ_c models that have been optimised with site-specific parameterizations, i.e. an R_w function fitted to reproduce local flux data. Nonetheless, the added value of dynamic chemistry approaches for the leaf surface is three-fold: (i) to better explain the temporal dynamics of emissions; (ii) to allow bi-directional cuticular exchange and NH_3 desorption, especially for the morning peak; and (iii) in theory, to predict the leaf surface sink/source strength in a generic and mechanistic fashion, mostly driven by the local pollution climate and atmospheric acid/base mixing ratios, without the need for site-specific, empirical parameterizations for R_w (Flechard et al. 1999). This means that such an approach is more suitable for regional-scale and global applications where the site-specific optimised parametrizations are not generally and systematically applicable.

Parameterization Schemes for χ_c Models

The canopy compensation point models presented above proposed generic frameworks, which for individual ecosystems or flux measurement sites require an optimisation with locally fitted parameters or functions (e.g. Γ_s, Γ_g, R_w). Loubet et al. (2012) argue that one drawback of model/flux comparisons at given measurement sites is the non-uniqueness of parameter vectors that best fit the NH_3 fluxes: it is for example often difficult to establish whether soil or stomata are the main sources.

To achieve this, it is typically necessary to add additional site evidence, such as bioassay estimates of Γ for different ecosystem compartments (e.g. Fig. 3) and to carefully analyze the time course of differences between measurements and the estimates provided by different model appraoches.

For generalisation and application of models at larger scales, typically within regional CTMs, several parameterization schemes have been proposed recently. The new parameterizations for the 1-layer ($\chi_s/\chi_w/R_w$) DEPAC 3.11 scheme by Wichink-Kruit et al. (2010) and Van Zanten et al. (2010) were based on a combination of the results of three years of ammonia flux measurements over a Dutch grassland (*Lolium perenne/Poa trivialis*) canopy and of existing parameterizations from the literature. Values of χ_w were derived from actual nighttime flux measurements and accounted for the pollution climate of the site, while their derived R_w function mostly reflected surface humidity effects. The observed seasonal variations in Γ_s at their grassland site (typically >5000 from autumn until early spring, decreasing to ~1000 in summer, see Fig. 2), presumably reflecting photosynthetic activity and GS/GOGAT activity, and were parameterized as a function of temperature with an exponential decay fit. (Note that Loubet et al. (2012) found a similar exponential decay for Γ_c in a triticale canopy in spring). The spatial variations of Γ_s were linearly linked to atmospheric pollution levels through the long-term NH_3 concentration for given sites, based on a review of literature values. Two linear regressions were proposed, either based on literature Γ_s values derived from micrometeorological flux measurements, to be used in 1-layer χ_s/R_w or $\chi_s/\chi_g/R_w$ models, or based on Γ_s values from apoplastic extraction, to be used in 2-or multilayer (e.g. $\chi_s/\chi_g/R_w$) models (see Fig. 7). This distinction was based on the recognition that bioassay-derived Γ_s values were typically a factor of 3 lower than micrometeorologically derived values (e.g. Fig. 1d), presumably due to additional contributions by litter and soil emissions to the latter estimates.

Zhang et al. (2010) proposed parameterizations for their 2-layer $\chi_s/\chi_g/R_w$ model within AURAMS based on an extensive literature review. Their approach was to compile a large database of published χ_s and χ_g values, and to create a model look-up table (cf Table 5 in Zhang et al. 2010) for both parameters. For each of their

26 land-use classes (LUC), they derived representative model input values based on statistics of literature data. For LUC classes with fertilized vegetation, a much larger value was used (typically factor 10–100) for both χ_s and χ_g than for semi-natural ecosystems. For the former (fertilized), one single value was used throughout, while for the latter (semi-natural), both Γ_s and Γ_g can take either one of two default values, either "high" or "low", depending on the background atmospheric N input by wet and dry deposition. The parameterization for R_w (leaf cuticle) was unchanged from Zhang et al. (2003) and based on canopy wetness, leaf area, and meteorological conditions (relative humidity, friction velocity), but did not account for differences in pollution climate. Initial model runs showed that typical summer daytime χ_c values (at a temperature of 25 °C), assuming a low N status, were less than 2 $\mu g\ m^{-3}$ over forests and other semi-natural canopies, below 5 $\mu g\ m^{-3}$ over grasslands, and between 5 and 10 $\mu g\ m^{-3}$ over agricultural crops. In the winter, these values decreased to almost zero over the forests and to below 3 $\mu g\ m^{-3}$ over the crops. The application of this new bi-directional air-surface exchange model in replacement of the original dry deposition model will reduce the dry deposition fluxes simulated in the regional scale air-quality model for which it was designed, especially during the daytime and for canopies with high-N status. The reductions in simulated dry deposition fluxes will also be larger at higher temperatures, stronger wind speeds, and drier conditions (Zhang et al. 2010).

Massad et al. (2010b) also made a very comprehensive review of the NH_3 flux literature, in order to derive a generalised parameterization scheme for the 2-layer $\chi_s/\chi_g/R_w$ model by Nemitz et al. (2001a). Although their parameterizations were intended for application in any CTM, their scheme was to some extent taylored to fit the LUC of the EMEP model (Table 6 in Massad et al. 2010b; Simpson et al. 2012). The meta-analysis confirmed that nitrogen input was the main driver of apoplastic $[NH_4^+]$ and bulk tissue $[NH_4^+]$. For managed ecosystems, the parameterizations derived for fertilization were reflected in peak value of Γ_s and Γ_g a few days following application, followed by a gradual return to background values. Fertilizer amounts determined the magnitude of the Γ_s response, regardless of fertilizer form (mineral, organic, grazing), and also the scale of the Γ_g response for mineral fertilizer. The initial Γ_g response to slurry application was equal to the Γ_{slurry} value, while animal grazing resulted in an initial Γ_g value of 4000. The sharp temporal decrease in Γ_s and Γ_g following the initial fertilization or grazing peak was parameterized by an exponential decay function with an e-folding time constant (Γ) of 2.88 days. Forunmanaged ecosystems, as well as managed agrosystems in background conditions, Γ_s was parameterized as a power law function of total N input (N_{in}) to the ecosystem, i.e. atmospheric N deposition (N_{dep}) plus annual fertilizer application (N_{app}) if applicable. Although the meta-analysis had demonstrated that the relationship of Γ_s to bulk tissue $[NH_4^+]$ was more robust than to N_{in} across a wide range of plant species (see also Mattsson et al. 2009a), the use of N_{in} as a proxy for Γ_s was deemed more convenient than bulk tissue $[NH_4^+]$, which by contrast would not be easily available as spatial input fields for CTMs. The parameterization derived by Massad et al. (2010b) for the leaf surface resistance R_w is discussed above in Section "Process/Component Scale Models: Soil, Manure, Fertilizer, Leaf Litter, Leaf, Cuticle, Air Column Chemistry” and Fig. 6. One of the major advantages of the Massad et al. (2010b) scheme, compared to the parameterization by Zhang et al. (2010), is the mechanistic linkage of Γ_s and Γ_g to atmospheric N deposition and to agricultural practices, allowing ecosystems to respond dynamically to changes in emissions and deposition patterns and to land management events.

Cooter et al. (2010) presented an upgrade of the earlier R_c-based NH_3 dry deposition approach of Wesely (1989) that had been used within CMAQ (Byun and Schere 2006), into a bi-directional χ_c model based on the $\chi_s/\chi_g/R_w$ approach by Nemitz et al. (2001a). The work was motivated by the realisation that the CMAQ representation of the regional nitrogen budget was limited by its treatment of NH_3 soil emission from, and deposition to, underlying surfaces as independent, rather than tightly coupled, processes. At the same time, it was recognized that NH_3 emission estimates from fertilized agricultural crops needed to respond to variable meteorology and ambient chemical conditions. These objectives were met by the integration of the $\chi_s/\chi_g/R_w$ approach together with elements of the EPIC model (see Section “Process/Component Scale Models: Soil, Manure, Fertilizer,Leaf Litter, Leaf, Cuticle, Air Column Chemistry”), which was calibrated using data collected during an intensive 2007 maize field study in Lillington, North Carolina (Bash et al. 2010; Walker et al. 2013). More recently, regional simulations of CMAQ coupled with EPIC have provided dynamic continental (US) scale NH_3 emission estimates from fertilizer applications with a tight coupling between emissions, deposition and agricultural cropping practices (Cooter et al. 2012; Bash et al. 2013) (see Section “Ammonia Exchange in Chemical TransportModels (CTMs) at Regional Scales”).

Landscape Scale Models

The specificity of the landscape scale, especially in agricultural areas, with respect to surface/atmosphere NH_3 exchange modelling is characterised by the close proximity of large agricultural point sources, or “hotspots” (Loubet et al. 2009a) and of semi-natural NH_3 sink areas such as forests, moorlands and wetlands. Hotspots induce large horizontal NH_3 concentration gradients downwind from sources, typically an exponential decay with distance (Walker et al. 2008), and a large spatial heterogeneity in NH_3 concentrations (e.g. Dragosits et al. 2002; van Pul et al. 2008) and exchange fluxes (Sommer et al. 2009). This fine-scale variability occurs at spatial scales (typically 100 m to 1 km) much smaller than, and therefore not “seen” by, regional CTMs (resolution typically 5 × 5 km^2 to 50 × 50 km^2); from a regional modelling viewpoint the (unresolved) landscape scale generally falls under the header “sub-grid issues” (Dragosits et al. 2002). Modelling studies have been applied to determine the fraction of emitted NH_3, which is recaptured locally downwind from the source (Fowler et al. 1998; Asman et al. 1998). The results vary widely, showing recapture fractions within the first 2 km between 2 % and up to 60 %, but in most cases in the range between 10 and 40 % (Loubet et al. 2006, 2009a).

The variability is in part due to variations in vegetation types, roughness and LAI over the patchwork of land uses, but also due to the nitrogen enrichment associated with large NH_3 deposition rates close to sources (animal houses, manure storage facilities, fertilized fields) (Pitcairn et al. 2006). Given an otherwise homogeneous, large field (a few hectares) cropped with, say, wheat or maize, and located just outside a large point animal production facility, one may expect a 10- or 20-fold higher NH_3 deposition at a distance of 20 m from the source than 200 m further downwind (Loubet et al. 2009a). One may thus also expect much higher bulk tissue N or $[NH_4^+]$ and higher Γ_s close to the farm buildings, as well as higher NH_x concentrations in soil (Γ_g) and especially on leaf surfaces (Γ_d), together with higher pH, which theoretically lead to less efficient NH_3 removal by vegetation (per unit ambient NH_3 concentration) (Jones et al. 2007). Such feedbacks of cuticular saturation and apoplastic NH_4^+ enrichment on NH_3 deposition rates (Walker et al. 2008) can potentially affect spatial NH_3 deposition budgets very significantly at the scale of the landscape, but uncertainties are very large, datasets are few, and parameterizations to account for N enrichment feedbacks for landscape-scale models have yet to emerge.

These processes and their coupled emission/dispersion/deposition modelling have recently been thoroughly reviewed by Loubet et al. (2009a), and earlier by Hertel et al. (2006) and Asman (1998, 2002), and thus only a brief overview is presented here. Loubet et al. (2009a) provided a technical comparison of 7 existing local atmospheric transport and deposition models for NH_3: DDR (Asman et al. 1989); TREND/OPS (Asman and van Jaarsveld 1992), LADD (Hill 1998), DEPO1 (Asman 1998), FIDES-2D (Loubet et al. 2001), MODDAAS-2D (Loubet et al. 2006), and OML-DEP (Olesen et al. 2007). All models except MODDAAS-2-D (multi-layer, see Loubet et al. 2006) used a 1-layer (big leaf) surface exchange architecture, and most models used a uni-directional dry deposition R_c/V_d scheme by default. However, both MODDAAS-2-D and FIDES-2D (Loubet et al. 2001) allowed bi-directional exchange with stomata, though they did not account for any potential soil emissions.

Theobald et al. (2012) presented the first intercomparison of 4 short-range atmospheric dispersion models (ADMS, Carruthers et al. 1999; AERMOD, Perry et al. 2004; LADD; and OPS-st, van Jaarsveld 2004), which they applied to the case of ammonia emitted from agricultural sources. The intercomparison focused on atmospheric NH_3 concentration prediction in two case study farms in Denmark and the USA. Wet deposition processes were not included in the simulations because dry deposition is likely the dominant deposition mechanism near sources (Loubet et al. 2009a; Pitcairn et al. 2006). Similarly, chemical processing of NH_3 in the atmosphere were also assumed to be negligible for short-range dispersion. Thus the only NH_3 removal mechanism involved was surface dry deposition, with all models using R_c/V_d schemes. The performance of all of the models for concentration prediction was judged to be "acceptable" according to a set of objective criteria, although there were large differences between models, depending on which source scenarios (area or volume source, elevation above ground, exit velocity) were tested. The findings highlight that the rate of removal by dry deposition near such a source leads to a rather small effect on simulated near-source NH_3 concentrations, which largely depended on sound treatment of source characteristics and dispersion rates.

Ammonia Exchange in Chemical Transport Models (CTMs) at Regional Scales

Despite unequivocal evidence and widespread concensus that NH_3 exchange is bi-directional in most climates and ecosystem types, including unfertilized vegetation, most CTMs operating at national, regional and continental scales still use R_c/V_d deposition-only schemes for NH_3 (see model review by van Pul et al. 2009): e.g. unified EMEP MSC-W model (Simpson et al. 2012) and EMEP4UK 5 × 5 km (Vieno et al. 2010); a Wesely (1989) approach is used in CHIMERE (Vautard et al. 2001; LMD 2011); DEPAC is used in OPS-Pro 4.1 (van Jaarsveld 2004); EMEP R_c/V_d approach is used in the coupled Danish Ammonia Modelling System DAMOS (DEHM/OML-DEP) (Geels et al. 2012); combined DEPAC and EMEP parameterizations in MATCH (Klein et al. 2002); and LUC-specific values of R_c are used in FRAME (Singles et al. 1998). Nevertheless, a few instances of χ_c model implementation in CTMs have recently been reported, using new χ_c parameterization schemes (see Section "Canopy/Ecosystem Scale Models"): e.g. the LOTOS-EUROS model (using revised DEPAC 3.11) (Wichink-Kruit et al. 2012); the coupled CMAQ-EPIC model (Cooter et al. 2010, 2012; Bash et al. 2013); and AURAMS (Zhang et al. 2010). Other CTMs have meanwhile focused on improving the treatment of sub-grid variability (DAMOS; Geels et al. 2012) or the spatial and temporal distribution of NH_3 emissions by field-applied mineral fertiliers (CHIMERE/Volt'Air, Hamaoui-Laguel et al. 2012).

Canopy Compensation Point Implementations in Regional CTMs

The first test implementation of a χ_c approach within a CTM was made by Sorteberg and Hov (1996) using an early version of the EMEP model and the χ_s/R_w model by Sutton et al. (1995b, 1998a), but the parameterizations were very crude, with only 2 fixed Γ_s values, 946 and 315 for grassland/cropland and other vegetation types, respectively.

In their LOTOS-EUROS model runs at the European scale (25 × 25 km^2 resolution), Wichink-Kruit et al. (2012) found that by using the bi-directional NH_3 exchange scheme by Wichink-Kruit et al. (2010), the modeled ammonia concentrations increased almost everywhere (compared with the R_c-based model), in particular in agricultural source areas. This was largely due to increased NH_3 life time and transport distance. As a consequence, NH_x deposition decreased in source areas, while it increased in large nature areas and remote regions (e.g. S. Scandinavia). The inclusion of a compensation point for sea water restricted dry deposition over sea and better reproduced the observed marine background concentrations at coastal locations. Over the land area, the model predictive capability improved slightly, compared with NH_3 network data, but concentrations in nature areas were slightly overestimated, while concentrations in agricultural source areas were still underestimated. The authors also discuss the issue of model validation using measured NH_3 concentration, related to the representativeness of a single measurement point within a heterogeneous landscape, compared with the modelled grid square average NH_3.

As in most other CTMs, the treatment of the atmospheric NH_x budget in CMAQ v4.7 traditionally relied on: (i) a unidirectional R_c approach, and (ii) estimates of fertilizer NH_3 emission that were independent of the physical and chemical variables and components of the CTM that simulate atmospheric transport, transformation and loss processes. The coupling of CMAQ v5.0 with EPIC and the Nemitz et al. (2001a) $\chi_s/\chi_g/R_w$ model to simulate the bi-directional exchange of NH_3 (Bash et al. 2013) allowed for the direct estimation of NH_3 emissions, transport and deposition from agricultural practices, with dynamic interactions between weather, soil, vegetation and atmospheric chemistry (Fig. 8). The CMAQ-EPIC coupled model thus shifted the NH_3 emissions modeling paradigm for fertilizer application from static or seasonal emission factors to a more dynamic, process-based approach. Some parameterizations were borrowed from Massad et al. (2010b), but unlike their exponential decay function to adjust Γ_g as a function of time after fertilization, the soil NH_4^+ budget in CMAQ v5.0 was simulated as being dynamically coupled to hourly soil NH_4^+ losses due to evasion and nitrification, and increases in soil NH_3 due to deposition. Values of Γ_s for crops and of Γ_g for

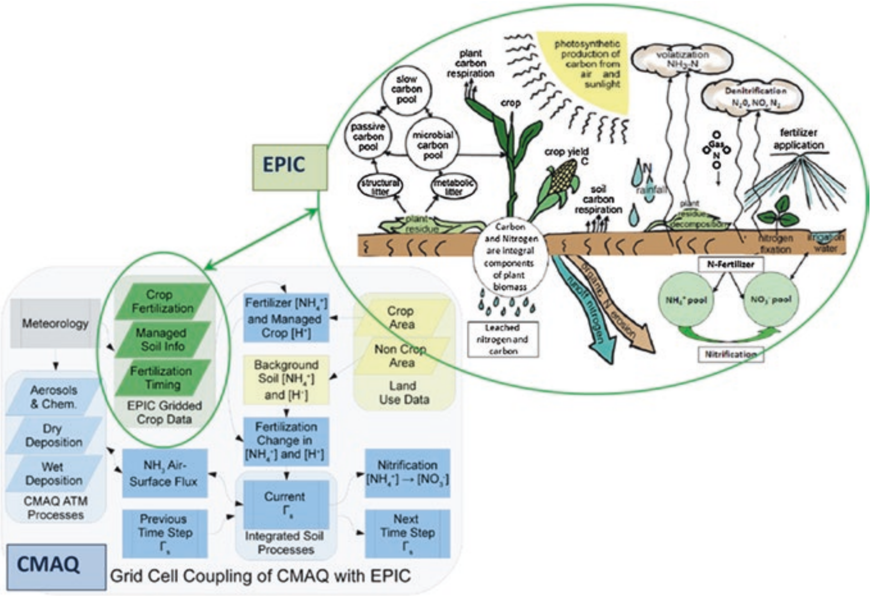

Fig. 8 Example of coupled CTM (CMAQ) and crop (EPIC) models for NH_3 exchange, modified from Cooter et al. (2012). *Top* Biogeo-chemical components of the carbon and nitrogen budgets in EPIC; *bottom* flow chart of EPIC coupled with CMAQ bi-directional NH_3 exchange. *Arrows* represent the flow of information, meteorological processes are shown in *grey*, EPIC processes in *green*, land use and land use-derived data in *tan*, and CMAQ processes in *blue*

non-agricultural soils were modeled as a function of land cover type and ranged from 10 to 160, which were at the low end of published values (e.g. Massad et al. 2010b; Zhang et al. 2010). The new coupled approach improved the predictive capability of CMAQ for NH_x wet deposition and for ambient nitrate aerosol concentrations. The largest improvements in the aerosol simulations were during the spring and fall, when the US EPA's national emission inventory estimates at these times are particularly uncertain. In Cooter et al. (2012), the EPIC agro-ecosystem and CMAQ models were used to assess agro-ecosystem management and changes in biogeochemical processes, providing more robust model assessments of future land use, agricultural, energy and climate change scenario analyses.

Improved Treatment of Sub-grid Variability and Spatial and Temporal NH_3 Emissions

High spatial resolution deposition modelling is crucial to determine the frequency of occurrence and magnitude of N critical loads and levels exceedances, since many sensitive nature areas and sites of special scientific interest (e.g. wetlands, heathlands, etc.) are very small, say a few hectares, and often located close to agricultural NH_3 sources (Dragosits et al. 2002). As noted above (Section "Ammonia Exchange Models and Parameterizationsfrom the Leaf to the Globe: State-of-the-Art"), this is a landscape scale issue, but it is also a CTM issue, because (i) failing to reproduce local NH_3 budgets affects the predictive capability of regional modelling, and (ii) CTMs must be used to derive critical loads exceedance maps at national and regional scales in support of environmental policy development. Improving the performance of high-resolution local-scale models requires high quality emission inventories with sufficiently high spatial resolution (Skjeth et al. 2011). In addition, a high temporal resolution for emissions is also crucial for the performance of CTMs, and dynamic calculations of NH_3 emissions are needed for a better prediction of high particulate matter episodes (Menut and Bessagnet 2010; Henze et al. 2009). This is especially relevant as NH_3 emissions in winter will lead to a higher contribution to particulate matter than NH_3 emissions in summer.

Data requirements for such models are access to detailed information about activity data and the spatial distribution in emissions on annual basis. Such requirements are met in very few countries, e.g. in Denmark and the Netherlands, where the ammonia emission inventory relies on highly detailed national agricultural registers, containing the exact location of farm houses, storages, and associated fields, as well as data on type and number of livestock, and information about applied production methods (Skjeth et al. 2004). In many other countries agricultural activity and NH_3 emission data are either very crude, based on e.g. default emission factors, and/or confidential at resolutions finer than typically $10 \times 10\ km^2$.

To address both spatial and temporal issues, the Danish Ammonia Modelling System (DAMOS) has been established as a coupled system consisting of the Danish 3-D Eulerian Hemispheric Model (DEHM) CTM covering the Northern Hemisphere ($6 \times 6\ km^2$ resolution) and of the local-scale (up to ca. 20 km)

Gaussian plume dispersion and deposition model OML-DEP (400 × 400 m^2 resolution) (Geels et al. 2012). The model may be coupled to a code (Skjeth et al. 2011) for calculating ammonia emission on the European scale, accounting for local climate and local management, in which a modular approach is applied for deriving data as input to the temporally varying ammonia emission model. Comparisons between computed and measured ambient NH_3 concentrations demonstrated considerable improvements in model performance over Denmark when the high spatial and temporal resolution emission inventory was applied, instead of the conventional (static) seasonal variations approach (Skjeth et al. 2004). Further, Geels et al. (2012) showed that the coupled DEHM/OML-DEP model system captured the measured NH_3 time series in Denmark better than the regional-scale model alone, and that about 50 % of the modelled concentration level at a given location originated from non-local emission sources. However, the coupled DAMOS model still overestimated observed local ammonia concentrations across Denmark, which might in part be explained by overestimated national emissions, by underestimated rates of conversion to NH_4^+ and of dry deposition, and, as in the LOTOS-EUROS case (Wichink-Kruit et al. 2012), by the model grid square size.

Laguel-Hamaoui (2012) coupled the 1-D Volt'Air model (Genermont and Cellier 1997), originally developed for field-applied slurry and adapted here for mineral fertilizers, to the CHIMERE CTM (Vautard et al. 2001; LMD 2011), in order to assess the impact of fertilizer NH_3 emissions on PM10 and NH_4NO_3 aerosol at the national scale. Ammonia emissions were computed from mineral fertilizer spread over agricultural soils, using datasets of crop management practices, soil properties and meteorology. Considerable effort went first into collecting management practices data at the national level, together with data processing to derive their spatial distribution. Three sets of CHIMERE runs were made, using as NH_3 emission inputs to the CTM either (i) the official EMEP data under the CLRTAP convention, (ii) the French national emissions inventory (INS) data, or (iii) a combination of the coupled Volt'Air emissions for mineral fertilizers and INS data for other sources. The three options for NH_3 emission inputs had different impacts on aerosol concentrations, depending on HNO_3 concentrations. The comparison of modelled PM10 and NH_4NO_3 aerosol with observations showed that the new ammonia emission method lent a marginal improvement to the spatial and temporal correlations in several regions and a slight reduction of the negative bias (1–2 $\mu g\ m^{-3}$ on average).

Global Scale

Uncertainties in the global NH_3/NH_x cycle are very large, not least because the NH_3 emission factors typically used for global emission upscaling, and the parameterizations for surface exchange modelling, are heavily biased towards NW European and N American conditions. Some sources are rather well studied, such as livestock agriculture in temperate Europe, while others are based on very few atmospheric NH_3 flux measurements. The uncertainties are particularly large for natural emissions from terrestrial sources and oceans (Dentener and Crutzen 1994; Bouwman et al. 1997), biomass burning (Andreae and Merlet 2001) and for livestock sources and forests in tropical regions. There is a major lack of knowledge on agricultural management practices in many parts of the world and on the effect of the many climates and soils of the world on emission processes, especially the interplay of temperature and moisture. With 37 % of the world's population between them, China and India's collective NH_3 emissions account for around 13.5 Tg NH_3–N year^{-1} (Huang et al. 2012; Aneja et al. 2012), i.e. about one-third of the EDGAR (2011) global emission estimate of 40.6 Tg NH_3–N year^{-1}, but subject to huge uncertainty. Aneja et al. (2012) estimate that NH_3 emissions from livestock could be a factor of 2–3 higher than their best estimate, while emissions from fertilizer application could be up to 40 % lower than they estimated.

In global atmospheric CTMs, which are coupled to general circulation models (GCMs) or driven by analyzed meteorological fields, and by prescribed emissions of NH_3 (e.g. Bouwman et al. 1997) and of other trace gases, ammonia exchange over terrestrial vegetation is generally modelled using R_c/V_d resistance schemes, often following Wesely (1989) (e.g. TM5 model, Huijnen et al. 2010; Ganzeveld and Lelieveld 1995; STOCHEM, Collins et al. 1997; Bouwman et al. 2002; GEOS-Chem Bey et al. 2001; Wang et al. 1998). However, in the MOGUNTIA model at $10 \times 10°$ resolution, Dentener and Crutzen (1994)—who were the first to reconcile by modelling the consistency on a global scale of upscaled NH_3 emission inventories and atmospheric NH_3/NH_4^+ concentrations and deposition—did use a canopy compensation point to calculate NH_3 emissions from natural continental ecosystems. Their approach did not distinguish stomatal from non-stomatal (soil, leaf surfaces) contributions, as they applied one set value (equivalent to $\Gamma = 290$) for the canopy, corresponding to $[NH_4^+] = 46$ µmolL^{-1} and pH = 6.8 in the mesophyll, based on measurements over pine forest by Langford and Fehsenfeld (1992). To account for the short atmospheric lifetime and the sub-grid local deposition of NH_3, Dentener and Crutzen (1994) directly removed 25 % of all anthropogenic emissions over land, such that these emissions never entered the transport and chemistry calculations. Bouwman et al. (2002) similarly reduced their grid square emissions for the same reason; the fraction of the total emission deposited within a few kilometers from the source depended on many factors, including the height of the source and the surface roughness (Asman 1998), and the compensation point concentration of vegetation.

Dentener et al. (2006) reported a multi-model evaluation (23 global CTMs) of current and future (2030) deposition of reactive nitrogen (NO_y, NH_x) as well as sulfate (SO_x) to land and ocean surfaces. Models predicted that NH_3 dry deposition represents between 30 and 70 % of total deposition. Present-day deposition using nearly all information on wet deposition available worldwide showed a good agreement with observations in Europe and North America, where 60–70 % of the model-calculated wet deposition rates agreed to within ±50 % of quality-controlled measurements. However, models systematically overestimated NH_x deposition in South Asia compared with available bulk wet deposition measurements.

There were substantial differences among models for the removal mechanisms of NH_x, as well as for NO_x and SO_x, leading to $\pm 1\sigma$ variance in total deposition fluxes of about 30 % in the anthropogenic emissions regions, and up to a factor of 2 outside.

The evaluation/validation of global CTMs for NH_3 dry deposition (or surface exchange) is even more difficult than for regional CTMs, with scarce or no NH_3 concentration and wet NH_x deposition data in many parts of the world, and, where there are data, point measurements being largely de-coupled from the very large grid square modelled averages (typically $1° \times 1°$ to $10° \times 10°$). Satellite data providing atmospheric column integrated NH_3 concentrations have recently offered a very welcome addition (Clarisse et al. 2009; Shephard et al. 2011; R'Honi et al. 2013), but their interpretation can prove complex in a modelling context. Despite a good qualitative agreement between satellite (IASI/MetOp) measurements and simulations by the TM5 global CTM, Clarisse et al. (2009) found that the satellite data yielded substantially higher NH_3 concentrations north of 30°N compared with model projections, and lower concentrations than the model south of 30°N. They concluded that ammonia emissions could have been significantly underestimated in TM5 in the Northern Hemisphere, but there were also issues with IASI's detection limit, limited thermal contrast, and an unrepresentative morning orbit time.

Similarly, Shephard et al. (2011) compared the output of global high-spectral resolution nadir measurements from the Tropospheric Emissions Spectrometer (TES) on NASA's Aura with GEOS-Chem model runs; initial comparisons showed that TES/Aura values were higher overall. These authors also invoked the possible underestimation of NH_3 emissions in the GEOS-Chem inputs, but also possibly the over-representation of NH_3 values at the $2° \times 2.5°$ resolution coming from TES sampling NH_3 hotspots at the subgrid level. They argued that the better agreement between TES/Aura and GEOS-Chem seasonality over biomass burning regions, compared with agricultural source regions, suggested that the latter may be a more likely source of uncertainty in models.

Synthesis and Conclusions

The basic processes controlling surface/atmosphere NH_3 exchange are relatively well understood, at least qualitatively. A wide range of factors are important, including: thermodynamics, meteorology, surface and air column heterogeneous chemistry, plant physiology and N uptake, ecosystem N cycling, compensation points, nitrogen inputs via fertilization and atmospheric deposition, leaf litter decomposition, SOM and soil microbial turnover, soil properties. Most of the fundamental process understanding was gained during the 1980s and 1990s, while many advances in modelling logically followed from the late 1990s onwards, spurred by the canopy compensation point concept of Sutton et al. (1995b, 1998a). There has been a gradual increase in the complexity of surface/atmosphere NH_3

exchange models, from simple steady-state R_c models to dynamic, multiple layer, multiple sink/source, multiple chemical species exchange models. This reflects both the improvement in process understanding and the increasing availability of flux datasets, which are needed to parameterize models.

Yet there remain substantial challenges at all spatial scales (leaf to globe). The predictive capability of existing models at the field scale is often poor when tested against new flux measurement or at new sites, and a local re-parameterization is often necessary to describe observations satisfactorily (even accounting for potentially large errors in flux measurements, as shown by intercomparison exercises). Semi-empirical parameterization schemes that are developed on the basis of a literature review and many flux datasets (Massad et al. 2010b; Zhang et al. 2010; Segaard et al. 2002) should in principle, statistically, reproduce large-scale features of NH_3 exchange, as least within the multi-dimensional climate/vegetation/soil/management matrix, from which they derive. However, if their degree of empiricism is too large, they may prove unsuitable for generalisation to other conditions and for scenario simulations (e.g. climate change). On the other hand, the more mechanistic process-oriented models should in theory be applicable in all conditions, but they typically require more input data (some of which may not be available), are more difficult to parameterize (a greater number of parameters with no established reference), and are more computationally intensive (and thus less likely candidates for large-scale models).

The ideal surface/atmosphere NH_3 exchange model should treat all ecosystem NH_x-related processes, fluxes and pools dynamically (fertilizer volatilisation and recapture, soil biogeochemistry, plant biochemistry and physiology, air and surface chemistry, atmosphere exchange) within a multiple-layer canopy framework (in-canopy profiles of turbulence, radiation, temperature, humidity, green vs senescent leaves, soil layer). Such a coupling is possible and practicable at the field scale (e.g. coupled STAMP/CERES-EGC/Volt'Air/SURFATM over crops), with a view to investigating certain aspects of the exchange, their dynamics and interactions, in parallel with detailed measurements of fluxes and pools. Clearly the task is more complex at the regional scale, although the CMAQ/EPIC example (Bash et al. 2013; Cooter et al. 2012; Fig. 8) demonstrates that it is feasible to a degree. The level of complexity of surface exchange schemes must be taylored to suit the modelling objectives, the scale and the availability of input data, while the availability of measurement data for validation assessment may prove a limiting factor in model development.

Realistic NH_3 Exchange Frameworks for CTMs

The current level of complexity of NH_3 surface exchange schemes in most regional and global CTMs is low relative to the advances that have been included in field scale models, i.e. static emissions from inventories and R_c/V_d unidirectional deposition (with the exception of those few models mentioned in

Section "Ammonia Exchange in Chemical TransportModels (CTMs) at Regional Scales"), and clearly does not reflect the current level of process understanding. The following list highlights features that could realistically be implemented in $\chi_s/\chi_g/R_w$ two-layer schemes (Nemitz et al. 2001a; see Section "Canopy/Ecosystem Scale Models"; Fig. 7) within CTMs, at least at regional scales.

- Dynamic agricultural NH_3 emissions from field-applied manures and fertilizers. At present these emissions are typically prescribed from national or international inventories, and independent of meteorological conditions and crop development stage, but seasonal and diurnal distribution factors are applied. Dynamic emissions could be simulated using process-based models (Section "Process/Component Scale Models: Soil, Manure, Fertilizer,Leaf Litter, Leaf, Cuticle, Air Column Chemistry"), even if the treatment does not extend all the way to soil biogeochemistry, soil NH_4^+ pools and plant uptake.
- Soil/litter emission potential (outside fertilization events). This term is likely negligible in most temperate forests and semi-natural vegetation on acidic soils, but Γ_g can be very large in grasslands and crops during the growing season, and might also be important in tropical forests due to large mineralisation rates and higher temperatures.
- Canopy re-capture of soil-based emissions. Emissions from fertilizers and other ground-based sources are partially re-captured by foliage (stomatal and non-stomatal pathways in a two-layer model, Fig. 7c). The degree of re-capture is controlled by canopy closure and leaf density (LAI profile), wind penetration, leaf wetness.
- Bi-directional stomatal exchange; N input-dependent Γ_s. The analysis by Massad et al. (2010b, their Fig. 5) shows consistent and convincing relationships between N inputs and Γ_s for crops and grasslands, which could be implemented in CTMs. Because fertilization outweighs atmospheric deposition by a factor of 10 in such systems, the circularity issue (N inputs affect Γ_s, while Γ_s controls NH_3 deposition) is less critical than in seminatural vegetation, though this represents a potentially important long-term negative feedback on deposition. Nevertheless, the relationship of Γ_s to atmospheric N deposition remains rather uncertain.
- Photosynthesis-dependent stomatal resistance (R_s). The widely used multiplicative algorithm by Jarvis (1976), and other simplified empirical approaches (Wesely 1989), should be upgraded to a more mechanistic, photosynthesis-driven model (e.g. Ball et al. 1987), following the example of CTMs for O_3 (Anav et al. 2012).
- Pollution-climate dependent non-stomatal uptake (R_w). This feature is present in some CTMs via the (long- term) NH_3/SO_2 ratio, but likely most regional and especially global models do not account for the effects of surface chemical loadings on non-stomatal uptake rates. Accounting for NH_3 alone (Jones et al. 2007) is not sufficient away from the large agricultural point sources; rather, the ratio of Total Acids to NH_3 (Fig. 6; Massad et al. 2010b) should be used generically. Wind erosion of soil particles and leaf base cation leaching may raise leaf surface moisture pH significantly, but there are too few available data to account for this at present.

- Offline ecosystem and leaf surface chemistry modelling. Some CTM frameworks may not be able to accommodate coupled (online, interactive) ecosystem functioning together with the transport, chemistry and exchange calculations. However, soil/plant/ecosystem models (e.g. DNDC, STAMP, PaSim) could potentially be used offline to generate many values of Γ_s, Γ_g, $\Gamma_{litter,}$ Γ_{soil} in multiple simulations of ecosystems, seasons, soil and pollution climate conditions, representative of the region in which the CTM is applied. Such Γ values should first be validated versus values published in the literature, and could then be called during CTM simulations from look-up tables or multiple regression functions. This might prove a viable compromise between constant default values (Zhang et al. 2010), or empirical functions (e.g. exponential decay with time, Massad et al. 2010b), and fully coupled CTM/ecosystem frameworks (Cooter et al. 2012). A similar concept could be applied for dynamic leaf surface chemistry (Flechard et al. 1999), whereby typical T_d potentials could be simulated offline for a wide range of environmental conditions, and called up by the CTM in a $\chi_s/\chi_g/\chi_d/R_d$ scheme.

Further Needs for Flux Measurements, Model Input Data, and Validation Data

For regional and global representativeness, model development and parameterization rely heavily on new field-scale flux measurement datasets becoming available, but it is also clear that the availability of model input data and of spatially distributed validation data can be limiting factors for CTMs at regional and global scales. The most pressing data needs are summarised below.

- Flux measurements for under-represented ecosystems in temperate regions. The NH_3 flux literature is heavily dominated by grasslands, cereal crops, heathlands/moorlands and coniferous forests. There are few measurements over root crops, leguminous crops and legume-rich grasslands, deciduous forests, dry scrubland.
- Flux measurements in the tropics: data are needed for all ecosystem types including rain forests, savannah, tropical crops.
- Flux measurements near (<500 m) agricultural point sources in rural landscapes, together with a quantification of soil, apoplastic and epifoliar Γ values as a function of distance from sources. Errors in measured fluxes arising from NH_3 advection must be accounted for (Loubet et al. 2009b).
- Seasonal and spatial variations in bulk leaf N content and apoplastic Γ_s ratio for a range of ecosystems. Such measurements could be carried out at a large number of sites across a CTM modelling domain, without necessarily measuring NH_3 fluxes above ecosystems, and would be useful to explore temporal and spatial patterns of modelled NH_3 exchange and total N deposition.

- Measurements of Γ values for the dominant crops, ecosystems and land uses in different climates and for different agricultural practices. These experimental Γ estimates should be collected with a view to both (i) underpinning the development of empirical parameterizations for bi-directional models and (ii) validating process-based ecosystem model Γ predictions. Long-term (e.g. annual, growing season) flux and Γ datasets are needed to better represent background conditions, as campaign-based measurements over fertilised systems have traditionally tended to focus on emission events. Wherever possible, the determination of Γ_s values should be attempted using different techniques (micrometeorological surface concentration extrapolation; controlled gas exchange chamber experiments; apoplastic extraction), as they tend to yield different results and the discrepancies between techniques are as yet poorly understood, given the current paucity of parallel measurements.
- Collection of critical ancillary data wherever NH_3 flux are measured in the field. In addition to classical (micro-) meteorological data, measured ancillary data must include variables that are likely to be useful later for model parameterization or validation. Efforts should be made to measure the following according to the issues being addressed: LAI and leaf density profile; leaf wetness profile; soil texture, porosity, wilting point, organic matter content, pH, $[NH_4^+]$ and $[NH_3^-]$; slurry pH, TAN, dry matter content and application rate; bulk leaf N and NH_4^+ content; leaf litter pH and $[NH_4^+]$; leaf surface water (dew, rain) pH and $[NH_4^+]$. More difficult to measure, but equally important, would be apoplastic pH and $[NH_4^+]$, such as by the vacuum infiltration technique (Husted and Schjoerring 1995); in-canopy vertical NH_3 profiles; ambient concentrations of SO_2, HNO_3, HNO_2 and HCl, and particulate NH_4^+ and NO^-. Studies quantifying base cation and other ion exchange with leaf surfaces are also needed.
- Fundamental analytical research is needed to provide guidance on the most appropriate soil NH_4^+ extraction method for the development of representative soil Γ values. Many studies have demonstrated the variability of extracted/extractable NH_4^+ depending on the electrolyte used (e.g. KCl, $CaCl_2$) and its concentration in the extraction solution (see for example Fig. 1 in the Supplement on http://www.biogeosciences-discuss.net/10/C2954/2013/bgd-10-C2954-2013-supplement.pdf). Provided a better understanding of the relationships between extractable NH_4^+ and soil Γ, historical soil chemistry datasets from long-term ecological sites, agricultural experiment stations, soil surveys, etc., could be put to use within the context of soil/vegetation/atmosphere NH_3 modelling.
- Use of environmental microscopy (e.g. Burkhardt et al. 2012) as a powerful set of tools for improving our fundamental understanding of the chemical dynamics of leaf surface water during the transition from wet to dry conditions. Further testing and development of dynamic leaf surface chemistry models is currently hindered by the fact that the chemistry of microscale cuticular water layers present on leaves and needles during the day cannot be measured. In the absence of

suitable techniques for field measurements, such laboratory techniques should be encouraged.

- Development, testing, validation and deployment of low-cost instrumentation for long-term NH_3 flux estimates. Given the complexity and elevated costs associated with intensive and high-resolution NH_3 flux measurement campaigns, there have been endeavours to develop robust “low-cost, low-tech” methods for long-term flux estimates and parameterizations, such as the COTAG (COnditional Time-Averaged Gradient) system (Famulari et al. 2010). However, such systems have been successfully deployed at only a handful of sites to date, and further they lack consistent validation against established reference methods.
- Spatial fields of measured atmospheric NH_3 and NH_4^+ concentrations. Satellite-derived column NH_3 data offer much promise for CTM evaluation at regional and global scales, but there are still large uncertainties in the retrieved concentrations. Ground-based monitoring networks for both NH_3 and NH_4^+ by low-cost denuder/filter methods (Tang et al. 2009; Flechard et al. 2011; Adon et al. 2010) are available in only a handful of countries worldwide and should be encouraged, both for CTM evaluation and for ground truthing of satellite data. The vertical dimension of the concentration field in the atmospheric boundary layer should also be explored; aircraft measurements provide such information but are expensive; the extent to which low-cost measurement techniques could be deployed in profile configurations on tall towers should be investigated.
- Fine-resolution (~1 km^2) agricultural census data, and management practices. These model input data for CTMs are often only poorly known. The former are in many countries either classified information or not documented, and only available at much coarser resolution (>10 km × 10 km). Data on typical management practices with respect to manure and fertilizer application (timing, amounts, machinery) should be easier to obtain, but require extensive survey work.
- Development of methods for sub-grid assessments. The accuracy and evaluation of models close to sources is a source of uncertainty, since especially NH_3 deposition can occur at scales substantially smaller than the horizontal and vertical extent of CTMs (e.g. Section “Landscape Scale Models”, and Loubet et al. 2009a). Even where network data are available, the application and evaluation of CTMs for NH_3 concentrations is hindered by such local-scale gradients and variability (Wichink-Kruit et al. 2012). Use of plume or Lagrangian 1-D models close to the source (see Asman, 2001; Hertel et al. 2006, 2011) or coupling of sub-grid dispersion models to CTMs (e.g. Geels et al. 2012) should help bridge the gap between ground-based, single-point observations and spatially averaged CTM outputs, and could be used to help parameterize larger scale CTM models in future.

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Modelling Atmosphere-Biosphere Exchange of Ozone and Nitrogen Oxides

L. Ganzeveld, C. Ammann and B. Loubet

Introduction

Vegetation canopies are efficient in removing ozone (O_3) from the atmosphere making surface dry deposition an important process in air quality but also in climate change. O_3 is the 3rd most important greenhouse gas (IPCC) responsible for ~25 % of the total net radiative forcing attributed to human activities (Forster et al. 2007). In addition, there is an important role of O_3 vegetation uptake in climate change through its impact as a pollutant on photosynthesis resulting in an expected reduction in plant productivity and carbon sequestration (Sitch et al. 2007). The nitrogen oxide compounds nitric oxide (NO) and nitrogen dioxide (NO_2), collectively known as NO_x, are pollutants effecting human health. NO_x is also key to tropospheric O_3 photochemical production and abundance of the hydroxyl radical (OH), which determines the lifetime of pollutants and greenhouse gases such as methane (Fowler et al. 2009a). NO_x input to ecosystems can also further play a role in climate change through its role as a terrestrial nutrient that might potentially limit enhanced net primary production (NPP) in a future carbon dioxide enhanced climate (de Vries et al. 2009; Holland et al. 1997). Large NO_x deposition

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L. Ganzeveld (✉)
Earth System Science Group, Department of Environmental Sciences, Wageningen University, Wageningen, The Netherlands

C. Ammann
Air Pollution and Climate Group, Research Station Agroscope, Zurich, Switzerland

B. Loubet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

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fluxes on ecosystems can also result in forest decline and loss of biodiversity as a consequence of soil eutrophication and acidification (Bouwman et al. 1997; Galloway et al. 2008).

Because of the role of NO_x in the photochemical production of O_3, concentrations as well as fluxes of the three compounds are intrinsically related to each other inside vegetation canopies and the atmospheric boundary layer. This is also due to the fact that the time scale of (photo-) chemical reactions between NO_x and O_3 (and other reactive compounds involved in this photo-chemistry) is of the same order as the turbulent time scale (Lenschow 1982b). This implies the potential occurrence of a flux divergence: a change in the magnitude or even the direction of flux with height as a function of these chemical reactions. Due to this effect and the co-existence of in-canopy NO_x sources and sinks, the atmosphere-biosphere flux can be upward as well as downward. Consequently, rather than referring to surface emissions or dry deposition we hereafter refer to bi-directional atmosphere-biosphere NO_x exchange. In contrast, for O_3 in-canopy biological, physical and chemical sinks generally prevail resulting in observed O_3 atmosphere-biosphere fluxes being directed downward and reflecting surface dry deposition.

Here we review the current state-of-the art knowledge on atmosphere-biosphere exchanges of O_3 and NO_x presenting an overview of their main sink and source processes as a function of biogeochemical and meteorological drivers. We also present an overview of O_3 and NO_x atmosphere-biosphere exchange representations in models deployed at the field- to global scale. Finally we identify the main needs in terms of observations and model development to further improve our knowledge and O_3 and NO_x atmosphere-biosphere exchanges models for application at the field to global scale.

Sources and Sinks Processes Contributing to Biosphere-Atmosphere Exchange

Here we review the commonly applied model approaches to represent sink (uptake) and source (release) processes. However, potential deviations or additions to the classical schemes are also mentioned. The sink strength of individual uptake/deposition pathways is commonly described and quantified using a resistance scheme in all types of models: i.e. the sink flux is considered proportional to the difference in local air concentration between two locations of the respective trace gas divided by the transfer resistance (Hicks et al. 1987b). The three-pathway scheme (Figure) is often taken as a reference in most current O_3 and NO_x deposition models (Emberson et al. 2001b; Lamaud et al. 2009; Stella et al. 2011d; Zhang et al. 2002).

Most quantitative information and model parameterisations of source/sink processes have been derived empirically from exchange flux measurements by enclosure techniques (Altimir et al. 2006; Breuninger et al. 2012; Gut et al. 2002; Pape et al. 2009) or micrometeorological techniques (Duyzer et al. 1995; Lamaud et al.

2009; Rummel et al. 2002, 2007; Stella et al. 2011b). However, it must be noted that such measurements do not reflect individual processes but rather a combination of various sources and sinks located at the ground or in the canopy. Consequently, individual NO_x and O_3 source and sink processes have often to be determined (estimated) indirectly from measured fluxes using simplified assumptions and partitioning methods (models). Despite these limitations, it is essential to disaggregate the stomatal, cuticular and soil deposition pathways in order to assess the role of feedbacks involved in air quality and climate change interactions (see below).

Plant Leaf Processes: Stomatal and Non-stomatal Exchange

(a) Stomatal uptake of O_3

The exchange of O_3 and NO_2 on vegetated surfaces is dominated by the well-documented uptake through leaf stomates. For O_3 it is commonly assumed that, despite its small solubility, the inner-stomatal concentration is zero. Yet, some models consider O_3 adsorption in the apoplast and its reaction with ascorbate (Tuzet et al. 2011). These models tend to predict a smaller stomatal absorption of O_3 which is due to an additional "apoplastic" resistance R_{apo} which leads to a stomatal O_3 concentration up to half the external concentration. However, if the assumption of a zero inner-stomatal concentration is valid, O_3 stomatal uptake is fully controlled by stomatal aperture quantified as stomatal resistance against the diffusion of O_3 molecules into the sub-stomatal cavities (Emberson et al. 2000). This means, that the stomatal resistance for O_3 is directly proportional to the stomatal resistance for H_2O (by the inverse of the ratio of the O_3 and H_2O molecular diffusion coefficients). The resistance for H_2O (or CO_2) can be determined by leaf transpiration measurements (and/or photosynthesis measurements) or estimated from canopy-scale H_2O/CO_2 flux measurements by the Penman-Monteith approach or combined methods as proposed by Lamaud et al (2009). The non-stomatal resistance (or cuticular or external leaf resistance) is generally quantified as the residual of the measured total leaf O_3 uptake minus the (H_2O/CO_2-derived) stomatal uptake.

(b) Non-stomatal uptake of O_3

Non-stomatal ozone leaf uptake can be of similar magnitude as stomatal uptake. This is not only relevant to quantify the O_3 dry deposition flux but also to assess the impact of O_3 on plant functioning and carbon sequestration which depends on the appropriate partitioning between stomatal and non-stomatal O_3 removal. An overview of experimental results and current knowledge on non-stomatal uptake is given by Fowler et al. (2009b) (see also references therein). They conclude that the relevant controlling factors are temperature (increasing deposition by thermal decomposition of ozone), surface wetness (increasing deposition) and solar radiation. Temperature and solar radiation could potentially affect non-stomatal removal of O_3 through their role in leaf-surface ozone photolysis and reactions with emitted VOCs. However, Zhang et al. (2002), Lamaud et al. (2009) and Stella et al. (2011b) only retained the dependence on relative humidity.

(c) Stomatal and non-stomatal exchange of NO_2 and NO
For NO_2 the state of knowledge on the stomatal exchange is less consistent. In the most simple approach NO_2 is treated simply like O_3. However, a number of studies reported significant deviations in the behaviour of NO_2 and suggested the use of an additional mesophyllic resistance reducing the stomatal uptake (Ganzeveld and Lelieveld 1995) and/or the existence of an NO_2 leaf compensation point (Eller and Sparks 2006; Gut et al. 2002; Hereid and Monson 2001; Lerdau et al. 2000; Teklemariam and Sparks 2006; Thoene et al. 1996). This leaf compensation point reflects the threshold ambient NO_2 concentration above which deposition occurs whereas for ambient concentrations smaller than the compensation point the leaf actually provides a source of NO_2. Because of the uncertainty in the NO_2 stomatal exchange, both in chamber methods (Breuninger et al. 2012) or in micrometeorological methods (Stella et al. 2012), it is much more difficult to separate and study the non-stomatal exchange of NO_2. In a very simple approach, the non-stomatal deposition was quantified from nighttime/dark measurements assuming that it is constant in time and stomatal exchange is zero (Eugster and Hesterberg 1996).

The (potential) exchange of NO by plant leaves is even more controversial. Uptake rates of NO observed by Neubert et al. (1993) are about one order of magnitude lower than those for NO_2, consistent with the findings reviewed by Hanson and Lindberg (1991). The main reason for this significantly smaller deposition velocity is the relative large mesophyll resistance for NO (Neubert et al. 1993; Wesely 1989). Kisser-Priesack et al. (1987) concluded, based on measurements with radioactively labelled NO, that cuticular uptake should not be ignored (Hanson and Lindberg 1991), also because of the relatively small loss by deposition through the stomata. In contrast, Neubert et al. (1993) and Wesely (1989) find that the uptake of NO by the cuticle does not contribute significantly to the foliage uptake.

The existence of an NO_2 leaf compensation point implies a leaf-scale production process of NO_2. Hari et al. (2003) observed a considerable NO_x emission from pine shoots only with UV light present. Zhou et al. (2003) and Raivonen et al. (2006) found evidence, that this emission was caused by photolysis of HNO_3 or nitrate previously deposited on the surface. Since in this photolysis $OH + NO_2$ or alternatively HONO is formed, it may also have an impact on air chemistry (i.e. VOC oxidation) near the ground. It has to be noted that the above mentioned leaf compensation point is not comparable to the so-called "canopy compensation point" for NO_2 or NO_x (Flechard et al. 2011; Walton et al. 1997a). The canopy compensation point reflects the change in the direction of the NO_2/NO_x atmosphere-biosphere flux determined by the atmosphere-canopy concentration gradient. The canopy concentration reflects the net effect of canopy interactions involving NO soil (and foliage) emission, chemistry, NO_2 leaf uptake and turbulent transport.

Soil Emissions and Deposition

Soil emission of NO occurs as a by-product of soil nitrification and denitrification processes. The latter are a function of temperature, moisture, and substrate (nitrate and dissolved N) availability. For natural ecosystems, the substrate availability is mainly a function of productivity (plant residues input) and wet and dry deposition, while for managed ecosystems it also depends on fertiliser input (Bouwman et al. 2002; Ganzeveld et al. 2010). There exists a large number of field and lab incubation studies for individual sites (Fowler et al. 2009a), which have been used to derive semi-empirical emission models for different soil, vegetation, and land-use classes (Hudman et al. 2012; Ludwig et al. 2001; Parton and et al 2001; Rolland et al. 2010; Stehfest and Bouwman 2006; Steinkamp and Lawrence 2011; Yienger and Levy 1995).

Uptake/deposition of O_3 and NO_2 at the soil surface is often masked in the measurements by the activity and the transfer resistance of the vegetation cover. It can be investigated experimentally either by using specific soil chambers "below" the vegetation canopy (mainly for forest or other tall vegetation) (Gut et al. 2002; Pilegaard et al. 1998) or by making micrometeorological measurements over extended bare soil (mainly for arable fields after harvest/tillage) (Stella et al. 2011a). However, for certain ecosystems like permanent grasslands, both approaches are hardly applicable.

A literature review about ozone soil deposition is given by (Lee et al. 2004). In a more recent study, (Stella et al. 2011a) report that bare soil O_3 resistance mainly depends on increases with soil surface relative humidity (extrapolated from air humidity) but absolute values are site specific (Stella et al. 2011a). The underlying process is thought to be a diminishing soil surface availability under increasing humidity. Results on NO_2 deposition to the soil surface are scarce and mostly limited to forests (Gut et al. 2002; Pilegaard 2001), and no dependency on environmental drivers have been reported.

Chemical Reactions in the Canopy Airspace

Beside the leaf- and soil source/sink processes described above (that may also include heterogeneous chemical reactions at solid surfaces), the three trace gases of interest can also be consumed or produced by homogeneous gas-phase reactions in the canopy airspace. Most important are the direct reaction between the three compounds:

$$NO + O_3 \longrightarrow NO_2 \tag{R1}$$

$$NO_2 + O_2 \longrightarrow \text{UV rad.} NO + O_3 \tag{R2}$$

Since R2 is a photochemical reaction, it is generally less effective within the canopy due to light extinction and is not relevant during the night. Therefore R1 occurring within the canopy airspace is important for the fate of soil emitted NO and can increase the (observed) O_3 flux towards the canopy (e.g. up to 30 % for a spruce forest reported by Pilegaard et al. (1997). In addition, as shown by Heal et al. (2001) also the reaction of NO with peroxy radicals (HO_2, RO_2) can have a significant influence on NO and NO_2 concentrations inside and above the canopy:

$$NO + RO_2 \longrightarrow NO_2 + RO \tag{R3}$$

$$NO + HO_2 \longrightarrow NO_2 + OH \tag{R4}$$

Reactions of O_3 with a selection of VOCs, although usually slower than R1–R4, may also be relevant as an ozone sink. Experiments conducted over a Pine tree forest indicated that chemical interactions involving the ozonolysis of very reactive terpenes could explain a significant part of the O_3 deposition flux to this forest (Goldstein et al. 2004). It should be considered, that especially the gas-phase reactions R1 and R2 are not comparable to other source/sink processes because they do not permanently generate or destroy the molecules but rather allow them to interchange (Lenschow 1982a). Therefore it depends on the short-term fate of the respective air parcel (see next section), whether the chemical reaction can be counted as a sustained source/sink or not.

Turbulent Transport and Diffusion Inside the Canopy

In addition to the actual uptake and release processes by plants and soil, the biosphere-atmosphere exchange is limited by the transport between the active surfaces and the ambient air above the vegetation canopy. One part of this transport is the diffusion through the quasi-laminar boundary layer at the surfaces (Hicks et al. 1987a; Wesely and Hicks 2000) that depends mainly on the local air/wind velocity and the gas diffusivity but is also influenced by in-canopy turbulence and foliar movement which both decrease the boundary layer thickness and hence the leaf boundary layer resistance (Finnigan and Raupach 1987; Loubet et al. 2006).

The second part is the turbulent transport that is generally more complex and variable because it can be non-diffusive and may lead to counter gradient fluxes. Most experimental and modelling studies describe the turbulent mixing intensity inside the canopy as a function of the above-canopy wind speed and/or turbulence as well as of the canopy density (LAI). However the specific thermal stability conditions inside the canopy (which can be very strong and sometimes opposite to the stability above the canopy) are rarely considered. Two important phenomena characterise canopy turbulence: (1) depending on the ambient wind speed, vegetation density and thermal stratification, the entire canopy layer or only the lower part of it can be partly or fully decoupled from the overlying air during certain times of day (Foken et al 2012; Jacobs et al. 1994; Raupach et al. 1996); (2) the renewal of the canopy air, and hence the mass and heat transport, during certain conditions can be almost fully attributed to coherent turbulence structures typically of the size of the canopy that periodically (in the order of minutes) enter very quickly the canopy layer from above (Gao et al. 1993; Serafimovich et al. 2011). This latter phenomenon is critical in terms of modelling in-canopy transport of reactive species also since this introduces a non-linear relationship between the concentration and the flux and leads to non-diffusive transport and counter-gradient fluxes (Denmead and Bradley 1987; Raupach 1989a). The concentration is representative of calm episodes while the flux is driven by short and intensive exchanges. This makes it also difficult to define a single transport time scale.

The canopy turbulence/transport interlinks the different source/sink processes mentioned in Section "Plant leaf processes: stomatal and non-stomatal exchange" most of which depend on the trace gas concentrations. For choosing (limiting) the complexity of a model approach, it is important to know the characteristic time scales of the involved processes. If one process (e.g. chemistry) is much slower (by two orders of magnitude or more) than another one (e.g. transport, plant uptake), it may not be necessary to include an explicit representation of the slower process in the model.

Chemical and Transport Time Scales in the Canopy

The turbulent or diffusive transport time scale can simply be expressed in the resistance analogy framework as the product of the resistance of the layer with its thickness d_{layer}: $\tau_{\text{trans}} = R_{\text{layer}} \times d_{\text{layer}}$. This leads for instance to a typical transport time scale in a canopy, based on the canopy aerodynamic resistance as given by van Pul and Jacobs (1994), of $\tau_{\text{trans-incanopy}} = 14\ LAI\ h_{\text{c}}^2\ u_*^{-1}$ (where h_{c} was considered to be the canopy height). For diffusive transport through a given layer (leaf, soil boundary layer, stomatal aperture), since the resistance is the ratio of the layer thickness to the diffusivity, the transport time scale is simply $\tau_{\text{trans-diffusive}} = {d_{\text{layer}}}^2/D_g$, where D_{g} is the gas diffusivity.

The chemical reaction time τ_{chem} for the NO-O_3-NO_2 triad gives the characteristic time scale of reactions R1 and R2. τ_{chem} is the time at which the concentration of a compound significantly changes from a previous value. It can also be seen as the time required for reaching a new photo-stationary state following a change in a compound concentration or reaction constant. It was evaluated by Lenschow (1982a) as:

$$\tau_{chem} = \frac{2}{\sqrt{{j_{NO_2}}^2 + {k_r}^2\left([\overline{O_3}] - [\overline{NO}]\right)^2 + 2 j_{NO_2} k_r \left([\overline{O_3}] + [\overline{NO}] + 2[\overline{NO_2}]\right)}} \qquad (1)$$

The chemical depletion times for NO, O_3 and NO_2 can also be estimated as the asymptotic limits of Eq. (1) when either NO, O_3 or NO_2 are becoming the dominant specie (Vila-Gureau de Arellano and Duynkerke 1992):

$$\tau_{deplNO} = \frac{1}{k_r \cdot [\overline{O_3}]} \quad \tau_{deplO_3} = \frac{1}{k_r \cdot [\overline{NO}]} \quad \tau_{deplNO_2} = \frac{1}{j_{NO_2}} \qquad (2)$$

The ratio between τ_{trans} and τ_{chem} is defined as the Damköhler number (Damköhler 1940): DA = $\tau_{\text{trans}}/\tau_{\text{chem}}$. Whenever the Damköhler number has a value relatively close to one, implying that the turbulent and chemistry time scales are of comparable magnitude, it is anticipated that chemical transformations will affect the fluxes. A potentially important consequence of these simultaneous gas-phase chemical reactions and vertical turbulent mixing in the canopy are so-called “segregation effects” concerning the quantification of chemical reactions. Chemical reactions are usually calculated using (measured or modelled) mean trace gas concentrations. However vertical turbulent mixing e.g. by coherent structures produce variations in the trace gas concentrations that are correlated in time with the turbulent transport. Assuming a general O_3 sink within the canopy and an NO source at the soil surface, a renewal of the canopy air mass will always increase the O_3 concentration and deplete the NO concentration. The consequent short term variations of O_3 and NO concentration in the canopy are negatively correlated to each other. This creates a non-linear effect in reaction R1, which is not considered if only mean concentrations are used.

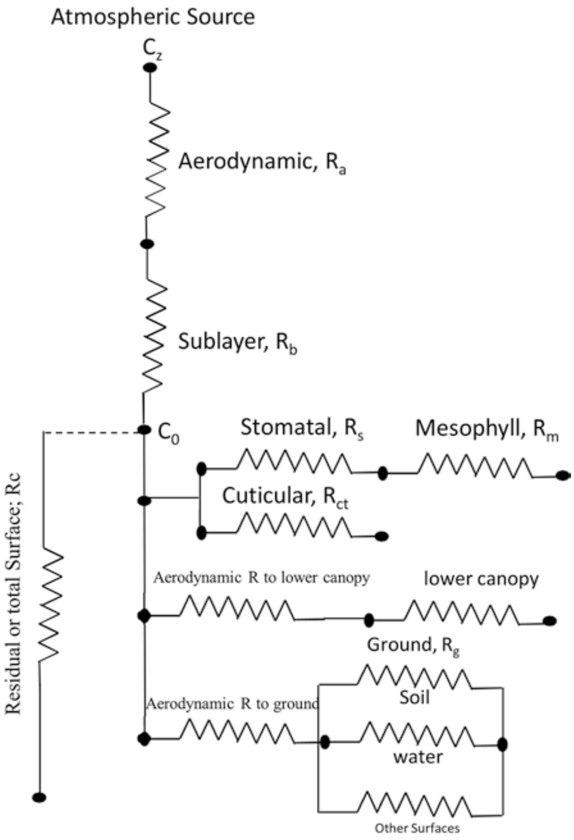
Existing Models

Big-Leaf Two-Layer Resistance Models

Field observations conducted in the 80’s and 90’s in the context of air quality research have resulted in the development of the so-called “big-leaf” dry deposition models (Ganzeveld and Lelieveld 1995; Hicks et al. 1987a; Wesely 1989). In such models the canopy removal of O_3 and other pollutants such as NO_2 and sulfur dioxide (SO_2) is being represented by the simulated uptake by one “average” leaf which is scaled up to the whole canopy either based on simple linear scaling or on a non-linear scaling by partitioning between sunlight and shaded leaves (Flechard et al. 2011). In addition, this approach also generally considers the removal by other canopy substrates, e.g., the soil and leaf cuticle through a number of representative parallel uptake resistances in the so-called resistance approach (see Fig. 1). The potentially limiting effect of turbulent transport of the trace gas from a reference height in the surface layer into the vegetation canopy and the diffusion towards the leaf surfaces is represented by aerodynamic resistance R_a and quasi-laminar boundary layer resistance R_b. Application of this approach (limited to one layer) to simulate O_3 dry deposition fluxes as the product of the dry deposition velocity, V_d, and surface layer O_3 concentration in large-scale models has demonstrated its merits (Ganzeveld and Lelieveld 1995).

More recent versions of the big-leaf resistance models (Lamaud et al. 2009; Stella et al. 2011c; Wesely and Hicks 2000; Zhang et al. 2002) consider a two-layer vegetation canopy with individual leaf resistances for the crown layer and the lower canopy including a turbulent transfer resistance between the two layers. The main limitation of these one- or two- layer big-leaf dry deposition models is that they rely on the non-divergence hypothesis being a fundamental assumption for the resistance analogy. Hence these approaches usually do not consider gas-phase chemical reactions inside the canopy. One noticeable exception is the

Fig. 1 Multi-resistance deposition model for O_3 and NO_2 after Wesely (1989) and Wesely and Hicks (2000). C_z concentration at height z; C_0, concentration at the roughness height ($z = d + z_0$); R_a aerodynamic resistance at height z; R_b canopy boundary layer resistance; R_s, stomatal resistance; R_{ct}, cuticular resistance; R_m mesophyll resistance. R_c is the equivalent surface resistance, that would replace the right hand side of the scheme. C_c is the canopy concentration



analytical resistance model proposed by Duyzer et al. (2005) with a very simplified O_3-NO-NO_2 chemistry considered in one canopy layer based on a mass balance approach, yet the model was not validated.

Large-scale chemistry and transport models, e.g., offline chemistry and tracer transport models and online chemistry-climate models, generally represent atmosphere-biosphere exchanges of O_3 and NO_x using the previously described big-leaf approach (Flechard et al. 2011; Ganzeveld et al. 2002b). This implies that the simulations of surface dry deposition and biogenic emissions are treated separately without considering the role of canopy interactions. Concerning biogenic NO_x emissions from soils, many of the global chemistry models actually use either a static inventory of global soil NO_x emissions by Yienger and Levy (1995) or an implementation of the model used to develop this global inventory. Yienger and Levy (1995) applied the so-called canopy reduction factor (CRF) approach to provide a first-order estimate of the role of in-canopy NO_x recycling (by deposition of NO_2 originating from local soil emitted NO) on the effective release of global soil NO_x emissions into the atmosphere. Improved representations of soil NO emissions, e.g., through enhancement in soil NO emissions associated with timing of fertilizer application (Jaegle et al. 2005) and pulsing associated with rainfall events (Hudman et al. 2012) have been introduced in such large-scale soil NO emission models also using remote sensing observations of the atmospheric NO_2 burden.

Multi-layer Canopy Models

Numerical multi-layer models including several layers for the vegetation canopy have been either derived as 1D models specifically intended to study near surface chemistry and biosphere-atmosphere exchange at the site-scale (Duyzer et al. 2004; Forkel et al. 2006; Gao et al. 1993; Jacob and Wofsy 1990; Walton et al. 1997b; Wolfe and Thornton 2011) or as an extension or integral part of a 1D-(Ganzeveld et al. 2002a) and a global atmospheric chemistry-climate model (Ganzeveld et al. 2002b, 2010). In the first case, the models are generally limited in height to the atmospheric boundary layer and run in a diagnostic mode needing a continuous forcing with (observed) weather variables as well as upper boundary conditions for all trace gas concentrations (referred to as "offline" model systems). In the second case, in so-called "online" modelling systems, the entire trace gas system (or a simplified set) as well as the physical atmospheric conditions are modelled in a prognostic way over time. It is important to make this distinction because of the difference in available input parameters required to simulate atmosphere-biosphere exchanges between those offline and online modelling systems (see below on issue of soil moisture).

In multi-layer models, the leaf and soil source-sink processes are usually represented similarly to the big-leaf models, yet the leaf resistances are specifically attributed to the different canopy layers. But in contrast to big-leaf models, the turbulent transport between the canopy layers is quantified and the gas-phase chemistry is calculated in each layer, assuming homogeneity in this layer considering the extinction in radiation and, consequently, photolysis rates. In some models (Duyzer et al. 2004; Walton et al. 1997b) chemistry for O_3 and NO_x has been very much simplified considering only reactions R1 and R2. However, as shown by Heal et al. (2001) the reaction of NO with peroxy-radicals (R3) cannot be neglected for the exchange of the NO_x compounds.

Shortcomings and Potential Improvements of Models

Shortcomings in Source/Sink Parameterisations (Similar for All Model Types)

Stomatal Resistance for O_3 and NO_2

Stomatal resistance in most models is derived by a Jarvis (1976) type function using a light response curve and additional dependencies on environmental parameters. Nevertheless, according to Flechard et al. (2011) a considerable variability of the bulk stomatal resistance (or conductance) can be observed among different (big-leaf type) models. According to Fowler et al. (2009a) many models do not include a soil-moisture limitation effect on stomatal resistance, which can be problematic in dry conditions. It is interesting to note that dependencies of stomatal uptake on soil moisture status in O_3 (and NO_x) atmosphere-biosphere exchanges are now included in the assessment of O_3 deposition plant impacts by the air quality community (Büker et al. 2012), while they have been considered in studies on chemistry-climate interactions already for quite some substantial time (Ganzeveld and Lelieveld 1995). This seems to also reflect the fact that, in contrast to chemistry-climate interaction studies, air quality assessments rely on the use of offline modelling systems that do not provide information on soil moisture status. Another essential coupling to be established in models is to connect O_3 (and NO_x) stomatal exchange to that of CO_2. A study by Sitch et al. (2007) actually showed that considering the ozone deposition impact on carbon uptake in a Earth system modelling scheme resulted in a simulated increase in atmospheric CO_2 inducing an enhanced radiative forcing as large as the radiative forcing effect of O_3 itself. Vice versa, one would anticipate a decrease in O_3 deposition with a decrease in stomatal exchange due to an increase in CO_2. Furthermore, a challenge in modelling stomatal exchange correctly is the potential for biases in water fluxes due to hygroscopic aerosols deposited on leaves surfaces that could drive water fluxes out of the apoplast Burkhardt (2010).

The appropriate seasonal course of the plant development stage and its influence on stomatal uptake may also need improvements in online models (Sakalli and Simpson 2012). For this purpose a coupling with vegetation growth models would be useful. Additionally, the plant capacity to adapt to changing water constraints is not well known and will be a key process to understand for long term studies on pollution-ecosystem interactions.

O_3 Non-stomatal Leaf Resistance and Soil Surface Resistance

Due to the lack of consistent experimental results for all main vegetation types, many models presently use generally constant non-stomatal resistance values (Emberson et al. 2001a; Ganzeveld and Lelieveld 1995). However, there has been a lot of experimental studies that have indicated that non-stomatal O_3 removal by leaves might be quite variable, depending on environmental parameters (Fowler et al. 2009a), and—more importantly—might be more efficient than what has been previously assumed and how it is commonly implemented in most model systems. There is strong evidence that non-stomatal O_3 deposition is dependent upon relative humidity (Lamaud et al. 2009; Stella et al. 2011a; Zhang et al. 2002). The cause of this empirically observed dependency is still to be determined, and in particular whether it can be explained by surface chemistry (Grontoft et al. 2004) or gas-phase chemistry (Wolfe et al. 2011). Anyway, the parameterisation of non-stomatal resistance could be revised to some extent based on the available experimental evidence. Furthermore the model values for soil resistance are still very uncertain and should be re-evaluated considering recent findings (Stella et al. 2011a, c). Yet it has to be considered that the effective contribution of soil deposition depends strongly on the efficiency of turbulence in transporting the ozone through the canopy down to soil surface (see below).

NO_2: Stomatal and Non-stomatal Leaf Exchange

Considering the large uncertainties in the knowledge of NO_2 deposition in general and leaf exchange in particular, there remain some key questions which are: (1) what is the magnitude of the mesophyll resistance? and (2) what is the role of potential emission processes (characterised by a compensation point effect)? More experimental data and a thorough survey of published results are necessary to establish an improved and generally valid model scheme for these processes. In particular many compensation point values reported in the literature may results from a misinterpretation of the NO_x-O_3 in canopy chemistry or biased measurements due to chemical reaction (Breuninger et al. 2012).

Interactions with VOCs

Wolfe et al. (2011) have suggested with a modelling study that non-stomatal ozone deposition (which is thought to be a surface reaction) could in fact be explained by reactions with hypothesised “very reactive” VOCs (VRVOC) which are assumed to be, not yet observed, unsaturated cyclic terpenoid hydrocarbons. Inclusion of this chemical sink of O_3 in their model system resulted in reproducing the observed large unexplained O_3 deposition velocities over a US Pine forest. The required VRVOC emissions accounted less than 2 % of the CO_2 uptake during this period, which is not unrealistic when compared to emissions of known BVOCs (up to 12 % of the net ecosystem exchange). The corresponding ‘chemical deposition velocity’ could be up to 0.25 cm s^{-1} (~25 % of a typical daytime removal rate for such a forest).

Shortcomings in Implementation of Processes (Model Type Dependent)

Explicit and Accurate Modelling of Environmental Drivers

As already previously mentioned, shortcomings in the implementation of the processes involved in atmosphere-biosphere exchange of O_3 and NO_x (and other reactive compounds and aerosols) are also related to the detail of the model representation of the main drivers. For example, leaf and soil surface temperature and relative humidity affect not only emissions, through biological activity (Laville et al. 2011) but also deposition processes through thermodynamic equilibrium (Tuzet et al. 2011) and surface site availability (Grontoft et al. 2004). Offline modelling systems often lack a detailed description of land-atmosphere interactions processes including a representation of the temporal variability in surface cover fractions, e.g., dry versus wet vegetation and snow cover, but also lack the information on the surface hydrological status. In this case, simulations of atmosphere-biosphere exchanges rely on the availability and quality of input datasets providing the information on the spatial and temporal variability in input data, e.g., biomass expressed by LAI or soil moisture fields. This limits application of such models to study feedback mechanisms because of the missing interaction between atmospheric and land surface processes, e.g., changes in biomass associated with O_3 and N deposition impacts. In online modelling systems, such as regional and global chemistry-climate models, such information is available and would allow assessing potentially relevant land-atmosphere interactions and feedback mechanisms. However, they may be biased too (especially water related variables, since simulation of rainfall in terms of temporal and spatial variability is still uncertain). It is therefore still essential to not only evaluate O_3 and NO_x concentrations/fluxes but also to assess the quality of such simulated drivers of O_3 and NO_x atmosphere-biosphere exchanges. For example, the mentioned important role of soil moisture in stomatal uptake is considered in simulations of atmosphere-biosphere exchanges in chemistry-climate modelling systems (Ganzeveld et al. 2010). However, recent studies on sites with extensive chemistry and micrometeorological observations indicate that the role of soil moisture in stomatal exchange is not always properly represented in such models. For modelling atmosphere-biosphere exchanges at the site-scale this information on soil moisture status relevant to stomatal exchange might also generally provide a limiting factor that can be partly dealt with by having indirect measurements of the influence of soil moisture status on atmosphere-biosphere exchanges, e.g., having H_2O and CO_2 flux measurements.

The quality of applied input datasets is also an issue that deserves critical evaluation. There are many remote-sensing based land cover products available that can be applied to constrain simulations of atmosphere-biosphere O_3 and NO_x exchanges. These high-resolution datasets suggest a lot of accuracy through the fine details seen in these products. However, comparison of a number of global biomass maps, expressed by LAI, showed that there are for example differences in the zonal mean LAI in tropical regions of up to 25 % (Gibelin et al. 2006).

Explicit Modelling of Transport and Chemistry Interactions

As mentioned in Section "Chemical and transport time scales in the canopy", big-leaf models cannot easily simulate chemical reactions and their interaction with turbulent transport inside the canopy. As a simple solution most large-scale atmospheric chemistry models use the canopy reduction factor (CRF) approach by Yienger and Levy (1995) to consider the decrease in the canopy-top NO_x flux compared to the soil NO emission. It is a simple empirical parameterization that uses the Leaf Area Index (LAI) and Stomatal Area Index (SAI) for the twelve soil NO emission classes of their emission algorithm to consider the amount of NO_2 being removed by leaf (needle) uptake. In this offline study it was assumed that the NO_x concentrations above the canopy are negligible compared to the in-canopy concentrations resulting from soil NO_x emissions. However, this does not apply for many continental locations except of remote and pristine sites far away from anthropogenic sources and with large soil NO emissions. This "flaw" of the CRF concept is to some extent corrected by the big-leaf dry deposition simulations in the large-scale models. However, it is not completely clear whether the net atmosphere-biosphere NO_x flux, calculated from the soil NO emission flux corrected with the CRF and the NO_x dry deposition is similar in magnitude and temporal variability to the flux calculated with a model that explicitly considers the role of canopy interactions. A study by Ganzeveld et al. (2002a), using a multi-layer canopy exchange model in a global chemistry and climate model, indicated that application of the CRF concept in large-scale models combined with dry deposition simulations (using the big-leaf concept) might provide reasonable estimates of atmosphere-biosphere NO_x fluxes in regions with high NO_x concentrations where dry deposition fluxes of NO_x are substantially larger compared to the soil NO emissions flux. However, the big-leaf approach seems to fail in representing the temporal variability in atmosphere-biosphere NO_x fluxes in regions where surface layer NO_x concentrations are being dominated by soil NO emissions. This calls for the application of explicit canopy exchanges models that include a representation of these canopy interactions involving the role of chemistry and turbulent transport.

In multi-layer models including explicit height dependent turbulence and chemistry processes, the shortcomings concerning these processes seem to be especially in understanding and correctly model the interaction between the turbulent transport and the chemical interactions. Most multi-layer models use K-type parameterisations for vertical exchange and are not able to describe "counter-gradient fluxes" observed in some conditions (Raupach 1989b) or the chemical segregation effects explained above. In addition, the stability effects on vertical mixing and decoupling effects due to distinct thermal stratification in the canopy are usually not taken into account in models. This would require the use of an energy balance model with full vertical resolution fully coupled with the dynamic models and accounting for free convection conditions. Existing (online) models also fail to properly represent the role of enhanced nocturnal mixing associated with the breakdown of the inversion layer due to enhanced shear production at the interface between the inversion layer and the nocturnal jet (Fitzjarrald and Moore 1990). Because of this underestimation of nocturnal mixing it appears that there is too strong nocturnal inversion present which also results in a misrepresentation of the night-to-day transition taking generally too long compared to observations (da Rocha et al. 2004; Ganzeveld et al. 2008). The latter implies that light dependent processes including foliage NO_x and HONO emissions, dry deposition, and photolysis operate in the limited volume of the canopy air space with a potential overestimation in the concentrations of emitted compounds and potential underestimation of O_3 dry deposition due to limited turbulent transport.

Assessment of the role of these issues and development of improved representations of turbulent transport in atmosphere-biosphere O_3 and NO_x exchanges could profit from recent development in Large Eddy Simulations (LES) that include boundary layer and in-canopy chemistry-turbulent transport interactions (Patton et al. 2001; Vinuesa et al. 2006). On the other hand, Fowler et al. (2009a)—comparing the different uncertainties and shortcomings in present models and the potential effect of chemistry-transport interactions within the canopy—concluded: "… although the interaction between atmospheric chemical reactions and exchange between the canopy and the atmosphere is easy to understand its importance may be limited. (…) In view of all the uncertainties hindering improved estimates in testing of models, the limited quality of the description of atmospheric transport processes within the canopy may not be a serious problem here." It illustrates that there are apparently contrasting opinions regarding the priorities on research activities focussing on atmosphere-biosphere O_3 and NO_x exchanges.

Data Needed for Model Validations

In order to validate models that simulate atmosphere-biosphere exchanges of O_3 and NO_x at the site- to air quality or chemistry-climate model scale it is not sufficient to collect only information on O_3 and NO_x fluxes. This would suffice if the only aim of such combined experimental and modelling activities would be to quantify O_3 and NO_x atmosphere-biosphere fluxes. However, is also essential to understand the underlying mechanisms that control temporal and spatial variability in O_3 and NO_x atmosphere-biosphere fluxes. Consideration of these mechanisms allows the use of the air quality and chemistry and climate modelling systems to conditions not represented by those observations, e.g., future climate and global change. Based on our assessment of the main limitations in processes that are involved in O_3 and NO_x atmosphere-biosphere fluxes it calls for more detailed observations of good quality data for coupled NO_2, NO and O_3 fluxes measurements (which are scare and not representative of all ecosystems) complemented with micrometeorology and surface hydrology measurements that will improve our understanding and model representation of:

- Surface hydrology, more particularly soil moisture and its effect on stomatal exchange
- Turbulent exchanges inside and above the canopy including the morning transition, stability effects and intermittency
- Substrate scale interactions between depositing and emitted species and their links with environmental factors (especially surface humidity of soils and leaves)

Links to Exchange of Other Reactive Compounds and Aerosols

(a) The considerations concerning uncertainties and possible improvements in the modelling of canopy transport and interaction with chemistry (see Sections above) similarly apply to the biosphere-atmosphere exchange of other reactive species like the NH_3-HNO_3-NH_4NO_3 triad, reactive biogenic VOCs through the role of O_3 and NO_x in OH production, and the potential release of very reactive compounds associated with O_3-VOC chemical interactions in/at the canopy air-leaf interface

(b) The considerations concerning uncertainties and possible improvements in the modelling of stomatal conductance (Section "Big-Leaf two-layer resistance models") similarly apply to other trace gases with relevant stomatal uptake (e.g. NH_3)

(c) The process of NO_2 emission by HNO_3 photolysis on leaf surfaces (see Section "Plant leaf Processes stomatal and non-stomatal exchange/Non-stomatal uptake of O_3") represents a direct link to the understanding and modelling of NO_3/HNO_3 deposition.

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Bidirectional Exchange of Volatile Organic Compounds

A. Guenther

Introduction

Volatile organic compounds (VOC) are a relatively minor component of the atmosphere and yet are widely recognized to have important roles in air quality and climate. With the exception of methane, an important greenhouse gas, atmospheric VOC are primarily of interest because of their impact on other atmospheric constituents, including oxidants and aerosol. Most of the global annual VOC emission is from biogenic sources but biomass burning, fossil fuel combustion and industrial activities dominate in some regions. Each of these major sources can be further categorized, e.g., biogenic sources include plant chloroplasts, plant specialized tissues, microbes, and animals. The processes for removing VOC from the atmosphere include VOC surface deposition, VOC deposition to particles, and surface deposition after oxidation to CO or CO_2. Regional to global atmospheric chemistry and transport models (CTMs) routinely include at least some VOC emission and removal processes but in a highly simplified form. Climate models have previously included just methane but as they evolve into more comprehensive earth system models, other VOC are being included although the sources and sinks may be prescribed or highly simplified.

A comprehensive characterization of atmospheric VOC is challenging due to the overwhelming number of compounds. Tens of thousands of VOC have been measured in the atmosphere and there may be hundreds of thousands more that have not been measured (Goldstein and Galbally 2007). There are many ways of classifying VOC including source types, chemical characteristics, and atmospheric impacts. Surface-atmosphere exchange behavior is typically not considered

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A. Guenther (✉)
Atmospheric Chemistry Division, National Center
for Atmospheric Research, Boulder, CO, USA
e-mail: alex.guenther@pnnl.gov

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when categorizing VOC for surface exchange models and yet this could facilitate the development of effective VOC modeling approaches. A simple scheme is presented here for classifying VOC into three major categories based on their surface-exchange behavior: reduced VOC (RVOC), atmospheric oxidation products (AOVOC) and bidirectional VOC (BDVOC).

Reduced VOC

Reduced VOC are produced at or near the earth surface and emitted into the atmosphere but are not produced in the atmosphere. RVOC include hydrocarbons such as alkanes (e.g., methane), alkenes (e.g., isoprene) and arenes (e.g., benzene). VOC containing sulfur or nitrogen can be included in this category but any oxygenated VOC that are produced in the atmosphere would not be included. There are oxygenated VOC that are emitted from vegetation, e.g., the hemiterpene, methyl-butenol, and the monoterpene, linalool, but are not produced in the atmosphere and so would be considered RVOC. Soils and litter are sources of several VOC (furfural, butanoic acid, methanol, …) but these sources have not yet been well quantified (Insam and Seewald 2010; Leff and Fierer 2008). Similarly composts and slurry applications may be sources of nitrogen containing VOC like trimethylamine (TMA) (Seewald et al. 2010; Twigg et al. 2011). Since RVOC are not produced in the atmosphere, any RVOC deposition flux is due to molecules that were at one time emitted into the atmosphere and are now returning to the surface, although most likely to a different location.

Methane and isoprene are the dominant VOC emissions and are both emitted into the atmosphere at rates of ~550 Tg per year (Guenther et al. 2006). These two RVOC are widely recognized as two of the most important VOC in the earth system and VOC surface exchange research has focused on these two compounds. There has primarily been investigations of emissions resulting in the development of relatively sophisticated models describing the processes controlling emissions of these two compounds. However, it has also been noted that surface sinks of these two compounds are not negligible and may account for about 5 % of the methane and isoprene emitted into the atmosphere (Cleveland and Yavitt 1997; Neef et al. 2010). This loss mechanism is usually incorporated into CTMs using an emission model and a deposition model that are independent of each other even though they have similar driving variables. The emission models are driven by landcover and weather variables including light, temperature and soil moisture (Guenther et al. 2006). The deposition models are driven by landcover and weather variables along with atmospheric concentrations (Wu et al. 2012).

Although a 5 % uptake is small compared to the uncertainties in the net fluxes of methane, isoprene and other RVOC, an accurate representation of the deposition of these compounds may be important. Megonigal and Guenther (2008) note that the upland ecosystems, that are primarily sinks of methane, cover a far greater area than the wetland areas that are a source of methane. The potential shift of these upland landscapes between source and sink regions could significantly impact the global methane budget and should be considered in earth system models. The fraction of isoprene and other reactive RVOC emitted by a forest canopy that is taken up before it can escape to the above canopy atmosphere is highly dependent on the oxidizing capacity of the canopy airspace and the canopy residence time. Surface exchange models currently do not simulate these processes although in some cases a net flux and a variable sink term is used to account for these losses (Guenther et al. 2006). An accurate representation of these processes is necessary especially for highly reactive RVOC, such as the sesquiterpene β-caryophyllene, that have large and variable fraction of emission that is removed in the canopy before reaching the above canopy atmosphere. The presence of these highly reactive VOCs in the canopy is also essential to quantify as they may play a significant role in yet unexplained non-stomatal removal of O_3 (Wolfe et al. 2011).

Atmospheric Oxidation Products

The chemical degradation of RVOC in the atmosphere produces a large variety of oxidized VOC. The oxidation of a single compound, the five carbon isoprene, produces a diverse array of AOVOC starting with four carbon first generation products, including methyl vinyl ketone (MVK) and methacrolein (MAC), that can react to form second generation products and so on until the carbon has been oxidized to CO_2. CTMs do not use explicit schemes to represent all of these AOVOC, due to the complexity and computational resources required, but most at least consider the first generation products MVK and MAC, which account for about 80 % of the carbon in the initial stage of isoprene oxidation. Some models represent them as specific species while others represent them as a lumped isoprene product. In either case, these molecules or their lumped sum are typically included in the dry deposition schemes of CTMs but this has been accomplished by assigning a dry deposition velocity that is based on measurements of other compound such as SO_2 and ozone. Karl et al. (2010) used above canopy flux measurements to demonstrate that the assumed canopy resistance for MVK and MAC used in CTMs is overestimated by about a factor of 5. They proposed that this high deposition rate was the result of active removal by leaves in order to eliminate these toxic compounds. The incorporation of a more accurate canopy resistance in a CTM results in substantial changes in simulated AOVOC deposition rates and atmospheric concentration distributions.

Jardine et al. (2010) observed emissions of oxidized VOC, including MVK and MAC, from vegetation enclosures and suggested that leaves could be a significant source of atmospheric MVK and MAC. The relative importance of foliar MVK and MAC emissions is not yet understood but the Karl et al. (2010) observations of higher than expected net deposition of MVK and MAC contradicts the suggestion that vegetation is a major direct source of MVK and MAC. However, we should consider that these compounds could be emitted at substantial rates under certain conditions, such as high temperatures and other stresses. The potential importance of AOVOC emission, and thus bidirectional exchange, should be recognized and a better understanding of the rates and controlling processes is needed.

Bidirectional VOC

The final category of VOC have substantial source and sink terms at both the earth surface and in the atmosphere. Emission and deposition processes are of similar importance for these BDVOC and so the accurate estimation of the net flux requires consideration of both. Kesselmeier (2001) identified four low molecular weight oxygenated VOC (acetaldehyde, formaldehyde, acetic acid, and formic acid) as compounds that are both emitted and taken up by plants in substantial quantities. These compounds can also be of anthropogenic origin and are produced in the atmosphere from the oxidation of RVOC. Kesselmeier recognized that the surface-atmosphere exchange of these compounds is bidirectional and their fluxes should be incorporated into models using an approach that includes a compensation point where emission occurs when ambient concentrations are below a certain level and deposition occurs with higher ambient concentrations. The compensation points reported by Kesselmeier indicate that plants are likely to be a source of these compounds in a clean remote environment and a sink in a polluted environment. While some simple approaches have been used to integrate emission and uptake into a unified model to account for BDVOC fluxes (Millet et al. 2010) these fluxes are typically represented in CTMs as separate emission and deposition models and one or the other may be completely neglected. A uniform approach for modeling BDVOC exchange between terrestrial ecosystems and the atmosphere is needed.

Of the four BDVOC identified by Kesselmeier, acetaldehyde tended to have the highest leaf level emissions and this has also been observed for net ecosystem fluxes (Schade and Goldstein 2002). Acetaldehyde emission sources in terrestrial ecosystems include soil and leaf litter in addition to plant canopies (Warneke et al. 1999). Jardine et al. (2009) used a stable carbon isotope as a tracer for characterizing multiple pathways for producing acetaldehyde in plants and also report that emissions were elevated following both leaf anoxia and mechanical stress. These findings highlight the complexity associated with accurately simulating the processes controlling just the emissions component of acetaldehyde emissions. Above canopy acetaldehyde fluxes from three forests were compared by Jardine et al. (2008). Acetaldehyde was emitted from a forest canopy with an LAI of 3 but there was a net deposition observed for canopies with LAI of 4.6 and 5.3. Vertical profiles of acetaldehyde gradients within and above these canopies showed that acetaldehyde was emitted by the upper canopy and taken up by the lower canopy. This is in agreement with previous observations by Kesselmeier (2001) showing that acetaldehyde and other BDVOC can be emitted from sunlit leaves and taken up by shaded leaves. Jardine et al. (2008) proposed a modeling approach based on ambient acetaldehyde concentration, a compensation point that is a function of light and temperature, and stomatal resistance to acetaldehyde but this technique was not implemented in a CTM. A simpler approach described by Millet et al. (2010) was used in a CTM to estimate global distributions of acetaldehyde as a function of LAI, light and temperature. The model simulated maximum acetaldehyde emissions for an LAI of 2 with decreasing emissions for lower or higher LAI.

The above canopy atmosphere is not the only location where RVOC can be oxidized. The canopy air space contains oxidants that can react with RVOC to produce oxidized VOC but it is a relatively small volume in comparison to the atmospheric boundary layer and so has previously been thought to be a relatively small source of oxidized VOC. DiGangi et al. (2011) recently measured a surprisingly large flux of formaldehyde from a forest canopy into the atmosphere. Branch and soil enclosure measurements indicated that these direct emission sources could only account for ~15 % of the observed ecosystem flux. They concluded that the remainder was due to the oxidation of biogenic VOC within the canopy airspace. The canopy they studied was an open woodland with a relatively short residence time which would minimize the production of formaldehyde. On the other hand, the open canopy has more light penetration which would stimulate photochemistry and VOC oxidation.

Methanol is the predominant oxidized VOC in the global atmosphere with an annual global emission rate that is thought to be the third largest of any VOC, after methane and isoprene (Guenther et al. 2012). High rates of biogenic methanol emission were first reported by MacDonald and Fall (1993) who noted that emissions were especially high from young expanding leaves. Heikes et al. (2002) compiled methanol sources and sinks into a global budget and estimated that about a fourth of the emitted methanol is dry deposited to terrestrial surfaces and another fourth is dry deposited to the ocean. Millet et al. (2008) developed a global budget using additional observations and estimated that dry deposition is responsible for about half of the methanol sink but that the ocean sink is 2.5 times greater than for land. These analyses indicate that methanol uptake by terrestrial ecosystems is important and should be considered as a BDVOC in surface exchange models. Stavrakou et al. (2011) proposed and implemented a simple CTM algorithm that included both emission and deposition.

After methanol, acetone is thought to be the next most dominant oxygenated VOC in the atmosphere. An analysis of the global acetone budget by Jacob (2002) concluded that surface deposition was responsible for only 12 % of the total acetone sinks. However, this deposition is ~20 % of the emission from a terrestrial ecosystem since nearly half of the acetone is produced by atmospheric oxidation of RVOC. This indicates the complexity of acetone sources and sinks and argues for classifying it as a BDVOC that should be represented in CTM with a unified emissions and deposition model.

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Surface/Atmosphere Exchange of Atmospheric Acids and Aerosols, Including the Effect and Model Treatment of Chemical Interactions

E. Nemitz

Introduction

This review forms one of a set of background papers for an expert workshop organised jointly by Cost Action ES0804 (ABBA) and the EU FP7 ECLAIRE project. This workshop aims to review the existing state-of-the-art in modelling the surface/atmosphere exchange of pollutants and to facilitate the exchange of expertise between the different research communities that have worked on different chemical compounds or compound families.

This background document attempts to provide a review of our understanding of the surface/atmosphere exchange of atmospheric acids and compounds found in the aerosol phase and with some reference to their treatment in current chemical transport models. These compounds are treated together in the same background document, because it is increasingly becoming evident that the gas-aerosol partitioning of some volatile compounds changes during the deposition process and that the deposition of some compounds cannot be considered without considering the behaviour of the chemically or physico-chemically interacting compounds. This is in particular true for the compounds that take part in the highly dynamic and fast NH_3–HNO_3–NH_4NO_3 equilibrium. Clearly, this also includes ammonia (NH_3). However, because NH_3 originates from different sources, undergoes different chemistry (as a base) and dominates the N deposition in many parts of Europe, a fully separate background paper is dedicated to the discussion of NH_3 (Flechard et al. 2013) Nevertheless, its interaction with the acids is treated in Sect. Chemical interactions of this chapter. Similarly, the chemistry of one of the main acids treated here (nitric acid, HNO_3) is

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E. Nemitz (✉)
Center for Ecology and Hydrology (CEH), Edinburgh, Penicuik, UK
e-mail: en@ceh.co.uk

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closely linked to the fluxes and chemistry of NO_x, which, together with O_3, is again treated in a separate background document.

The influence of chemistry on fluxes should be borne in mind when reading this document, because the process understanding of the behaviour of the various compounds was in general developed without taking into account the effects of chemistry during measurement and interpretation.

Generally, the dry deposition flux in chemical transport models (CTMs) is parameterised by multiplication of the concentration of compound i (i.e. c_i) in the lowest model layer with the dry deposition velocity of this compound.

$$F_i = -V_{d,i}(z) \times c_i(z) \tag{1}$$

Here we follow the convention that F_i is negative if directed towards the ground (deposition) as this provides a sink for the lowest model layer. In general, V_d is the reciprocal of the resistance towards dry deposition. The aerodynamic resistance (R_a) describes the vertical transport through the turbulent part of the atmosphere and limits the deposition of all substances, except large particles, for which gravitational settling contributes to the deposition process. Gases also have to overcome the laminar sub-layer that forms around all surface elements and this process is described through a further resistance (laminar sub-layer resistance, R_b) in series with R_a. Due to their physical properties (size, inertia) particles have additional processes to overcome this layer, so that a modified parameterisation of R_b must be used or, more often, the deposition of particles is described without the use of R_b. In addition, the deposition of gases is further restricted by the interaction with the canopy itself, which in the simplest approach may be described by a bulk canopy resistance (R_c). In more complex approaches R_c may be replaced by a network of resistances, parallel and in series, that describe the various alternative pathways that exist for the deposition of a given compound, and the resistances involved. Thus, in the simplest case V_d for gases may be written as:

$$V_d(z) = (R_a(z) + R_b + R_c)^{-1} \tag{2}$$

A different, more complex approach, may need to be applied for compounds that undergo bi-directional exchange such as NH_3, because Eqs. (1) and (2) cannot describe emission. Since $R_C \geq 0$ Eq. (2) implies that even if a canopy provides a perfect sink for a given compound, its deposition velocity cannot exceed

$$V_{max} = (R_a(z) + R_b)^{-1}. \tag{3}$$

Although the R_b approach is sometimes extended to particles, descriptions of the deposition efficiency of particles really addresses the mechanisms by which they overcome the laminar boundary layer and interact with surface elements at the same time. Thus, it is more in keeping with the terminology used for the gas exchange, to parameterise the surface interaction of particles through the surface value of the deposition velocity ($V_{ds} = V_d(z_0)$), which for gases would equate to $V_{ds} = (R_b + R_c) - 1$. In addition, large particles also deposit by gravitational settling at the terminal settling velocity (V_{ts}) at which gravity is balanced by the drag force. This is not constrained by turbulence and thus R_a. Thus, the overall V_d for particles can be written as:

$$V_d(z) = \left(R_a(z) + V_{ds}^{-1}\right)^{-1} + V_{ts}. \tag{4}$$

Deposition of Acids

Nitric Acid (HNO_3)

Importance and Sources

Nitric acid is produced by oxidation of NO_x, primarily emitted from fossil fuel combustion. Daytime production proceeds through NO_2 reaction with the OH radical, while a night-time source is the reaction of the N_2O_5 radical (unstable during daytime). HNO_3 reacts with NH_3 to form ammonium nitrate (NH_4NO_3) and is thus a key precursor for secondary aerosol production. With the decrease in European SO_2 emissions, in NW Europe concentrations of ammonium nitrate now exceed those of ammonium sulphate, and is a major contributor to the aerosol chemical composition during regional pollution episodes (Charron et al. 2006). The radiative effect of European nitrate is at least of the same magnitude as that of sulphate. Nitric acid makes a considerable contribution to the N deposition and acid loading to sensitive (semi-)natural ecosystems.

Measurement Approaches

Measurement of surface/exchange fluxes of HNO_3 is still challenging with current technology. In most cases, HNO_3 exchange is derived from gradient measurements using either manual denuders included in filter-packs (Harrison et al. 1989; Müller et al. 1993), or automated denuders at several heights (Meixner et al. 1990; Neftel et al. 1996; Twigg et al. 2011). Fast response measurements as required by eddy covariance approaches are still difficult to realise and instrumentation is not commercially available. Farmer et al. (2006) measured the eddy-covariance flux of several groups of oxidised N (NO_y) compounds with a laser induced fluorescence (LIF) NO_2 sensor with several inlets at different temperature and derived the HNO_3 flux by difference. However, their diurnal pattern in HNO_3 emission still needs to be reconciled with other observations. Instruments have also been developed to measure fluxes of total oxidised N (Turnipseed et al. 2006) or even total N (Ammann et al. 2012; Marx et al. 2012) based on thermal conversion followed by fast chemiluminescence NO detection. While these measurements do not provide chemically speciated information to foster the process understanding of individual N compounds, in many situations HNO_3 will make a substantial contribution to the flux measured by this approach, due to its fast deposition rate (see below). The idea of the application of NO or NO_2 detection is to convert HNO_3 at the sampling point into a less sticky compound that can more easily be transported to an analyser without losing fast fluctuations.

Relaxed accumulation is an alternative single-height flux measurement approach that avoids the need for fast chemical sensors, by rapidly directing up- and down-draft air into two accumulation reservoirs which can then be analysed with slow techniques. This approach has been applied to HNO_3 (Myles et al. 2007; Pryor and Klemm 2004), but care needs to be taken that the response of the inlet system is sufficiently fast.

A further challenge in measuring fluxes of HNO_3 is its potentially rapid exchange with its aerosol counterpart (NO_3^-), resulting in the potential for sources and sinks below the measurement height. For this reason, a flux measurement at a single height does not necessarily reflect the exchange with the vegetation and soils. For the gradient approach the situation is even more complex: because the flux is derived from concentration measurements at various heights and the gradient is modified by the chemistry, it is not clear to which height (if any) the derived flux applies. If chemistry and turbulent transport proceed with comparable time constants, the flux-gradient relationship itself is altered and a modified 'effective' eddy diffusivity needs to be used (Galmarini et al. 1997). Because of this complication through chemical interactions of the NH_3–HNO_3–NH_4NO_3 system, some authors only provide fluxes of total nitrate ($TN = HNO_3 + NO_3^-$) and total ammonium ($TA = NH_3 + NH_4^+$), which are conserved with height (Wolff et al. 2010). The majority of measurements have been reported without taking account of chemistry and some of the data needs to be interpreted as such.

Behaviour Regarding Surface/Atmosphere Exchange

Nitric acid is highly water soluble, with an effective Henry coefficient of 2.1×10^5 M atm^{-1}. This means that even over slightly wet surfaces, it is thought to deposit with a zero canopy resistance ($R_c = 0$) (Dollard et al. 1987; Huebert and Robert 1985; Meyers et al. 1989; Müller et al. 1993). As a result, its deposition is only governed by the atmospheric resistances.

Despite this general view that HNO_3 should deposit at V_{max}, a significant number of observations have contradicted this paradigm as summarised by Nemitz et al. (2004a) and Twigg et al. (2011), showing either deposition at $V_d > V_{max}$ and $V_d < V_{max}$ or even emissions ($V_d < 0$). Where statistically significant, such observations have been attributed to non-conserved fluxes, i.e. fluxes that change with height, due to the formation/evaporation of ammonium nitrate aerosol (NH_4NO_3). The process is explained in more detail in Section "Topical Research Questions to be Discussed".

Reduced deposition rates and apparent emissions have been reported more often than apparent overly fast deposition (Huebert et al. 1988; Kramm and Dlugi 1994; Neftel et al. 1996; Nemitz et al. 2004a; Zhang et al. 1995). An example time series for such behaviour of HNO_3 (and also HCl) was observed over a Dutch heathland as shown in Fig. 1.

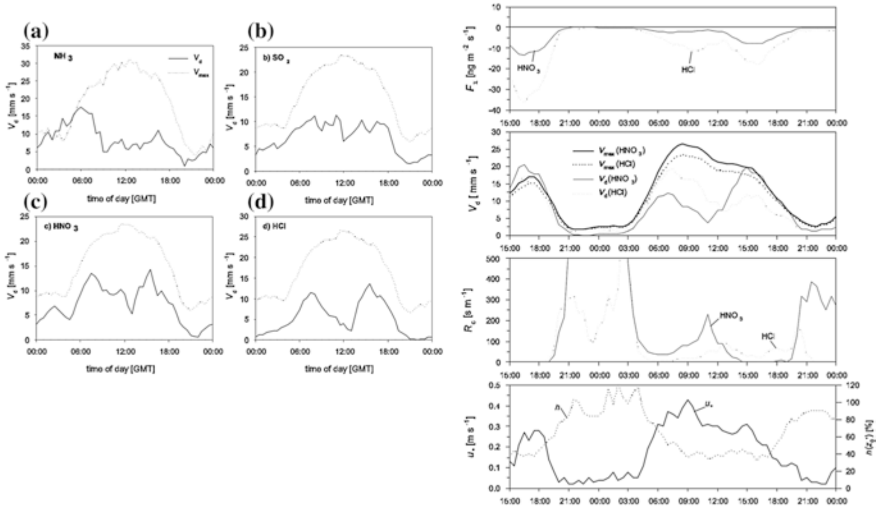

Fig. 1 Example time-series of HNO_3 and HCl fluxes measured above a heathland indicating $V_d < V_{max}$ ($R_c > 0$) during the day (Nemitz et al. 2004a)

This observation is consistent with airborne NH_4NO_3 evaporation during the aerosol deposition process, and this is further supported by the observation of fast NO_3^- and NH_4^+ deposition rates during some of these studies (see below). There are, however, alternative explanations for reduced deposition/emission of HNO_3. Evaporation of HNO_3 can potentially not only occur from particles containing NH_4NO_3 in the air, but also from NH_4NO_3 aerosol previously deposited to leaf surfaces, or from leaf surfaces as water layers evaporate, thus remobilising some of the deposited N. Recently, Zhou et al. (2011) suggested that photolysis of HNO_3 on forest canopy surfaces may provide a further HNO_3 sink and, at the same time, an important daytime source for HONO, again remobilising some of the deposition of N and acidity. However, much of the deposited HNO_3 and NH_4NO_3 is probably not remobilised. There is some evidence that some HNO_3 may be taken up by the plant through the leaf cuticle (Cadle et al. 1991; Marshall and Cadle 1989), however, in wet climates most of it is likely to be washed off the surfaces into the ground.

Parameterising HNO_3 Exchange

Because HNO_3 is readily taken up by vegetation surfaces, the flux of this compound is more sensitive to the calculation of R_a and R_b than most other compounds, for which the canopy interaction provides the limiting factor and represents the dominating component resistance. In fact, studies have used HNO_3 flux measurements to assess the validity of parameterisations of R_b by inverting Eq. (1)

(Müller et al. 1993; Pryor and Klemm 2004). There is general consensus to link R_b to the sublayer Stanton number (B) as

$$R_b = (B\,u_*)^{-1}. \tag{5}$$

Various parameterisations of B have been proposed (Businger 1986; Hicks et al. 1987; Jensen and Hummelshoj 1995; Meyers et al. 1989), which lead to similar predictions for short vegetation (Sutton 1990), but divert more significantly for tall vegetation (forests) (Pryor and Klemm 2004).

A commonly used parameterisation for short vegetation is

$$B^{-1} = Sc \times Re^{0.5} \tag{6}$$

where Sc is the Schmitt number (the ratio of kinematic viscosity of air to the molecular diffusivity of the gas under consideration) and Re is the Reynolds number ($Re = u_* z_0/\nu$). The exponent of the dependence on Re of 0.5 appears to be reasonable for short vegetation. However, based on a review of previous publications, Jensen and Hummelshoj (1995, 1997) recommended a revised formulation for forest, which implies a weaker dependence on z_0, accounting for the fact that the surface elements in forests are much smaller than the canopy height:

$$B^{-1} = \nu/D_i\,[c/\mathrm{LAI}^2 \times l u_*/\nu]^{1/3} \tag{7}$$

with $c = 100$. Kramm and Mölders (2005; and references therein) also pointed out that the standard equations for B^{-1} can fail over very smooth surfaces such as ice and water.

Because HNO_3 cannot generally be considered a chemically conserved species, with chemical sources and sinks occurring below the measurement height (cf. Chap. 5), its use for deriving parameterisations of R_b may be problematic, at least in some situations.

Hydrochloric Acid (HCl)

Importance and Sources of HCl

Hydrochloric acid is an inorganic acid that is released by anthropogenic combustion processes (e.g. incineration chlorine containing wastes such as PVCs and chlorine rich coals) as well as the substitution reaction of HNO_3 with NaCl, the main constituent of seasalt. HCl is not treated by most chemical transport models (CTMs), presumably for two main reasons: first, although it is a potential precursor for secondary inorganic aerosol, the vapour pressure of NH_4Cl is considerably higher than that of NH_4NO_3 (see below) and it is therefore considered not important in governing the aerosol load. Recent measurements by Aerosol Mass Spectrometer, of the Cl^- (which is thought to reflect NH_4Cl in most environments) have confirmed relatively low concentrations, apart from in some industrial/heavily urban sites (e.g. Mexico City). Second, HCl concentrations have traditionally been thought to be relatively small and thus its contribution to acid deposition has often been ignored. Consequently, fewer measurements exist than for HNO_3. This view has recently been challenged and the decrease in HCl deposition (associated with the phasing out of chlorine rich coals and introduction of emission abatement technologies in coal power plants) may have been one of the drivers for the decrease in acidification in the UK (Evans et al. 2011).

Emerging measurements of HCl, which is one of the compounds measured by online denuder measurement approaches such as the MARGA (Thomas et al. 2009) and URG AIM instruments start to challenge the notion that HCl concentrations are now very small and governed by the HNO_3–NaCl reaction Fig. 2 shows the relative contribution of HNO_3, HONO, HCl and SO_2 to total inorganic acid loading (in eq m^{-3}) at four European sites measured during the EMEP Intensive measurement campaign June 2006 measured with the MARGA technology and its different forerunners (GRAEGOR, SJAC-WAD), demonstrating that HCl can at times account for >40 % off the acidity, and can make a considerable contribution even if the PM_{10} Cl^- loading (taken as a proxy for seasalt influences) is low. There are a number of caveats to this assessment: (i) the HONO measurement

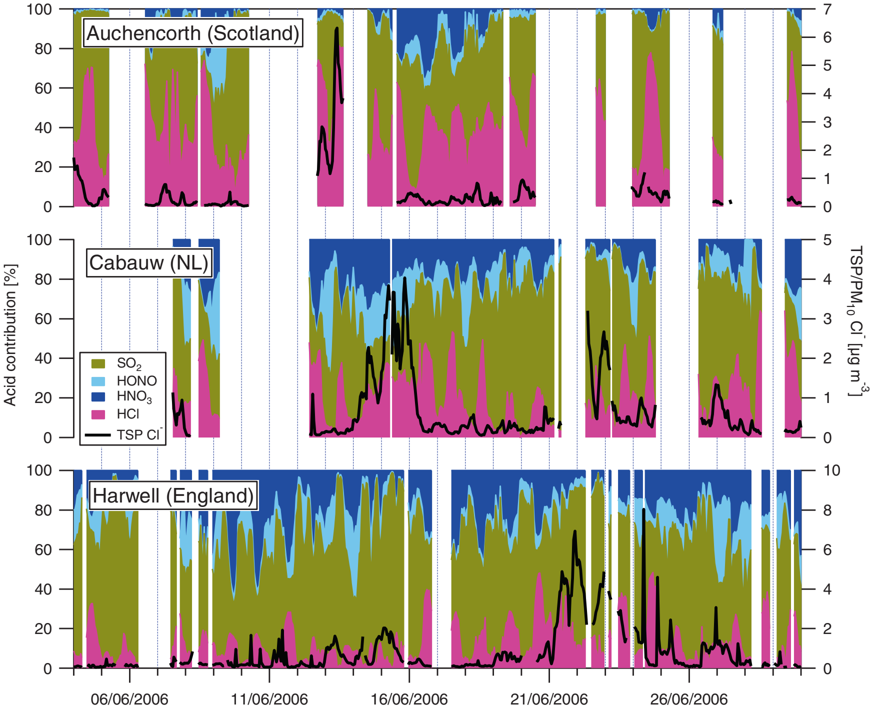

Fig. 2 Breakdown of total measured inorganic acidity into its components. Data from MARGA instruments operated during the EMEP IMP June 2006 at two UK and one Dutch site. Also shown is a measurement of aerosol chloride contained in total suspended particulate (TSP) or PM_{10} to indicate conditions when seasalt reached the measurement site

with this technology is not artefact free and may be over-estimated; similarly the HNO_3 measurement might include N_2O_5. (ii) Recently, several studies, using more specific instrumentation, have revealed considerable concentrations of nitryl chloride ($ClNO_2$) in the atmosphere both at marine impacted (Phillips et al. 2012) and continental sites (Thornton et al. 2010). Although this compound has limited direct water solubility, it may dissociate rapidly increasing its effective solubility. Thus, some of it may be captured by the wet rotating MARGA denuder and dissociate into Cl^- and NO_2^-/NO_3^-. Its interference with the gaseous Cl^- measurement, usually attributed to HCl, remains to be assessed. (iii) There is theoretically the potential for the release of HCl from HNO_3 reaction with NaCl that may have deposited to the inlet surfaces. However, significant amounts of HCl are also found if the instrument is run with a very short (10 cm) inlet cone and no further size-segregating inlet. In this configuration this effect should be minimised. Independent of whether it represents HCl or $ClNO_3$, the measurements indicate much larger sources of gaseous Cl^- than previously thought.

Behaviour of HCl

HCl is thought to behave like HNO_3, although even less measurement evidence exists (Harrison et al. 1989; Nemitz et al. 2004a, b). Its Henry coefficient is very much smaller than that of HNO_3 (Table 1), but both acids dissociate so readily in water that for practical purposes, both are highly soluble. HCl also reacts with NH_3 to form a dynamic equilibrium with NH_4Cl. The volatility of NH_4Cl is lower than that of NH_4NO_3 (Harrison et al. 1990; Mozurkewich 1993), but ambient air concentrations also appear to be much lower as evidenced by measurements by Aerosol Mass Spectrometer (AMS), the Cl^- reported of which is thought to mainly represent NH_4Cl in most conditions.

Parameterisation of HCl Exchange

Much fewer CTMs treat HCl than HNO_3 because HNO_3 is a precursor to the important aerosol NH_4NO_3, which plays a major role for the climate system, the human health impact of PM and the long-range transport of nitrogen. By contrast,

Table 1 Effective Henry coefficients (*H*) and molecular diffusivities (*D*) of atmospheric acidic compounds (modified from Wesely 1989)

Acidic compound	D (cm^2 s^{-1})	H (M atm^{-1}) at pH 7
SO_2	0.114	1×10^5
HNO_3	0.114	1×10^{14}
HCl	0.170	NA
HONO	0.136	1×10^5
HCOOH (formic acid)	0.136	4×10^6

concentrations of NH_4Cl are comparably small. As with HNO_3, HCl deposition is usually modelled with a zero (or notional, very small) value of the canopy resistance (R_c).

Nitrous Acid (HONO)

Nitrous acid (HONO or HNO_2) concentrations tend to be somewhat smaller compared with HNO_3 and HCl but HONO still appears to be important (and overlooked) in terms of its contribution to N or acid deposition. Even more importantly, the daytime photolysis of HONO is thought to be the main source of the OH radical in the atmosphere, especially during sunrise, and OH is one of the key oxidants in the atmosphere. As a consequence has received more attention by the atmospheric research community than by the community working on air pollution and their effects on ecosystems.

Sources of HONO are poorly understood. Because during day its photolysis to NO and OH is rapid, daytime concentrations have long thought to be very small. With the development of more sensitive and artefact free measurement approaches such as LOPAP (Heland et al. 2001), it has become clear that considerable amounts of HONO must be produced during daytime. Production has been observed to occur on humic substances (Stemmler et al. 2006) and upward (emission) gradients have been observed in the urban environment, above grassland, above manured land and in forests (Harrison and Kitto 1994; Hesterberg et al. 1996; Stutz et al. 2002; Twigg et al. 2011; Zhou et al. 2011). It is therefore clear that HONO exchange is generally bi-directional. It has been suggested that some of the HONO emission originates from the photolysis of deposited HNO_3 and thus would need to be taken into account when deriving deposition budgets (Zhou et al. 2011). Currently, too few flux measurement studies exist to derive a mechanistic understanding of both the deposition and chemical production mechanisms.

Sulphur Dioxide (SO_2)

Sulphur dioxide (SO_2) is not a major focus of this background document, which is focussed on those acidic compounds that interact with the aerosol phase. SO_2 does contribute to the formation of aerosol through reaction in a two step process: first sulphuric acid is produced through reaction by OH. In the next step, sulphuric acid may condense to form aqueous highly acidic aerosol, but more likely it is neutralised by NH_3 to ammonium bisulphate (NH_4HSO_4) and, eventually, ammonium sulphate ($(NH_4)_2SO_4$). Both ammonium sulphates (AS) are thermally stable at ambient temperatures and thus AS does not evaporate during surface/atmosphere exchange. AS *production* on the other hand is not limited by NH_3, but by OH, and therefore does not respond to emissions of NH_3.

The surface/atmosphere exchange of SO_2 received considerable interest in the 1980s and 1990s, when it was identified as a major contributor to forest acidification. In fact it is one of the two 'stereotypical' compounds from whose behaviour early deposition schemes were generalised. It represents a compound whose deposition was believed to be governed by water solubility, while the deposition of the other compound (O_3) was thought to be governed by chemical reactivity (e.g. Wesely 1989; Zhang et al. 2002).

In Europe and America, the interest in SO_2 has declined greatly and measurements of dry deposition rates appear to be rare. SO_2 concentrations have declined greatly over the pasts 20 years, with the consequences that (a) the importance of SO_2 deposition in controlling acid deposition has declined relative to NH_3 and NO_x, and (b) concentrations have reached the detection limits of standard instrumentation making measurements increasingly difficult. Therefore, few long-term measurements of SO_2 dry deposition have emerged over the past 10 years. The few time-series that do exist suggest that, unlike HNO_3 and HCl which tend to stick to any natural surface, SO_2 deposition responds to leaf wetness and leaf water chemical composition, reflecting its lower solubility in water (Table 1). Even when there is no visible leaf water (rain, dew, guttation) present, microscopic leaf water layers exist as a function of relative humidity (or water vapour pressure deficit) and the hygroscopicity of the surface. These water layers represent highly concentrated solutions and dissolution of SO_2 into these small reservoirs is therefore self-limiting, unless it is accompanied by the dissolution of a neutralising agent, mainly NH_3. This effect of SO_2/NH_3 co-deposition has been postulated as early as the 1980s and simulated in a mechanistic model (Flechard et al. 1999), but long remained somewhat elusive to be found in the field (e.g. Erisman and Wyers 1993). In a re-analysis of long-term measurement datasets at a Scottish moorland site and a Dutch forest, we showed that the non-stomatal resistance of SO_2 uptake decreased with increasing RH, but increased with increasing acid/base (SO_2/NH_3 ratio) (Fig. 3), and this parameterisation is implemented in the EMEP CTM, and has led to better agreement between modelled and measured SO_2 concentrations.

A simpler parameterisation of the effect is included in the Dutch IDEM model. A further recent long-term study of SO_2 exchange above a Belgian forest has corroborated these findings and reported a long-term trend of a decreasing canopy resistance of SO_2 as a response to the long-term trend of a declining SO_2/NH_3 ratio (Neirynck et al. 2011).

Using data from a European network; we have elsewhere illustrated the fact that the acid ratio in Europe is no longer dominated by SO_2 and that other acidic gases now need to be incorporated into the analysis and parameterisation and this is further supported by the analysis shown in Fig. 2 (Fowler et al. 2009).

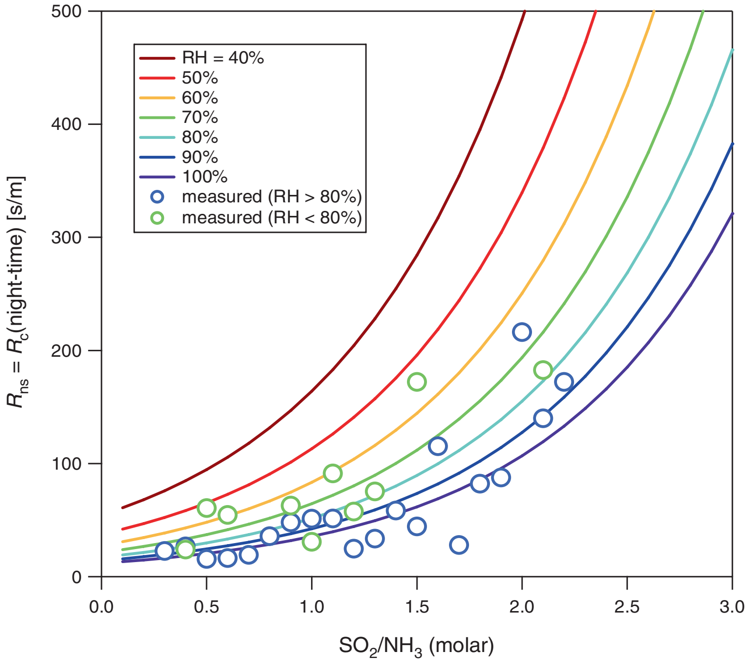

Fig. 3 Parameterisation of the non-stomatal deposition resistance of SO_2 in response to *RH* and acid ratio as implemented in the EMEP model

Organic Acids

Organic acids are a subgroup of oxygenated volatile organic compounds (OVOCs). They cover a range of volatilities and therefore partition between the gas and aerosol phase to variable degree. Formic (HCOOH), acetic (CH_3COOH) and propionic (aka propanoic acid, CH_3CH_2COOH) acid are the most abundant carboxylic acids and oxalic acid ($HOOC_2OOH$) the most common dicarboxylic acids in the atmosphere. All these are found to be >90 % in the gas phase, but propionic acid has been found to exist up to 30 % in the aerosol phase, pyruvic acid up to 15 % in the aerosol phase, propanoic 7–32 % in aerosol and methanosulphonic acid (MSA) is found in aerosol. While the deposition parameters of some of these compounds have been derived theoretically (e.g. Zhang et al. 2002), virtually no dry deposition measurements currently exist and these parameterisations have therefore not been validated. Some of these compounds are covered in the background paper on VOCs.

Deposition of Aerosols

Particle Number Fluxes

Measurements and Current Understanding of the Deposition Process

Measurements
Particle number fluxes have been measured and parameterised for some forty years and several papers have reviewed the results and current understanding (Petroff et al. 2007a; Pryor et al. 2007; Sehmel 1980; Zhang et al. 2003). Early measurements used wind tunnels and surrogate surface collectors to study deposition processes. With the advent of fast response aerosol counters direct micrometeorological flux measurements have been performed in the real atmosphere. Particle number flux measurements are methodologically limited by two factors: (a) Counting statistics are always limited because these counters count typically only tens of particles per 100 ms (a typical eddy-covariance sampling period). Size-segregated measurements have the additional challenge of aerosol number concentrations changing logarithmically with size: a particle counter optimised to measure the small number of larger particles would be overwhelmed by the large number of small particles. (b) Deposition velocities of particles are very small (typically 0.1–10 mm s^{-1}) and thus any small measurement artefact may have a large relative effect.

Initially, measurements were made with fast laser-based optical particle spectrometers, typically covering the size range 0.1–1 μm (Gallagher et al. 1997; Nemitz et al. 2002; Sievering 1983, 1987) and more recently 0.25–2.5 μm (Ahlm et al. 2010; Vogt et al. 2011) and down to 0.06 μm (Deventer et al. 2011; Harrison et al. 2011). A range of aerodynamic and electromobility spectrometers have also now been used (Damay et al. 2009; Grönholm et al. 2007; Nemitz et al. 2000a; Pryor 2006; Pryor et al. 2009; Schmidt and Klemm 2008). All these approaches derive the particle number flux for various aerosol size-bins. In parallel, condensation particle counters (CPCs) have been used for the flux measurements, which derive the 'total' particle number flux, typically over a size range of 10 nm to 1 μm, depending on the model of the CPC and the inlet configuration (e.g. Buzorius et al. 1998, 2001; Martin et al. 2009; Nemitz et al. 2009, 2002).

A part of the limitation of the physical transport is the transfer through the laminar sub-layer that surrounds all surface elements, which gases can only overcome by Brownian diffusion (parameterised through R_b). Particles have a much reduced Brownian diffusivity (decreasing with increasing particle size), but additional ways by which they can overcome this layer. These are primarily impaction (the effect of particle inertia on the inability to follow strongly bent streamlines) and interception (the effect of particle size on making physical contact with the surface elements while following streamlines). Not every particle that makes physical contact with surface elements 'sticks' to the surface and rebounce can be important. In addition, gravitational settling becomes important for super-micron particles. This process is not a diffusive transport and does not require a gradient in the atmosphere to occur. The gravitational deposition flux is therefore not captured by turbulent flux measurements.

Interpretation of Emission and Fast Deposition Fluxes

Emissions have repeatedly been observed during particle flux measurements. There are clearly situations in which emissions take place. Urban flux measurements represent the emission from combustion sources and (wind-driven and vehicle induced) resuspension (Deventer et al. 2011; Dorsey et al. 2002; Järvi et al. 2009; Martin et al. 2008; Schmidt and Klemm 2008; Vogt et al. 2011). Measurements over deserts and snow quantify the resuspension of surface-derived material (Fratini et al. 2007) and in some forest environments the release of primary biological aerosol particles (PBAP) such as spores, pollen and leaf fragments can cause upward fluxes, especially of super-micron aerosol (Ahlm et al. 2010).

However, large aerosol emission fluxes have been reported for situations in which no emissions sources should exist. There is the general understanding that there is no effective primary source of submicron particles from vegetation, except for the release of some small PBAP. Re-suspension is inefficient for these small particles. Secondary aerosol formation is via condensation of pre-cursors gases onto existing aerosol or through nucleation. The former does not create new particles, while the particles created through the latter process inside the canopy are smaller than the detectable size-range of the instrumentation normally used for these measurements. Besides, measurements show that during nucleation events particle concentrations are larger at higher heights than in the forest canopy, suggesting that the canopy is not a source region for nucleation (Gordon et al. 2011; Pryor et al. 2008a, 2009). There are several potential explanations for the detection of emissions:

(a) A large random error on a small positive deposition velocity would lead to a probability distribution including both positive and negative values. To obtain the mean deposition velocity, some authors have averaged over the positive values only (e.g. Damay et al. 2009; Gallagher et al. 1997), but Nemitz et al. (2002) demonstrated that this approach can severely bias the results towards larger deposition velocities when flux measurements are noisy.

(b) Several authors have attributed apparent emissions to negative storage errors due to the entrainment of clean air from the free troposphere as the boundary layer expands (Pryor et al. 2008a). Because deposition to vegetation is very small, air with a higher concentration may reside in the canopy air space, while the aerosol concentration above the vegetation is lowered due to the downward mixing of cleaner air into the boundary layer. An apparent emission results, which reflects venting of the more polluted air out of the canopy, rather than a physical emission. Again, omitting these periods from the analysis is not without problems, because this negative storage error ($\mathrm{d}c_N/\mathrm{d}t < 0$)

would have been preceded by a positive storage error ($dc_N/dt > 0$), during which the concentration built up inside the canopy, which is more difficult to detect.

(c) Whenever particle fluxes are measured for a limited size-range, the micrometeorological flux measurement approach is effectively applied to a quantity that may not be conserved with height. If the instrument measures the wet diameter, this may change with height as particles move through a gradient of relative humidity (*RH*) gradient, which often increases close to vegetation canopies. Where particles take up water and increase in size during the deposition process, they may move from one size bin to another. Thus, potentially, a particle following an eddy motion may be detected in one bin on its way down and in another bin on its way up, unless the particle counter dries the particles prior to detection. If the *RH* gradient and the aerosol growth factor are known, a correction can be applied (Fairall 1984; Vong et al. 2003, 2010). Just as the uptake and release of water vapour causes changes in size, so does the condensation or evaporation of chemical material to/from the particles and this effect is much more difficult to correct for and it cannot be avoided by drying the sample air. Arguably the most important airborne source/sink of aerosol material is the dynamics of the NH_3–HNO_3–NH_4NO_3, as shown since the advent of robust techniques to measure the flux of individual aerosol chemical compounds (see next section).

It should be noted that the process of aerosol growth and shrinkage can cause both positive and negative artefacts, depending on the gradients in chemical drivers and the size of the aerosol distribution. While (a) and (c) effect the measurement of the correct local flux at the measurement height, (b) relates to the difference between the flux at the measurement height and the exchange with vegetation.

Aerosol Chemical Components

Robust flux measurements of individual aerosol chemical components have traditionally been rare. A number of studies has used surrogate surface dry deposition samplers, which were then analysed for individual chemical compounds, to measure dry deposition rates of individual aerosol chemical species (e.g. Bytnerowicz et al. 1987). However, these surfaces are usually considered unrepresentative of vegetation. Some micrometeorological flux measurements of aerosol chemical components were made with manual filter pack gradients (e.g. Duyzer 1994; Wyers and Duyzer 1997), and sulphate fluxes were measured by eddy-covariance with a fast chemiluminescence detector as early as the 1980s (Wesely et al. 1985b). In the meantime, relaxed eddy accumulation has also been used for aerosol flux measurements (e.g. Meyers et al. 2006).

During the last ten years two continuous online analysers have been used to measure fluxes of aerosol chemical components. The GRAEGOR wet-chemistry gradient analyser is based on a combination of wet annular denuders and steam jet aerosol collectors (SJAC) and measures water soluble aerosol components (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-) at two heights (Thomas et al. 2009). Two groups have used this instrument for flux measurements (Twigg et al. 2011; Wolff et al. 2007, 2010). The Aerodyne Aerosol Mass Spectrometer (AMS) is an alternative approach to probe the aerosol chemical composition, providing a fast-response measurement of the non-refractory (operationally defined as aerosol that flash-vapourise at 600 °C) aerosol components over the aerosol size range dictated by the transmission of its aerodynamic lens inlet, which approximates PM_1. This means it is thought to detect virtually all ammonium nitrate, chloride and sulphates, but is comparably insensitive to seasalt (NaCl), reacted seasalt ($NaNO_3$) and crustal material. It also provides a quantitative measurement of total submicron organic aerosol mass and the organic mass spectra (70 eV electron impact ionisation), from which time-series of primary combustion aerosol and secondary oxidised aerosol may be inferred. Special fast data acquisition modes have been developed (Crosier et al. 2007; Kimmel et al. 2011) that allow its application for eddy-covariance flux measurements (Gordon et al. 2011; Nemitz et al. 2008; Thomas 2007; Zalakeviciute et al. 2012).

Half of the applications of the AMS flux system have targeted urban aerosol fluxes. However, measurements emerging from both techniques over vegetation suggest that deposition rates of aerosol vary greatly between chemical compounds. Deposition rates of SO_4^{2-} tend to be small and in the range of model predictions. In particular, NO_3^- and NH_4^+, however, tend to show high apparent deposition rates that are inconsistent with model predictions and larger than those of SO_4^{2-}. While differences in the size distributions would be a potential explanation, the difference also holds for the AMS non-refractory PM_1 flux measurements, with the AMS indicating very similar size-distributions for NO_3^- and SO_4^{2-}. Moreover, while the GRAEGOR gradient measurements are often operated to also detect coarse aerosol, they indicate fast NO_3^- deposition fluxes even at continental sites, where a major contribution of coarse $NaNO_3$ is unlikely. Bulk chemical deposition velocities as a function of u_* obtained with the GRAEGOR and AMS flux systems are summarised in Fig. 4. Thomas (2007) and reported AMS flux measurements over an English oak forest during warm summertime conditions and Nemitz et al. (unpublished) applied the approach to a Dutch Douglas fir stand and, most recently, to a mixed deciduous forest in the Italian Po Valley. Nemitz et al. (2004b) applied a GRAEGOR-style instrument to measure fluxes of NH_4^+ over a Dutch heathland.

Wolff et al. (2010) measured fluxes of water soluble aerosol components and gases by GRAEGOR gradients and reported the results for TA and TN. However, if interpreted ignoring chemical interactions, like in the other experiments, apparent fluxes may be derived for the aerosol components (Wolff et al. 2011). As expected, the compilation of these measurements (Fig. 4) indicates that V_d increases with u_*, however, even the average deposition velocities very much exceed what current models predict on the basis of the physical aerosol interaction with the canopy alone. On individual days, many of the NO_3^- deposition

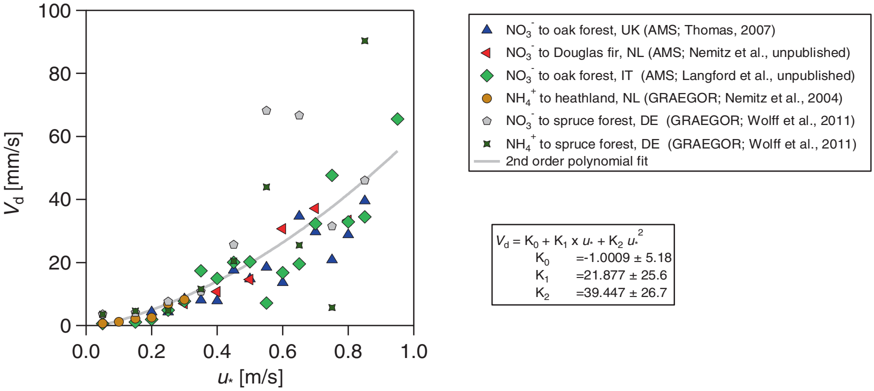

Fig. 4 Apparent nitrate and ammonium deposition velocities, enhanced by ammonium nitrate evaporation near the surface, averaged according to u_* (from Fowler et al. 2009, expanded)

velocities may reach values of up to 100 mm s^{-1}. By contrast, the deposition rate of sulphate is much smaller and in line with model predictions. In fact deposition rates are often so slow that they are within the experimental error.

Some of the first observations of high deposition rates of NO_3^- were made with filter pack gradients over a Dutch forest, with V_d sometimes exceeding $1/R_a$. At the same time SO_4^{2-} showed much slower deposition (Wyers and Duyzer 1997). A subsequent modelling study (Van Oss et al. 1998) showed that this observation was consistent with the evaporation of NH_4NO_3 during deposition, releasing NH_3 and HNO_3 gas that sometimes showed unexpected emission gradients at this site. Similarly, using a continuous gradient measurement, Nemitz et al. (2004b) observed high deposition rates of NH_4^+ to a Dutch heathland, at the same time as observing an apparent non-zero canopy resistance of HNO_3 (cf. Fig. 1) and bi-directional particle number fluxes as measured with an optical particle spectrometer eddy-covariance system. The authors again demonstrated that the likely cause was evaporation of NH_4NO_3 during deposition and simultaneously showed that the volatilisation induced shrinkage of the aerosol would indeed cause the bi-directional number fluxes, with apparent emission in size-bins < 0.3 μm and deposition of larger particles (Nemitz and Sutton 2004). As will be discussed in more detail in Chapter 5, the conversion between NH_4NO_3 and NH_3/HNO_3 represents the fastest and most important aerosol sink/source in addition to water vapour uptake/release. As a result, NO_3^- fluxes are directly impacted by this process. The NH_4^+ is partially associated with NO_3^-, the other main neutralising ions being SO_4^{2-} and Cl^-, thus NH_4^+ is affected by the NH_4NO_3 equilibrium, but not to the same extent as NO_3^-.

Analysis of the fluxes of other aerosol chemical components measured by the newer AMS techniques also suggests elevated deposition rates of NR-PM_1 Cl^- (representing mainly NH_4Cl) and those organic aerosol components that are known to be more volatile.

Parameterisation of the Deposition Process

As with gaseous compounds, aerosol deposition in CTMs is typically calculated as the concentration in the lowest model layer, multiplied by a deposition velocity (V_d). The description of the aerosol differs between CTMs: in the *bulk description* a chemical aerosol compound is treated as a single species with a notional implied mean diameter, without explicitly modelling the size. In the *modal description* the aerosol is described as the composite of typically three aerosol modes, describing the nucleation, accumulation and coarse mode. A simplified description of aerosol microphysics allows particles to move from one mode to another and often the average size of the modes is adjusted accordingly. Finally, in the fully resolved *sectional model* the aerosol is distributed over a large number of size bins and full microphysics can be resolved.

The size resolved models require a parameterisation the deposition velocity as a function particle diameter ($V_d(D_p)$). For the bulk model, compound specific deposition rates can be derived either by multiplication of $V_d(D_p)$ (from models or size-resolved measurements) with the typical size distribution of the compound or, more empirical, from measurements of chemically resolved flux measurements. While most parameterisations can be traced back to a numerical formulation of $V_d(D_p)$, the latter approach was followed e.g. by Ruijgrok et al. (1997).

Parameterisations of the different aerosol deposition processes (Brownian diffusion, impaction, interception, gravitational settling) have been around since the 1980s (e.g. Slinn, 1982). However, often measurements suggest larger deposition rates than predicted by these parameterisations, especially to rough surfaces such as forests (e.g. Gallagher et al., 1997), indicating that either the description of the deposition process is incomplete or that measurements are biased. There is plenty of scope for both possibilities. Uncertainties in the parameterisation include:

(a) The processes of impaction and interception are sensitive to the characteristic size of the surface elements (leaves/needles, leaf hairs), the orientation of these elements and the vertical structure of the canopy. For example, Davidson et al. (1982) showed that particle collection efficiencies can differ greatly between grass species. Using a state-of-the-art multi-layer deposition model, Petroff et al. (2007b) showed that the gap between model results and observations can partly be closed if the canopy structure is correctly accounted for in forest models. Results of $V_d(D_p)$ of this model are shown in Fig. 5.

(b) Recently Katul et al. (2010, 2011) showed that the inclusion of the process of turbophoresis into Petroff's model further improved the model/measurement intercomparison (cf. Fig. 6). Turbophoresis is the tendencies of particles to migrate towards region of lower turbulence associated with their inertia. It enhances deposition rates and is not considered in conventional parameterisations.

(c) There are additional processes that are not usually considered in deposition modelling of particles, but which may have an impact on the deposition rate:

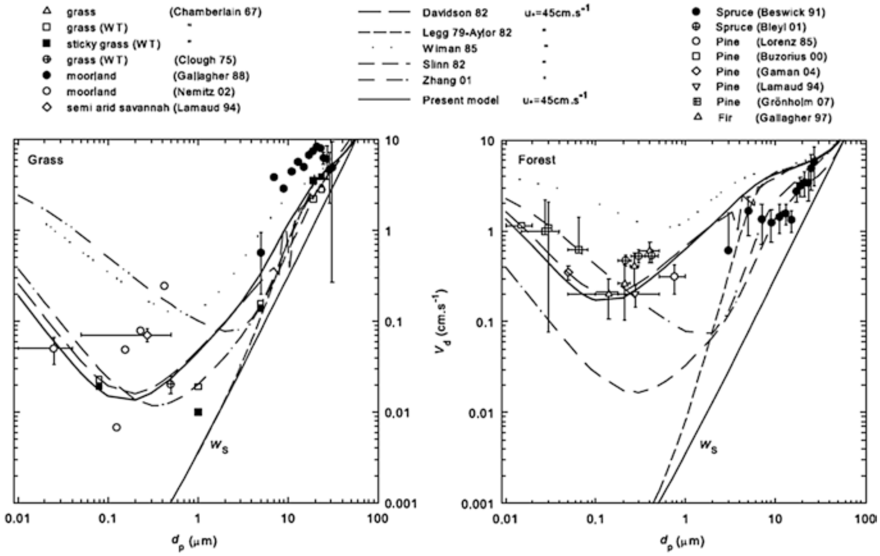

Fig. 5 Evolution of the deposition velocity V_d with the particle diameter D_p on grass and grass-like canopies (*lhs*) and coniferous canopies (*rhs*) for friction velocity between 0.35 and 0.56 m s^{-1}, as given by various measurement campaigns and six existing models from the literature. Canopy characteristics used by models are $h_c = 0.07$ m, $z_0 = 0.01$ m, $LAI = 4$, $d_n = 3$ mm, $a = 1.78$ for grass and $h = 17$ m, $h_c = 7$ m, $z_0 = 1$ m, $LAI = 22$, $d_n = 1$ mm, $a = 3.81$ for forest. Deposition velocities are recalculated at the same reference height $z_R = 100z_0$. The parameters of Slinn's model (1982) are $f_{IN} = 0.01$, $d_r = 20$ mm, $c_v/c_d = 1/3$, $b = 2$. The model of Zhang et al. (2001) is applied on Land Use Categories #6 (grass) and #1 (evergreen-needle-leaf trees), the corresponding parameters being, respectively, $f_{IM} = 1.2$ and 1, and $f_B = 0.52$ and 0.56; from Petroff et al. (2007b). Reproduced from Fowler et al. (2009)

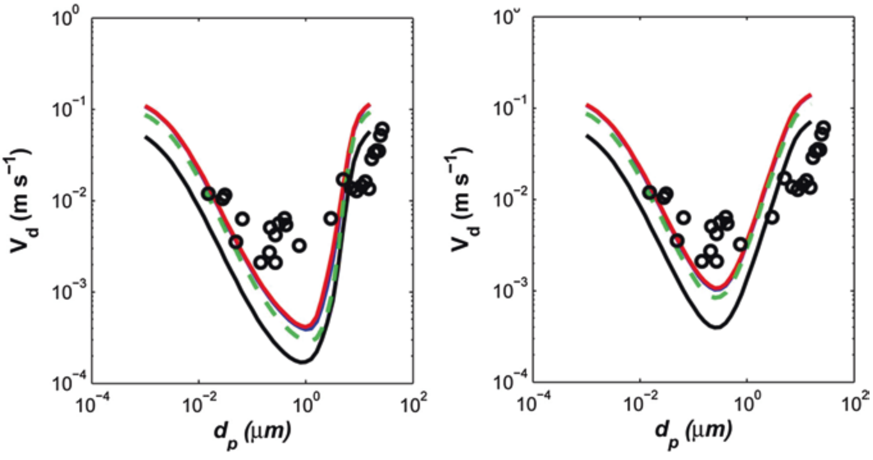

Fig. 6 Prediction of $V_d(d_p)$ with a multi-layer model (**a**) ignoring and (**b**) accounting for thermophoresis compared with measurement data. The *different lines* represent runs for different leaf area density profiles, with were either flat (*black*) or weighted towards the top (*green*), middle (*blue*) or bottom (*red*) of the canopy (from Katul et al. 2011)

as with turbophoresis, thermophoresis (the tendency of particles to migrate along a temperature gradient), may affect deposition rates. In addition, atmospheric particles are often charged and may interact with the electric fields in the boundary layer.

Some uncertainties in the flux measurements have been discussed in the previous section. For size-segregated flux measurements it also needs to be considered that different spectrometers measure different diameters (e.g. optical, aerodynamic, vacuum aerodynamic, electromobility) which cannot always easily be translated into each other. Overall it appears that factors that may affect flux measurements have not always been taken sufficiently into account when flux measurement data have been used to derive parameterisations of $V_d(D_p)$. Parameterisations have recently been reviewed in several papers (e.g. Pryor et al. 2008b) and this is not repeated here.

Several authors have shown that on average measurements of V_d scale with u_* in approximate agreement with the models. If the ratio of V_d/u_* is plotted against stability, however, many measurements reveal an increase in this ratio under unstable conditions (e.g. Fig. 7). This phenomenon was first reported by Wesely et al. (1985b) and, on first impression, appears to be in agreement with similarity theory of turbulence, which explains a similar behaviour of standard deviations of turbulence and concentrations, if normalised by u_*. While these are affected by turbulence, the deposition rate of aerosols is limited by the physical interaction with the vegetation and it is unclear why the processes of Brownian diffusion, impaction and interception would reveal similar dependencies on atmospheric stability.

An alternative explanation of this effect has been suggested by Langford et al. (2010) stability may provide a proxy for the conditions under which evaporation is particularly pronounced. The stability parameter ($1/L$) is proportional to sensible heat flux (H) and inversely proportional to u_*^3. Thus, unstable conditions are

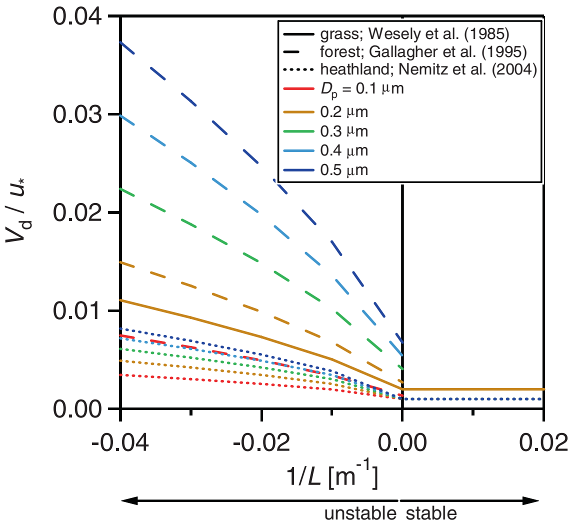

Fig. 7 Summary of the dependence of aerosol deposition velocity on the Monin-Obukhov length (L), indicating a sharp increase of normalized deposition velocity (V_d/u_*) in unstable conditions. Reproduced from Fowler et al. (2009)

associated with (a) large temperature gradients with elevated temperatures at the canopy top, and (b) extended transport times reduced turbulence and consequently long transport times. While several datasets that have been found to be strongly affected by aerosol evaporation show a strong dependence of V_d/u_* on $1/L$, this explanation is not fully consistent with the initial observation by Wesely et al. (1985a),who reported the effect for sulphate, a non-volatile aerosol component. Also, while $1/L$ has skill in explaining some of the variability in V_d/u_* it may not be the most appropriate parameter to use in analytical model parameterisations. It might just happen to be the parameter that has most often been assessed. Finally, H is not necessarily an easy parameter to predict accurately for each CMT land cover type on the basis of the information available from the NWP model.

Alternatively, the effect may be simulated more mechanistically in explicit multi-layer exchange/chemistry models. This approach is discussed in the following chapter.

Chemical Interactions

Effects on Fluxes

The effect of chemical interaction has necessarily run as a common thread through the preceding chapters. As it is becoming increasingly evident that many measurements of acid gas and aerosol deposition reported in the literature are affected by chemical interactions, it cannot be ignored when interpreting measurement results and, in this light, some of our understanding of exchange processes needs to be reviewed.

Chemical interactions affect fluxes if two factors combine: (a) there needs to be chemical source or sink for this compound in the air space below the height at which a flux is measured or at which the reference concentration in a deposition model is taken and (b) this reaction needs to be sufficiently fast for occur during the time it takes an average molecule to be transported between this reference height and the ground surface. This time-scale analysis is usually conducted using the Damköhler number, the ratio of the time-scales of transport and chemistry ($D_a = \tau_t/\tau_c$). Chemistry and transport are usually thought to interact for $0.1 < D_a < 10$ (cf. dashed lines in Fig. 8). For smaller values chemistry is too slow to have an impact, while for larger values chemical local equilibrium is thought not to be disturbed by transport (Kramm and Dlugi 1994). This approach is useful to assess how chemistry and transport interact locally, at a given height. It does, however, not quantify the overall potential of chemical sources and sinks to alter significantly the flux between the reference height and the ground (or vegetation). First, under conditions where chemistry is too fast for transport to disturb chemical equilibria (i.e. $D_a > 10$) it still leads to very significant vertical flux divergence. An example is the oxidation of many sesquiterpenes which is so rapid that most are thought to have reacted away during transport to a height where their canopy

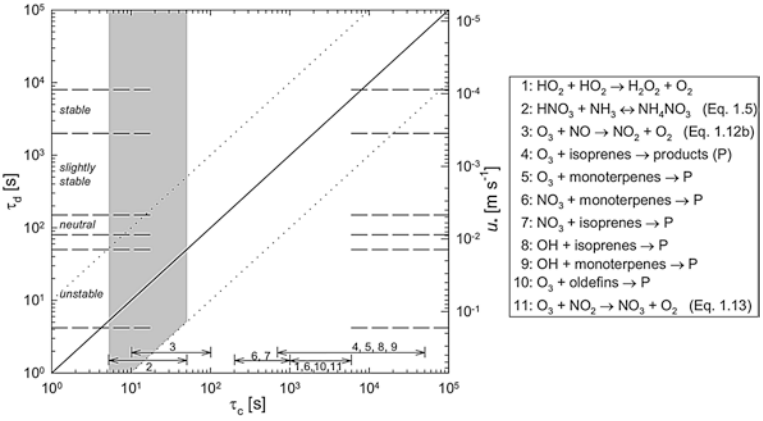

Fig. 8 Comparison of the typical chemical time-scale for various reactions with the turbulent diffusive time scale in the surface layer for typical conditions (Dlugi 1993; modified). The *shaded area* indicates the range of conditions for which fluxes of NH_3, HNO_3 and NH_4NO_3 could be affected by their chemical interaction

scale flux can be measured by micrometeorological flux measurement approaches. Second, during their transport the molecules or particles experience a range of time-scales which cannot be expressed by one single value of D_a. (First-order) chemical time-scales often depend on the concentration of the other reactants, aerosol surface area (in the case of heterogeneous reactions) and meteorological parameters (e.g. radiation, temperature) all of which change with height. The transport time-scales can be very much longer for the transport within plant canopies and within the laminar sub-layers than in the turbulent atmosphere above, for which the transport time-scale is usually derived. Thus, the assessment whether fluxes may be affected by chemistry cannot purely be based on the assessment of the Damköhler number at the measurement height. However, this approach has been used in the literature to rule out chemical effects on bulk chemical fluxes (e.g. Yamulki et al. 1996).

The summary of the chemical time-scales (Fig. 8) demonstrates, however, that the equilibration of the NH_3–HNO_3–NH_4NO_3 system represents one of the fastest sources or sinks in the atmosphere. For pure NH_4NO_3 aerosol, the vapour pressures of NH_3 and HNO_3 seek to form an equilibrium with the aerosol phase, which increases with increasing temperature and decreasing humidity (Mozurkewich 1993) (Fig. 9):

$$NH_4NO_3 \leftrightarrow NH_3 + HNO_3 \quad K_e = [NH_3] \times [HNO_3] = f^n(T, RH) \tag{8}$$

NH_4Cl forms the equivalent equilibrium with NH_3 and HCl, which is, however, of less relevance under most atmospheric conditions.

For an aqueous or mixed phase aerosol the picture is more difficult, because each gas will be subject to an equilibrium surface pressure which is dictated by other solutes. In particular, the vapour pressure of NH_3 is strongly reduced in the

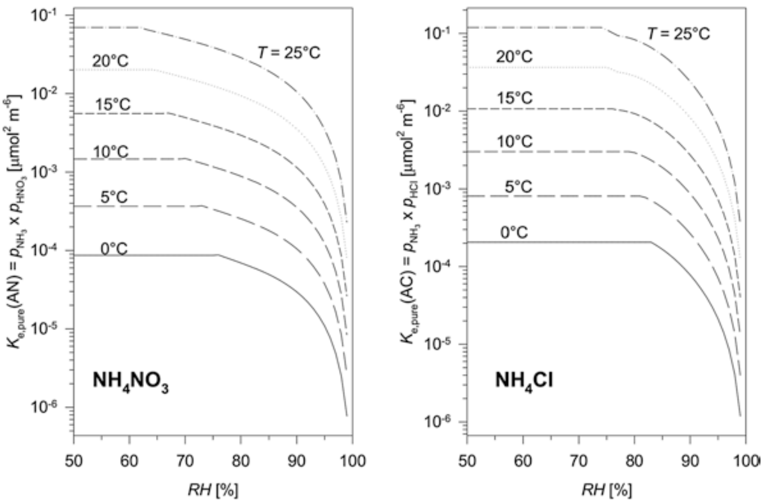

Fig. 9 Equilibrium vapour pressure products (K_e) of NH_3 and HNO_3 as well as NH_3 and HCl over pure NH_4NO_3 and pure NH_4Cl, respectively

co-presence of SO_4^{2-}. Nevertheless, qualitatively dependence on *T* and *RH* still holds, together with the tendency for NH_3 uptake to promote acid uptake and vice versa.

The fast chemistry of the NH_3–HNO_3–NH_4NO_3 system in and near vegetation canopies has several effects:

Flux divergence and error on flux measurements

For an individual compound, the flux at the measurement height above the vegetation no longer represents the actual exchange with the surface (vegetation), because chemical sources/sinks exist between measurement height and the ground, resulting in vertical flux divergence. A single height flux measurement (e.g. by eddy-covariance or relaxed eddy-accumulation) would still measure the correct local flux at the measurement height. For HNO_3, deposition rates with $V_d > V_{max}$ may be observed where gas phase HNO_3 is destroyed near the surface, below the flux measurement height, due to incorporation into aerosol (gas-to-particle conversion). In this situation the HNO_3 does not need to overcome the full atmospheric resistance. This process is most likely to be the case over surfaces where the NH_3 concentration increases sharply near the ground, e.g. due to fertiliser emissions. In this case, deposition of NO_3^- and NH_4^+ aerosol would be suppressed or emission may be observed.

Conversely, reduced deposition or emission of NO_3 may be the effect of NH_4NO_3 evaporation during the aerosol deposition. Near and within the canopies temperatures tend to be elevated during daytime, compared with the atmosphere above. In addition, concentrations of HNO_3 and (at least over semi-natural vegetation) NH_3 are reduced near the ground. Both factors promote NH_4NO_3 evaporation which provides an additional (airborne) source of HNO_3 below the flux measurement height. The result is the observation of apparent reduced HNO_3 deposition or even upward gradients of HNO_3, although at the vegetation surface both NH_4NO_3 and HNO_3 continue to deposit. At the same time, NH_4^+ and NO_3^- would show increased deposition rates at the measurement height, because some of the NH_4NO_3 is lost before it interacts physically with the surface. The NH_3 and HON_3 formed from the process deposit more effectively than the aerosol phase.

Where the flux is inferred from a measurement of the vertical concentration gradient, the situation is more complex, because the concentration profile is modified by the chemistry. The calculated flux is not representative for any height.

In addition to the effect on the bulk chemical species, the loss of NH_4^+ and NO_3^- from (or uptake onto) aerosol also affects size-resolved aerosol number flux measurements. In the case of aerosol evaporation, the particles shrink during the deposition process, which leads to a shift in the size distribution with height. If fluxes are derived from the fluctuations or gradients within a certain size-bin, the particles that are detected in this size bin at a lower height, may have been detected in a larger size-bin at the top height. In other words, the flux is derived from a quantity which is no longer conserved with height. The effect depends on the exact size-distribution at the time.

Effect on the total nitrogen exchange

In addition to affecting measurements and their interpretation, the gas-aerosol phase conversions affect the actual net exchange of nitrogen (N) in two different ways: where NH_4NO_3 evaporates near the ground, this process converts slowly depositing aerosol into fast depositing gaseous compounds, effectively increasing nitrogen deposition. In general, NH_3 exchange with vegetation is bi-directional and governed by the comparative magnitude of the air concentration and the various emission potentials of vegetation elements and soils, primarily the stomatal compensation point (Flechard et al. 2013). If NH_4NO_3 evaporates to form NH_3 near the ground, this will reduce the potential for NH_3 emission from the plants and increase N deposition. Where NH_3 is incorporated into NH_4NO_3 near the ground (usually in situations of strong NH_3 emission), this may lower NH_3 concentrations and further stimulate NH_3 emission.

While the foregoing discussion focuses on the chemistry of the NH_3–HNO_3–NH_4NO_3 system, it is not the only gas-aerosol partitioning that affects flux measurements and surface/atmosphere exchange. The equilibration of aerosol particles with surrounding liquid water is even faster than the chemistry described here. Because water vapour is so abundant, aerosol water activity adjusts very rapidly to the surrounding relative humidity. Thus, relative humidity gradients can also affect measurements of size-segregated aerosol fluxes unless the sample is dried prior to measurement (Fairall 1984; Kowalski 2001; Vong et al. 2003, 2010).

The chemistry of some organic compounds, probably primarily sesquiterpenes, may be sufficiently fast for these compounds to form oxidation products that partition into the aerosol phase, during the few minutes it takes between emission and their measurement above the canopy. The opposite effect may influence urban flux measurements of aerosols: particles contained in tail pipe emissions have been shown to evaporate as the exhaust gas is diluted (Robinson et al. 2007).

Treatment of Near-Chemistry in Deposition Schemes

As also discussed in the background paper on NH_3 several ‘modified gradient approaches’ have been developed to aid the interpretation of flux measurements of NH_3, HNO_3, NH_4^+ and NO_3^-. However, these have been applied only in targeted studies where a comprehensive dataset was available to constrain the models as much as possible and even in those studies some unconstrained parameters could be adjusted freely. Most datasets are far from being sufficiently complete for fluxes to be corrected for chemical interactions with current approaches. Prompted by the apparent HNO_3 emission and fast aerosol deposition observed by Huebert et al. (1988) in a mixed agricultural area, Brost et al. (1988) were the first to simulate the chemistry of this triad and confirmed that the observations were consistent with NH_4NO_3 volatilisation during deposition. Similarly, Van Oss et al. (1998) successfully reproduced the high nitrate deposition fluxes observed by Wyers and Duyzer (1997) and simultaneously showed that the NH_3 emission measured above the Dutch Douglas fir stand at (Speulderbos) may not originate from elevated foliar compensation points, but could be associated with NH_4NO_3 volatilisation near the warm canopy. In a further study, Kramm and Dlugi (1994) simulated formation of NH_4NO_3 in a modified inferential approach. They assumed equilibrium at the vegetation surface and disequilibrium well above, which, because both gases were deposited, meant exceedence of the equilibrium constant and therefore potential for aerosol formation. These scenarios appear to be non-representative of the real world, where disequilibrium is more likely to be driven by the surface exchange itself. This was pointed out by Nemitz (1998) who modelled NH_4NO_3 formation over a surface with large NH_3 emissions. All these models were similar in that they (a) used a big-leaf formulation of the biosphere/atmosphere exchange, (b) simulated steady-state conditions and (c) used a chemical rate that was fitted to the measurements or varied in sensitivity assessments. The exact description of the chemistry differed between models, deploying either a first order relaxation towards equilibrium conditions with a chemical time-scale, which could be estimated from the size-distribution of the aerosol (except for the accommodation coefficient) or using reaction rates. The models mirrored the early 1-D column models that simulated the $NO–NO_2–O_3$ triad (Duyzer et al. 1995; Galmarini et al. 1997; Kramm et al. 1991).

Nemitz and Sutton (2004) advanced this approach by implementing a size-distributed aerosol, which allowed an improved estimate of the chemical time-scales and the simulation of the effect of the gas/aerosol interactions on size-segregated flux measurements. They showed that the evaporation of NH_4NO_3 could qualitatively explain the observed behaviour of bi-directional aerosol number fluxes observed above a Dutch heathland (Nemitz et al. 2004b), with large V_d for the larger particles ($d_p > 0.3$ μm) measured and apparent emission of smaller particles.

The study of Ryder (2010) provided a further milestone in the modelling of the effect of NH_4NO_3 evaporation of bulk fluxes and size-segregated particle number fluxes, moving beyond earlier studies by (a) explicitly resolving aerosol fluxes

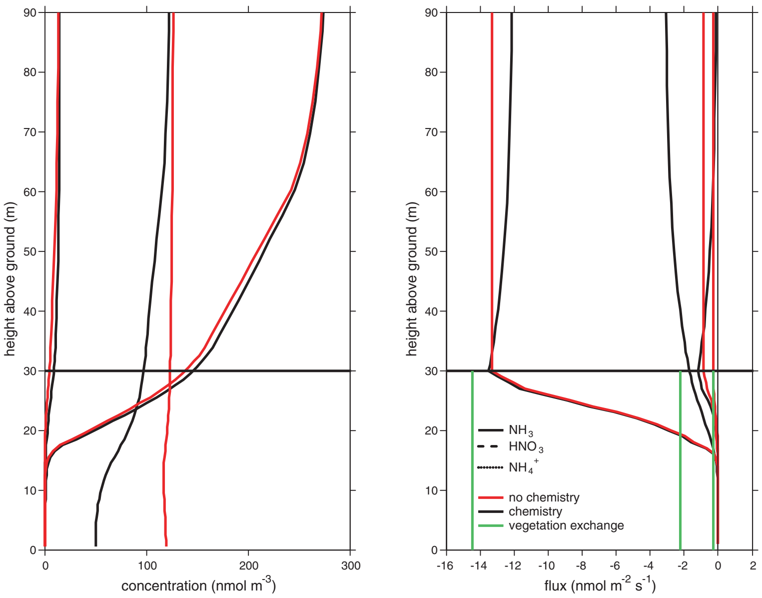

Fig. 10 Example vertical profiles of concentrations (*left*) and fluxes (*right*) modelled with the coupled chemistry/transport/exchange model of Ryder (2010) for a Dutch forest canopy

with plant canopies, (b) simulating full thermodynamics of mixed inorganic aerosols, (c) linking to gas-phase chemistry (e.g. HNO$_3$ production from soil NO), (d) making no equilibrium assumptions. The disadvantage of this fully coupled 1-dimensional chemistry/thermodynamics/aerosol microphysics/exchange/transport model is its computational cost, which makes it inappropriate for application in CTMs. Ryder (2010) applied the model to the Dutch heathland dataset of (2004a, b) and a more recent measurement dataset at the Dutch forest which was also studied by Wyers and Duyzer (1997) and Van Oss et al. (1998), including AMS eddy-covariance fluxes. He showed that at the forest up to 50 % of the NH$_4$NO$_3$ evaporation below the measurement height occurred *within* the canopy, while for the short heathland vegetation, the fraction was still significant at 30 %. He also showed that the effect of the evaporation could easily increase the apparent nitrate flux by a factor of 10 or 20 and is therefore responsible for the high deposition rates of NO$_3^-$ and NH$_4^+$ summarised in Fig. 10.

Figures 10 and 11 exemplify some of the results. Figure 10 shows an example results of the bulk chemical concentration and flux profiles simulated over the heathland. In this particular run, the deposition flux of NH$_4^+$ increases by a factor of 15 between the no-chemistry and chemistry run, while the evaporation results in much reduced apparent HNO$_3$ deposition at higher heights. As a general feature, because NH$_3$ fluxes tend to be much larger than those of HNO$_3$ and NH$_4$NO$_3$, the relative effect is smallest on NH$_3$.

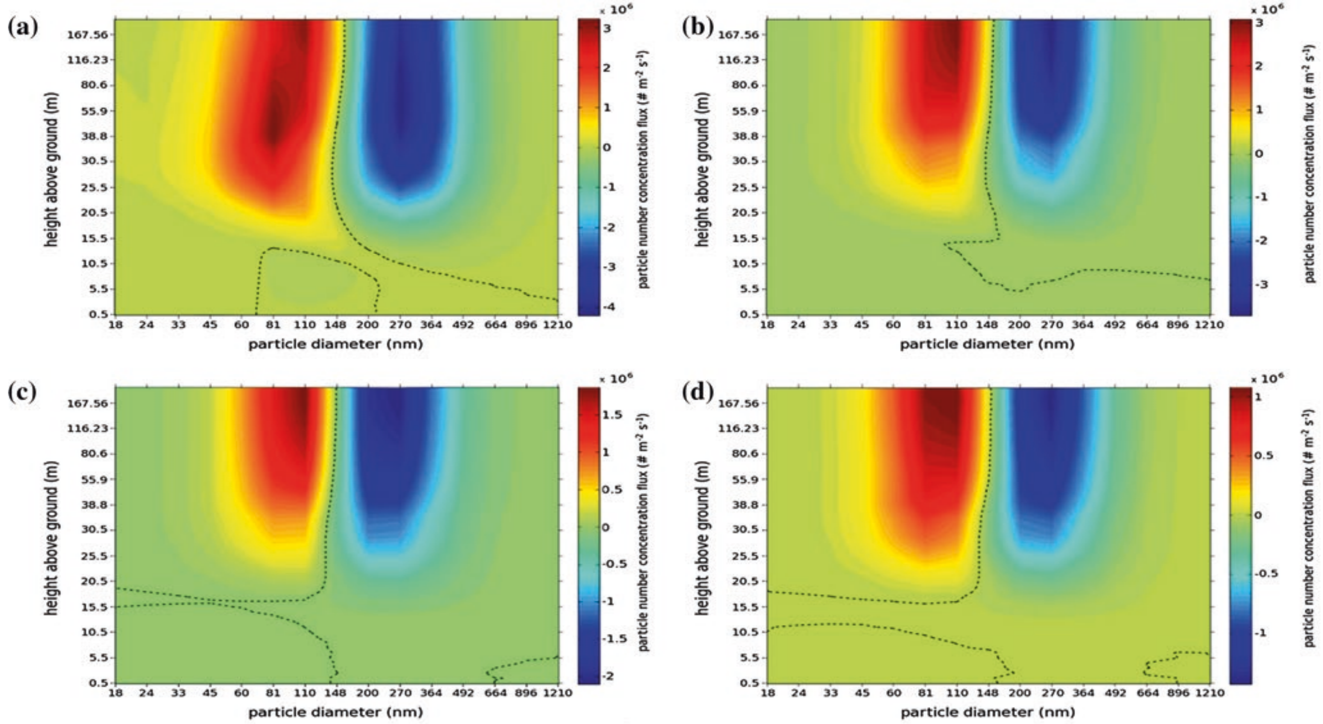

Fig. 11 Size segregated particle fluxes simulated for 2/7/2009 at: **a** 6:00, **b** 8:00, **c** 10:00, **d** 12:00. *Dotted line* denotes the canopy top (above which the vertical scale is logarithmic). *Dashed lines* denote the transition from positive to negative flux

Figure 11 shows the apparent size-segregated particle fluxes for four different times of the same day that originate from the particles moving between size-bins during the deposition process. The dotted line represents the size at which the apparent flux switches from deposition to emission and approximately reflects the peak in the number size distribution. To the left of the dotted line more particles shrink into a given size bin from the next larger size than are leaving the bin to the next smaller size. The result is an apparent emission flux. To the right of the line more particles shrink out of a given size bin than shrink into it from the next larger size bin, resulting in apparent fast deposition.

The study of the NH_4NO_3–NH_3–HNO_3 partitioning has recently been extended to the simulation of concentration profiles within the entire boundary layer, in response to vertical profiles in temperature (Aan de Brugh et al. 2012).

To date, no study appears to have deployed a modified inferential model that accounts for NH_3–HNO_3–NH_4NO_3 interactions spatially, within a CTM, similar to the NO–NO_2–O_3 chemistry that has been tested in a global model (Ganzeveld and Lelieveld 1995). Using the study of Ryder (2010) as a reference, future work should focus on the assessment on how much his approach can be simplified in terms of thermodynamics, vertical resolution and size-resolution of the aerosol.

Several authors have modelled *organic* chemistry within and near plant canopies to estimate the amount of flux divergence between the above-canopy flux measurement and the point of vegetation exchange including the processes inside the canopy, but most of these studies have been confined to gas-phase chemistry (Boy et al. 2011; Gao and Wesely 1994; Gao et al. 1993; Makar et al. 1999; Saylor 2012; Stroud et al. 2005). The main reason is that the modelling of biogenic secondary organic aerosol (BSOA) formation is still in its infancy and it remains difficult to include the hundreds or thousands of reactions and compounds involved even in the degradation of a simple compound as isoprene.

Topical Research Questions to be Discussed

HNO_3:

- How important is leaf surface chemistry for reducing the deposition of HNO_3?
- How can gradient flux measurements of HNO_3/NH_3/NH_4NO_3 efficiently and reliably be corrected for chemical interactions in the air space? What measurements are needed?
- How much of the deposited HNO_3 might be re-emitted as HONO?
- What are the measurement artefacts on current measurement techniques (HONO, NO_x, N_2O_5, $ClNO_2$) and what are the implications on the current understanding of the exchange process derived from these results?

HCl:

- What are the sources of HCl and what is its contribution to atmospheric chemistry and acid deposition?
- Should it be treated in more CTMs, also to close the mass balance of HNO_3/HCl against measurements?

HONO:

- How can HONO fluxes be measured reliably?
- What tools have we got to deconvolve the measured net fluxes of HONO into deposition and chemical production?

SO_2:

- Current formulations of SO_2/NH_3 co-deposition ignore other acids. How can these be taken into account?

Organic acids:

- What are the best parameterisations to use in the absence of measurement data?
- How could the measurement situation be improved?

Aerosols:

- How important are processes missing in deposition models (e.g. turbophoresis) and how could they best be taken into account, if required?
- How well can canopy morphology be described at the regional/global scale? What are the best 'mean' parameters to use?
- Different parameterisations need to be used for aerosol chemical compounds of different volatility. Could the effect of near-surface evaporation of NH_4NO_3 on the effective deposition rates of NO_3^- and NH_4^+ be parameterised in an empirical approach? What meteorological drivers could be used, that are accurately predicted in NWP models?
- Under what conditions is the effect considerable/negligible?
- What is the effect of evaporation on other (semi-)volatile compounds such as Cl^- and certain organic aerosol components? How can this be taken into account?

Modelling of chemical interactions:

- What is the minimum vertical resolution (2 or more in-canopy layers; resolution above the canopy?) required to model in-canopy chemistry mechanistically? What is the computational burden for the CTMs?
- How can we make sure that the multi-layer modelling approaches are consistent with the big-leaf models, e.g. in terms of R_b, R_s? How do we define the relationship?
- How far can we simplified state-of-the-art coupled transport/exchange/chemistry models in terms of aerosol size information, vertical resolution, complexity of chemistry and thermodynamics?

- What model complexity is appropriate in terms of input parameters, computational cost?
- Can we ignore chemistry for certain surfaces?
- How tightly linked is gas phase chemistry and gas/aerosol partitioning?

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Part II
Synthesis According to Compounds

Modelling the Air–Surface Exchange of Ammonia from the Field to Global Scale

J.O. Bash, C. Flechard, M. Adon, P. Cellier, J.L. Drouet, S. Genermont, B. Grosz, L. Horvath, R.-S. Massad, M.A. Sutton, M.R. Theobald and R. Wichink Kruit

Introduction

The Working Group addressed the current understanding and uncertainties in the processes controlling ammonia (NH_3) bi-directional exchange, and in the application of numerical models to describe these processes. As a starting point for the discussion, the Working Group drew on the background document prepared by Flechard et al. (2013) specifically for the workshop. Based on these discussions by the Working Group, the present report documents the assessment and recommendations for modeling of NH_3 exchange from the field to global scales.

J.O. Bash (✉)
National Exposure Research Laboratory, U.S. Environmental Protection Agency,
Research Triangle Park, NC 27711, USA
e-mail: Bash.Jesse@epa.gov

C. Flechard
INRA, Agrocampus Ouest, UMR1069 Sol Agro-hydrosysteme Spatialisation,
35042 Rennes, France

M. Adon
Laboratoire d'Aérologie, UMR 5560, Université Paul-Sabatier (UPS) and CNRS,
Toulouse, France

M. Adon
Laboratoire de Physique de l'Atmosphère, Université Félix Houphouët Boigny,
Abidjan, Cote d'Ivoire

P. Cellier · J.L. Drouet · S. Genermont · R.-S. Massad
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

B. Grosz
Department of Meteorology, Eotvos Lorand University, 1117 Budapest,
Pazmany Peter S. 1/a, Hungary

R.-S. Massad and B. Loubet (eds.), *Review and Integration of Biosphere-Atmosphere Modelling of Reactive Trace Gases and Volatile Aerosols*,
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Modelling NH_3 Air–Surface Exchange Processes

Progress in the understanding and modeling of NH_3 bi-directional exchange have been made at the field scale (Massad et al. 2010) and more recently the regional scale (Bash et al. 2013; Hamaoui-Laguel et al. 2014; Wichink Kruit et al. 2012). Current parameterizations of NH_3 bi-directional exchange typically rely on a two-layer (vegetation and soil) resistance model with compensation points for vegetation and soil surface (Nemitz et al. 2001). The compensation point is modeled as the gas phase equilibrium of NH_3 with the aqueous solution in surface media. In practice, the compensation point is modelled as an emission potential (Γ, the ratio of aqueous phase NH_4^+ to H^+ concentration) and the combined Henry and solubility equilibria (Nemitz et al. 2001). Models of process-based NH_3 exchange at vegetation surface incorporating C-N turn-over processes (Riedo et al. 2002), leaf surface chemistry (Flechard et al. 1999), and soil emission models (Génermont and Cellier 1997) have been developed but have not yet been integrated into a common framework. A more comprehensive process description is provided by (Flechard et al. 2013).

Recent regional scale modeling of NH_3 air-surface exchange has typically relied on estimates of NH_3 emissions from national inventories or estimates of livestock densities (Hellsten et al. 2007; Pinder et al. 2006; Skjøth et al. 2011) and the dry deposition of NH_3 in air-quality models without the consideration of bi-directional exchange. Improvements in the modelling of reduced nitrogen pools in environmental compartments has been performed at several levels of detail by (a) modeling NH_3 emissions using a more process based approach and linked to an atmospheric chemical transport model (CTM) without a bi-directional NH_3 exchange parameterization (Hamaoui-Laguel et al. 2014); (b) incorporating bi-directional exchange for semi-natural areas using empirical relationships in a CTM (Wichink Kruit et al. 2012); and (c) explicitly describing bi-directional exchange in a CTM by coupling to agro-ecosystem models for parameterizations of soil biogeochemistry and agricultural processes (Bash et al. 2013). Details of the regional scale bi-directional modelling approaches are discussed in the next section.

L. Horvath
MTA-SZIE Plant Ecology Research Group, Szent István University, Páter K. U. 1,
2103 Gödöllő, Hungary

L. Horvath
Hungary and Hungarian Meteorological Service, Gilice 39, 1181 Budapest, Hungary

M.A. Sutton
Center for Ecology and Hydrology (CEH) Edinburgh, Penicuik, UK

M.R. Theobald
Higher Technical School of Agricultural Engineering, Technical University of Madrid
(UPM), 28040 Madrid, Spain

R.W. Kruit
TNO, Climate, Air & Sustainability, 80015, 3508 TA Utrecht, The Netherlands

Regional Scale Implementations of Bi-directional NH_3 Exchange in CTMs

Currently two CTM systems have parameterized NH_3 bi-directional exchange the LOTOS-EUROS model (Wichink Kruit et al. 2012) and the Community Multiscale Air-Quality CMAQ model (Bash et al. 2013). These two modelling systems have taken different approaches to NH_3 bi-directional parameterizations at a regional scale. The LOTOS-EUROS model utilizes NH_3 fertilizer and animal housing emissions from a database and models the bi-directional NH_3 fluxes at stomatal and water surfaces using empirical relationships based on the mean monthly ambient NH_3 and annual total NH_x ($NH_3 + NH_4^+$) deposition respectively. A cuticular compensation point, C_w, is parameterized in LOTOS-EUROS as an empirical function of the ambient NH_3 concentration and temperature (Kruit et al. 2010). Bi-directional exchange in CMAQ estimates NH_3 emissions from agricultural soils from fertilizer application by coupling the soil geochemical processes in the Environmental Policy Integrated Climate (EPIC) agro-ecosystem model to define a soil Γ (Cooter et al. 2012). In CMAQ, the stomatal compensation point, C_s, is an empirical function of the annual total N deposition and fertilization application following Massad et al. (2010). The resistance to deposition on the leaf surface, R_w, in CMAQ is a function of the ambient NH_3 concentration and the relative humidity. These two parameterizations highlight some of the difficulties in regional scale applications of bi-directional NH_3 exchange: most notably, the use of reported annual national emission data, and the coupling of agro-ecosystem models for incorporating fertilizer NH_3 emissions in CTM. Emissions from manure storage and animals in these modeling systems rely on national estimates and are not dynamic. Currently, these models use empirical relationships to parameterize processes governing C_s and C_w that are not well understood. The use of national NH_3 emission databases, CTM coupling to ecosystem models or empirical relationships have to be balanced against the availability of model input data on the regional scale, computational limits, and the modeling systems ability to capture the observed dynamics of NH_3 bi-directional exchange.

Despite the recent progress in the modeling of NH_3 bi-directional exchange (Flechard et al. 2013), there are several processes that are either poorly understood or missing in local and regional scale models. These are primarily in the treatment of the dynamics of the NH_3 exchange from apoplast and cuticular vegetation sources, the treatment of emissions from leaf litter decomposition, the treatment of animal housing, and manure storage and application. Models of process-based NH_3 exchange at vegetation surface incorporating C-N turn-over processes have been proposed (Riedo et al. 2002), but are difficult to parameterize at the regional scale in CTMs. Similarly, process based models of NH_3 emissions from manure application and grazing have been developed for soil emissions (Génermont and Cellier 1997). The first stages of application for regional models have been explored (Hamaoui-Laguel et al. 2014), but have yet to be coupled to CTMs using a bi-directional exchange framework. Modelling of NH_3 fluxes at leaf litter surfaces has proven to be challenging because the leaf litter nitrogen pool is small and dynamic, relative to fertilized soils, but has some of the largest measured emission potential (Γ) (Sutton et al. 2009) and a process based model has yet to be developed. The modeling of pH is critical to the estimation of Γ and has proven to be challenging due to uncertainties in the buffering capacity and composition of the surface media solution. The complexity of how these processes are modelled will depend on the application, e.g. field scale modelling to interpret flux measurements, regional scale modeling of future agricultural scenarios, etc.

Development of Improved NH_3 Process-Based Bi-directional Exchange Models

Modelling of NH_3 bi-directional exchange is beneficial to experiments by providing a conceptual framework in which to interpret observed results. This interpretation of the observations can elucidate physical processes that cannot yet be measured. Likewise, the inclusion of an NH_3 bi-directional exchange framework in regional and global models improves the estimation of nutrient and acid deposition. Ideally field and regional scale NH_3 bi-directional models would use the same framework that could efficiently be adapted to each scale. This would also be beneficial for evaluating models improvements at the field scale on regional scale applications. Models developed in this framework should be community based and open source to reach the largest research community and draw upon their collective knowledge. Recommended model processes and parameterizations for both field and regional scale models are listed in Table 1, distinguishing current state-of-the-art and consensus on the need for future developments over the next 2–5 years.

Field Scale One-Dimensional (1-D) Model

Although substantial progress has been made in modelling the diurnal and temporal dynamics of NH_3 fluxes at the field scale, the Working Group recommends further development of these modeling efforts to investigate vegetation, litter, and soil processes on NH_3 exchange. This model should be built on a framework common to the four chemical species groups addressed in this workshop and be based on a modular concept to easily evaluate, change and update model algorithms as the understanding of these processes improves. The current bi-directional exchange models should be adapted for animal NH_3 emissions similarly to how it has been applied to model NH_3 global fluxes from seabird colonies (Riddick et al. 2012) to improve modeled climate feedbacks on emission estimates. There is currently uncertainty regarding the dynamics of the emission potential (Γ) and the nitrogen

Table 1 Current state-of-the-art and recommended future parameterizations of model variables needed to parameterize NH_3 bi-directional exchange for field scale and regional scale Chemistry and Transport Models (CTMs)

Model variable	Purpose	Future ideal model	Currently tenable model
Soil Γ	Soil ammonium pool	**Agricultural:** management model coupled to ecosystem and bi-directional exchange model	**Agricultural:** management model coupled to ecosystem and bi-directional exchange model
		Semi-natural: Ecosystem model coupled to a bi-directional exchange model	**Semi-natural:** Empirical parameterizations and look up tables
Litter Γ	Leaf litter N pool and pH	Litter decay/ammonification model coupled to a bi-directional exchange model	Empirical parameterization
Apoplast Γ	Leaf apoplast N pool and pH	Model of NH_3 transport in plant physiology model coupled to a bi-directional exchange model	Empirical parameterization of N deposition/fertilizer input or ambient NH_3 concentration (process model only demonstrated to date for grassland)
Cuticle resistance/Γ	Leaf surface N pool and pH	Cuticle Γ coupled to leaf surface chemical model	Empirical parameterization of cuticle resistance or cuticle Γ
Mineral fertilization	Soil inorganic N input	Ecosystem model coupling evasion, nitrification, and agricultural management	Ecosystem model coupling evasion, nitrification, and agricultural management
Manure/grazing fertilization	Soil organic N input	Manure Γ modeled form organic N decay and uric acid hydrolysis model	Empirical parameterizations and look up tables
Vegetation/soil pH	Γ parameterization	Dynamic empirical parameterization	Constant or lookup table
Animal NH_3 emissions	Atmospheric NH_3 source	Animal excretion Γ linked to organic N decay and uric acid hydrolysis model	Emissions database/ inventory
Fertilizer NH_3 flux	Atmospheric NH_3 source/sink	Bi-directional exchange model coupled to an agro-ecosystem model	Bi-directional exchange model coupled to an agro-ecosystem model or lookup table
Semi-natural NH_3 flux	Atmospheric NH_3 source/sink	Bi-directional exchange model coupled to an ecosystem model	Lookup table or empirical relationships

(continued)

Table 1 (continued)

Model variable	Purpose	Future ideal model	Currently tenable model
Sub-grid cell processes	Capture land scale heterogeneity*	Micrometeorological variables, fluxes, and ambient concentrations estimated for each land use	Micrometeorological variables and fluxes estimated for each land use
Soil–canopy–atmosphere exchange model	Estimation of transport processes	Multiple soil and canopy layer bi-directional resistance model	Two layer (soil and canopy) bi-directional resistance model

*Parameterization only needed for CTM

pools in leaf litter, vegetation and in the soil and how they contribute to the net NH_3 flux. A better understanding of the chemistry on the leaf surface building on the work of Flechard et al. (1999), the dynamics connecting apoplastic NH_4^+ with fertilization and nitrogen deposition, and soil decomposition and mineralization processes would likely reduce uncertainties. These processes should be investigated on a field scale utilizing flux measurements integrated with a comprehensive bi-directional NH_3 exchange model.

Regional and Global Scale Model

Modeling of bi-directional exchange requires agricultural management and ecosystem information to parameterize the dynamics of the soil–vegetation–atmosphere exchange processes that are typically not available at the regional scale. These data needs can be met by using empirical functions, look-up tables, or by coupling CTMs to ecosystem models that parameterize vegetation and soil biogeochemical processes. The coupling of CTMs to ecosystem and agricultural management models address the physical and biogeochemical processes more directly than empirical relationships or look-up tables. However, most of the ecosystem models with NH_3 exchange parameterizations have been developed and evaluated for managed agricultural ecosystems. Thus, the modelling of NH_3 bi-directional exchange in semi-natural systems will likely rely on empirical relationships until future measurements elucidate the seasonality and sensitivity of apoplastic, leaf litter, and soil emission potentials (Γ) to biogeochemical processes and nitrogen deposition.

Uncertain processes should be bound on a regional scale with observational constraints on modeled processes and by preserving the nitrogen mass balance in the modelled fluxes between the soil, litter, and vegetation NH_4^+ and atmospheric NH_3 pools. Process based modelling of NH_3 bi-directional exchange at a regional scale using a framework common to the other pollutants and processes considered in this workshop will present computational challenges. Faster numerical methods will need to be developed and sensitivity studies at both field and regional scales should be used to determine what processes can be generalized or may be represented empirically while still capturing the observed dynamics.

Uncertainty in Processes and Measurement Needs

Recently, advances have been made in the modeling of NH_3 in agricultural cropping systems on national, continental and global scales (Cooter et al. 2012; Hamaoui-Laguel et al. 2014; Paulot et al. 2014). However NH_3 emissions from agricultural cropping and animal operations are the largest source and the modelling of the processes governing these emissions on a regional scale dominate the overall uncertainty in NH_3 emissions and deposition. Ammonia emissions from animal operations are the largest source of agricultural ammonia emissions to the atmosphere and are typically modeled using empirical relationships (Skjøth et al. 2011). Simple process based NH_3 emissions models from animal excretions and volatilization dynamics (Riddick et al. 2012) have been developed and could likely be adapted to model emissions from manure storage and animal housing to capture environmental changes in future climate scenarios better than empirical relationships derived from observations taken under the current climatic conditions. How the dynamics of NH_3 emissions from manure and grazed agricultural systems and the dynamics of soil and litter pH (a critical component) evolve in response to organic and inorganic fertilizer application are currently not well represented in bi-directional exchange models. Large uncertainties also exist in the understanding of how ambient NH_3 concentrations and nitrogen deposition influence the apoplastic NH_4^+ concentration and how the chemistry on the leaf cuticle impacts NH_3 fluxes, although these uncertainties likely impact a smaller fraction of the NH_3 emissions budget than agricultural emissions.

Conclusion and Model Integration

A consistent set of assumptions in a common model framework governing NH_3 exchange is needed to interpret processes from flux measurements and provide measurement targets. Similarly, a common framework is needed in regional and global CTMs to unite NH_3 emissions and deposition processes. Effort should be devoted to making this framework modular so that processes can be easily updated or replaced as the community's knowledge of NH_3 exchange improves or more generalized parameterizations are developed for regional and global scale CTM applications. Modular land surface models have recently been incorporated into regional and global climate modeling systems to estimate land use change information and carbon, nitrogen, moisture and temperature fluxes (Lamarque et al. 2012; Lawrence et al. 2011). These land surface models have generally been applied for climate simulations and greenhouse gases. They could serve as an example framework that could be adapted for use for reactive trace gases and volatile aerosols.

The transport processes and receptors/pools in this modelling framework should be common to the other chemical species considered in this workshop. This will likely include the incorporation of a multi-layer canopy and soil/litter model. A common framework for multiple chemical species will allow connections in aerosol processes, in-canopy and leaf chemistry, and feed backs on vegetation and soil resistances and nitrogen pools to be parameterized on a more process-based level than it is currently feasible. Additionally, a common model framework may highlight areas of discrepancies in existing parameterizations and measurement needs.

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O_3 and NO_x Exchange

B. Loubet, C. Ammann, J.F. Castell, L. Emberson, L. Ganzeveld, A.S. Kowalski, P. Laville, L. Merbold, E. Personne, P. Stella, J.-P. Tuovinen and A. Tuzet

Introduction

This discussion was based on the background document "Review on modelling atmosphere-biosphere exchange of Ozone and Nitrogen oxides", which reviews the processes contributing to biosphere-atmosphere exchange of O_3 and NO_x, including

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B. Loubet (✉) · J.F. Castell · P. Laville · E. Personne · A. Tuzet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France
e-mail: loubet@grignon.inra.fr

C. Ammann
Air Pollution and Climate Group, Research Station Agroscope, Zurich, Switzerland

L. Emberson
Stockholm Environment Institute, University of York, YO10 5DD York, UK

L. Ganzeveld
Earth System Science Group, Department of Environmental Sciences, Wageningen University, Wageningen, The Netherlands

A.S. Kowalski
Department of Applied Physics, University of Granada, 18071 Granada, Spain

L. Merbold
Institute of Agricultural Sciences, ETH Zurich, 8092 Zurich, Switzerland

P. Stella
Biogeochemistry Department, Max Planck Institute for Chemistry, 55020 Mainz, Germany

P. Stella
Now at UMR SAD-APT, AgroParistech, Paris, France

P. Stella
AgroParisTech, UMR INRA/AgroParisTech SADAPT, Paris, France

J.-P. Tuovinen
Finnish Meteorological Institute, 503, 00101 Helsinki, Finland

R.-S. Massad and B. Loubet (eds.), *Review and Integration of Biosphere-Atmosphere Modelling of Reactive Trace Gases and Volatile Aerosols*,
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stomatal and non-stomatal exchange of O_3 and NO, NO_2. Non-stomatal exchange, including soil and chemical reactions in the canopy airspace is discussed, with a focus on how these processes are influenced by turbulent transport in the canopy. Existing models are reviewed, from big-leaf and two layer resistance to multi-layer models. Based on this background document, the discussion in the working group was organized to discuss the current gaps in modelling O_3–NO–NO_2 exchange and the ideal model that should be developed.

Product of the Discussion

Processes Involved in the O_3 and NO_x Exchange

As emphasised in the background document "Review on modelling atmosphere-biosphere exchange of Ozone and Nitrogen oxides", a first limitation in modelling biosphere-atmosphere exchange of the O_3–NO–NO_2 triad lays in some important gaps of knowledge on some key processes:

- Is O_3 deposition rather a thermodynamical adsorption or a chemical depletion process? The mechanism of O_3 deposition at the biosphere interface is yet not clearly understood. Especially at the soil surface, and in the plant leaves, there is still the uncertainty on whether the process is a thermodynamical equilibrium adsorption process or whether O_3 reacts with another compound in the gas phase (NO, VOCs) prior to surface deposition. This links to a second question as to whether O_3 is "destroyed" or only converted at the soil and plant surfaces. This second question is important in terms of atmospheric chemistry since chemical conversion would release a secondary product back to the atmosphere while the overall oxidation capacity could remain unchanged.
- Is the observed O_3 deposition dependence on wetness a surface or a volume process? Most of the experimental evidence suggests that non-stomatal O_3 deposition is a heterogeneous decomposition process, with a decomposition rate depending on the air relative humidity (Grontoft et al. 2004; Stella et al. 2011). Nevertheless these evidence are mostly empirical and do not explain the observed high affinity of O_3 to water layers.
- What is the role of VOCs in O_3 deposition? Some modelling exercises suggest that ozonolysis of very reactive terpenes could explain a significant part of the non-stomatal O_3 deposition fluxes to forests (Goldstein et al. 2004; Wolfe et al. 2011).
- Is the existence of a NO_2 compensation point confirmed? Although NO_2 compensation points have been reported in the literature (e.g. (Hereid and Monson 2001), it may result from a misinterpretation of the NO_x-O_3 in-canopy chemistry or from biased measurements due to chemical reactions (Breuninger et al. 2013; Chaparro-Suarez et al. 2011; Stella et al. 2013).
- What is the magnitude of NO_2 deposition to soils and what are its environmental drivers? Measurements of NO_2 deposition to soils are scarce and mostly limited to forests, no dependency on environmental drivers of NO_2 soil deposition has been reported (Gut et al. 2002; Pilegaard 2001).

The Ideal Biosphere-Atmosphere Exchange Model

Despite the gaps in knowledge exposed above, we consider that there is sufficient knowledge and empirical parameters to model O_3–NO–NO_2 biosphere-atmosphere exchange. The main model characteristics were discussed. The core model should contain a set of essential modules:

- The model should consider water, heat, O_3, NO and NO_2 together, and possibly other pollutants.
- A stomatal conductance module that is connected to water vapour exchange and photosynthesis and ideally differentiate between sunlight and shaded leaves.
- An energy balance module to determine canopy conductance, surface wetness, air temperature and relative humidity, all essential for simulating O_3 and NO_x exchange.
- A surface hydrology module including detailed soil moisture to account for water stress effects on stomatal conductance and soil moisture impacts on NO emissions by soils and O_3 deposition onto the ground.
- A multi-layer chemistry-transport model, simulating NO_x-O_3 chemical reactions in the canopy, would be necessary for NO_x, but not essential for O_3.
- A soil NO emission module should be included which would depend upon the soil water content and the ecosystem nitrogen status.
- The inclusion of (NO_x) leaf production processes and compensation point mechanisms in the model scheme should be considered with the need however to determine the parameter values.
- A coupling with a vegetation growth model would be necessary to allow evaluating feedback mechanisms of O_3 and NO_x exchange on biomass production (and hence leaf area and canopy height) and stomatal uptake.
- Two vegetation layers should be enough for O_3 and NO_x and could also be computationally efficient using an analytical approximation for in-canopy transport.
- In order to ease model calibration and parameter evaluation it would be preferable to develop a single or a few common conceptual model schemes.
- These schemes should be implemented in an easy-to-use offline one-dimensional model version which should be available to experimentalists (cf. available user interface of DO3SE model).

Datasets for Model Parameterisation and Validation

The discussion also emphasized the need for comprehensive datasets for validating NO–NO_2–O_3 exchange, which should include fluxes and concentrations at several levels inside and above the canopy.

Moreover specific experimental datasets should be obtained to develop parameterisations of:

- Non-stomatal leaf deposition of O_3
- Soil and snow deposition of O_3 and NO_2
- NO emissions from litter plant residues, green manure and litter.

The model would require land cover properties (vegetation and land use types).

Areas of Uncertainty

As already mentioned, an essential area of uncertainty lays in the processes themselves: what is the non-stomatal deposition process for O_3? Is there an NO_2 compensation point? Are O_3 chemical interactions in the canopy of first or secondary importance, and what are the main compounds involved (VOCs, R–OH, aerosols?).

In terms of parameterisation, O_3 and NO_2 soil deposition and how they change with soil type and wetness are key unknowns. Similarly, the in-canopy transfer resistance and diffusion time are key parameters which would require homogenisation. In particular several transport times may be considered which would represent transfer to and from the soil or vegetation.

The lack of good comprehensive datasets was also pointed out in the discussion and especially for European ecosystems.

It was considered that NO_x deposition models should be sufficient in non-tropical regions but full coupling with O_3 would be required in tropical forests as they exhibit a large decoupling between inside and outside the canopy.

Conclusions

The consensus arising from the discussion was that most of the model components, required for O_3–NO_x exchange modelling, are available and that the efforts should be concentrated on filling the gaps concerning three main areas:

1. To develop a shared, open access, easy-to-use model framework including a model for the exchange of the three compounds cited above, an energy balance model, an in-canopy chemical-transport model, and a canopy functioning model. This model is required both by modellers to develop specific parameterisation (soil, cuticle) and experimentalists to interpret their data.
2. To perform dedicated process studies to better understand them and derive extended parameterisation on (a) O_3 and NO_2 deposition to the soil and how this process depends on soil texture and moisture; (b) NO emissions from litter and organic amendments; (c) cuticular O_3 deposition and its response to leaf wetness; and (d) leaf O_3 detoxification.
3. To compile comprehensive datasets including flux and concentration-profile measurements of the triad O_3–NO–NO_2 over major ecosystems, especially in Europe, to validate the models.

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Bi-directional Exchange of Volatile Organic Compounds

R. Forkel, A. Guenther, K. Ashworth, C. Bedos, C. Delon, J. Lathiere, S. Noe, E. Potier, J. Rinne, O. Tchepel and L. Zhang

Introduction

Volatile organic compounds (VOC) are a relatively minor component of the atmosphere and yet are widely recognized to have important roles in air quality and climate. With the exception of methane, an important greenhouse gas, atmospheric VOC are primarily of interest because of their impact on other atmospheric constituents, including oxidants and aerosol. Most of the global annual VOC emission is from biogenic sources but biomass burning, fossil fuel combustion and industrial activities dominate in some regions. Each of these major sources can be further categorized, e.g., biogenic sources include plant chloroplasts, plant specialized tissues, microbes, and animals. The processes for removing VOC from the

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R. Forkel (✉)
Karlsruhe Institute of Technology (KIT)—Institute for Meteorology and Climate Research,
IMK-IFU, Kreuzeckbahnstraße 19, 82467 Garmisch-Partenkirchen, Germany
e-mail: renate.forkel@kit.edu

A. Guenther
National Center for Atmospheric Research, Boulder, CO 80301, USA

PresentA. Guenther
Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory,
Richland, WA 99352, USA

K. Ashworth
Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

C. Bedos · E. Potier
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

C. Delon
Laboratoire d'Aérologie, Université Paul-Sabatier (UPS) and CNRS,
UMR 5560 Toulouse, France

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atmosphere include VOC surface deposition, VOC deposition to particles, and surface deposition of their oxidation products including oxidized VOC, CO and CO_2. Regional to global atmospheric chemistry and transport models (CTMs) routinely include at least some VOC emission and removal processes but in a highly simplified form. Climate models have previously included just methane but as they evolve into more comprehensive earth system models, other VOC are being included although the sources and sinks may be prescribed or highly simplified.

A comprehensive characterization of atmospheric VOC is challenging due to the overwhelming number of compounds. Tens of thousands of VOC have been measured in the atmosphere and there may be hundreds of thousands more that have not been measured (Goldstein and Galbally 2007). Treatment of these compounds could be simplified however by categorizing them with respect to their surface-atmosphere exchange characteristics: reduced VOC (RVOC), atmospheric oxidation products (AOVOC) and bi-directional VOC (BDVOC).

Reduced VOC (RVOC)

Reduced VOC are produced at or near the earth surface and emitted into the atmosphere but are not produced in the atmosphere. RVOC include hydrocarbons such as alkanes (e.g., methane), alkenes (e.g., isoprene) and arenes (e.g., benzene). VOC containing sulfur or nitrogen could be included in this category. Oxygenated VOC that are emitted from vegetation, e.g., the hemiterpene, methyl-butenol, and the monoterpene, linalool, but are not produced in the atmosphere would be considered RVOC; but any oxygenated VOC that are produced in the atmosphere would not be included.

Soils and litter are sources of several VOC (furfural, butanoic acid, methanol, …) but these sources have not yet been well quantified (Insam and Seewald 2010; Leff and Fierer 2008). Similarly composts and slurry applications may be sources

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J. Lathiere
Laboratoire des Sciences du Climat et de l'Environnement, IPSL, UVSQ, CEA, CNRS,
Gif-sur-Yvette, France

S. Noe
Department of Plant Physiology, Institute of Agricultural and Environmental Sciences,
Estonian University of Life Sciences, Tartu, Estonia

J. Rinne
Department of Physics, University of Helsinki, Helsinki, Finland

O. Tchepel
CESAM and Department of Environment and Planning, University of Aveiro, 3810-193
Aveiro, Portugal

L. Zhang
Air Quality Research Division, Science and Technology Branch,
Environment Canada, Toronto, ON, Canada

of nitrogen containing VOC like trimethylamine (TMA) (Seewald et al. 2010; Twigg et al. 2011).

Since RVOC are not produced in the atmosphere, any RVOC deposition flux is due to molecules that were at one time emitted into the atmosphere and are now returning to the surface, although most likely to a different location. Methane and isoprene are the dominant VOC emissions and are both emitted into the atmosphere at rates of ~550 Tg per year (Guenther et al. 2006; Neef et al. 2010). These two RVOC are widely recognized as two of the most important VOC in the earth system and VOC surface exchange research has focused on these two compounds. This has primarily been investigations of emissions resulting in the development of relatively sophisticated models describing the processes controlling emissions of these two compounds. However, it has also been noted that surface sinks of these two compounds are not negligible and may account for about 5 % of the methane and isoprene emitted into the atmosphere (Cleveland and Yavitt 1997; Neef et al. 2010).

Atmospheric Oxidation (AOVOC) Products

The chemical degradation of RVOC in the atmosphere produces a large variety of oxidized VOC. For example, the oxidation of a single compound, the five carbon isoprene, produces a diverse array of AOVOC starting with four carbon first generation products, including methyl vinyl ketone (MVK) and methacrolein (MAC), that can react to form second generation products and so on until the carbon has been oxidized to CO_2. CTMs do not use explicit schemes to represent all of these AOVOC, due to the complexity and computational resources required, but most at least consider the first generation products MVK and MAC, which account for about 80 % of the carbon in the initial stage of isoprene oxidation. Some models represent them as specific species while others represent them as a lumped isoprene product. In either case, these molecules or their lumped sum are typically included in the dry deposition schemes of CTMs but this has been accomplished by assigning a dry deposition velocity that is based on measurements of other compound such as SO_2 and ozone. Karl et al. (2010) used above canopy flux measurements to demonstrate that the assumed canopy resistance for MVK and MAC used in CTMs is overestimated by about a factor of 5. They proposed that this high deposition rate was the result of active removal by leaves in order to eliminate these toxic compounds. The incorporation of a more accurate canopy resistance in a CTM results in substantial changes in simulated AOVOC deposition rates and atmospheric concentration distributions.

Jardine et al. (2010) observed emissions of oxidized VOC, including MVK and MAC, from vegetation enclosures and suggested that leaves could be a significant source of atmospheric MVK and MAC. The relative importance of foliar MVK and MAC emissions is not yet understood but the Karl et al. (2010) observations of higher than expected net deposition of MVK and MAC contradict the suggestion that vegetation is a major direct source of MVK and MAC. However, we should consider that these compounds could be emitted at substantial rates under certain conditions, such as high temperatures and other stresses. The potential importance of AOVOC emission, and thus bi-directional exchange, should be recognized and a better understanding of the rates and controlling processes is needed.

Bi-directional VOC (BDVOC)

The final category of VOC have substantial source and sink terms at both the earth surface and in the atmosphere. Emission and deposition processes are of similar importance for these BDVOC and so the accurate estimation of the net flux requires consideration of both. Kesselmeier (2001) identified four low molecular weight oxygenated VOC (acetaldehyde, formaldehyde, acetic acid, and formic acid) as compounds that are both emitted and taken up by plants in substantial quantities. These compounds can also be of anthropogenic origin and are produced in the atmosphere from the oxidation of RVOC. Kesselmeier (2001) recognized that the surface-atmosphere exchange of these compounds is bi-directional and their fluxes should be incorporated into models using an approach that includes a compensation point where emission occurs when ambient concentrations are below a certain level and deposition occurs with higher ambient concentrations. The compensation points reported by Kesselmeier (2001) indicate that plants are likely to be a source of these compounds in a clean remote environment and a sink in a polluted environment.

Of the four BDVOC identified by Kesselmeier (2001), acetaldehyde tended to have the highest leaf level emissions and this has also been observed for net ecosystem fluxes (Schade and Goldstein 2002). Acetaldehyde emission sources in terrestrial ecosystems include soil and leaf litter in addition to plant canopies (Warneke et al. 1999). Jardine et al. (2009) used a stable carbon isotope as a tracer for characterizing multiple pathways for producing acetaldehyde in plants and also report that emissions were elevated following both leaf anoxia and mechanical stress. These findings highlight the complexity associated with accurately simulating the processes controlling just the emissions component of acetaldehyde emissions. Above canopy acetaldehyde fluxes from three forests were compared by Jardine et al. (2008). Acetaldehyde was emitted from a forest canopy with an LAI of 3 but there was a net deposition observed for canopies with LAI of 4.6 and 5.3. Vertical profiles of acetaldehyde gradients within and above these canopies showed that acetaldehyde was emitted by the upper canopy and taken up by the lower canopy. This is in agreement with previous observations by Kesselmeier (2001) showing that acetaldehyde and other BDVOC can be emitted from sunlit leaves and taken up by shaded leaves.

The above canopy atmosphere is not the only location where RVOC can be oxidized. The canopy air space contains oxidants that can react with RVOC to produce oxidized VOC but it is a relatively small volume in comparison to the atmospheric boundary layer and so has previously been thought to be a relatively small source of oxidized VOC. DiGangi et al. (2011) recently measured a surprisingly large flux of formaldehyde from a forest canopy into the atmosphere. Branch and soil enclosure measurements indicated that these direct emission sources could only account for ~15 % of the observed ecosystem flux. They concluded that the remainder was due to the oxidation of biogenic VOC within the canopy airspace. The canopy they studied was an open woodland with a relatively short residence time which would minimize the production of formaldehyde. On the other hand, the open canopy has more light penetration which would stimulate photochemistry and VOC oxidation.

Methanol is the predominant oxidized VOC in the global atmosphere with an annual global emission rate that is thought to be the third largest of any VOC, after methane and isoprene (Guenther et al.). High rates of biogenic methanol emission were first reported by MacDonald and Fall (1993) who noted that emissions were especially high from young expanding leaves. Heikes et al. (2002) compiled methanol sources and sinks into a global budget and estimated that about a fourth of the emitted methanol is dry deposited to terrestrial surfaces and another fourth is dry deposited to the ocean. Millet et al. (2008) developed a global budget using additional observations and estimated that dry deposition is responsible for about half of the methanol sink but that the ocean sink is 2.5 times greater than for land. These analyses indicate that methanol uptake by terrestrial ecosystems is important and should be considered as a BDVOC in surface exchange models.

After methanol, acetone is thought to be the next most dominant oxygenated VOC in the atmosphere. An analysis of the global acetone budget by Jacob (Jacob 2002) concluded that surface deposition was responsible for only 12 % of the total acetone sinks. However, this deposition is ~20 % of the emission from a terrestrial ecosystem since nearly half of the acetone is produced by atmospheric oxidation of RVOC. This indicates the complexity of acetone sources and sinks and argues for classifying it as a BDVOC that should be represented in CTM with a unified emissions and deposition model.

As can be seen from the above consideration of the best-studied VOCs, even such an apparently simple categorization approach would present many challenges. The approaches currently used in numerical models are described in Section "Current Parameterizations in CTMs for Reduced VOC and Atmospheric Oxidation Products" and the major deficiencies associated with these approaches are described in Section "Gaps and Disadvantages of Current Parameterizations". A brief description of key features of an ideal model is given in Section "The Ideal Model" and the conclusions are presented in Section Conclusion.

Current Parameterizations in CTMs for Reduced VOC and Atmospheric Oxidation Products

Reduced VOC (e.g., isoprene, α-pinene) emissions are estimated with approaches based on simple mechanistic (semi empirical) approaches that include algorithms describing emission response to variations in environmental conditions (Guenther et al. 1993; Niinemets et al. 1999) and the calculation of landscape average emission factors. The models consider the major processes driving variations in emissions. For isoprene emissions, this includes a light response that is based on electron transport, a temperature response based on enzymatic activity, and a CO_2 response based on changes in metabolite pools, enzyme activity and gene expression. The emission activity factors can account for emission response to light, temperature, leaf age, soil moisture, leaf area index and CO_2 inhibition (Guenther et al. 2012).

The surface sinks of methane and isoprene, which may account for about 5 % of the amounts emitted into the atmosphere, is either neglected or incorporated into CTMs using an emission model and a deposition model that are independent of each other even though they have similar driving variables. The deposition models are driven by land cover and weather variables along with atmospheric concentrations (2012). Although a 5 % uptake is small compared to the uncertainties in the net fluxes of methane, isoprene and other RVOC, an accurate representation of the deposition of these compounds may be important, particularly on a regional or local level as the heterogeneity of source and sink processes can result in significant net transport of these compounds. Megonigal and Guenther (2008) note that the upland ecosystems, that are primarily sinks of methane, cover a far greater area than the wetland areas that are a source of methane. The potential shift of these upland landscapes between source and sink regions could significantly impact the global methane budget and should be considered in earth system models.

The fraction of isoprene and other reactive RVOC emitted by a forest canopy that is taken up before it can escape to the above canopy atmosphere is highly dependent on the oxidizing capacity of the canopy airspace and the canopy residence time. Surface exchange models currently do not simulate these processes although in some cases a net flux and a variable sink term is used to account for these losses (2006). An accurate representation of these processes is necessary especially for highly reactive RVOC, such as the sesquiterpene β-caryophyllene, that have a large and variable fraction of emission that is removed in the canopy before reaching the above canopy atmosphere. The presence of these highly reactive VOCs in the canopy is also essential to quantify as they may play a significant role in yet unexplained non-stomatal removal of O_3 (Wolfe et al. 2011).

As outlined above, CTMs do not use explicit schemes to represent all AOVOC, due to the complexity and computational resources required. Those molecules or their lumped sum that are represented are typically included in the dry deposition schemes of CTMs by assigning a dry deposition velocity that is based on measurements of other compound such as SO_2 and ozone. As outlined previously, Karl et al. (2010) showed that the incorporation of a more accurate canopy resistance in a CTM results in substantial changes in simulated AOVOC deposition rates and atmospheric concentration distributions.

The flux of atmospheric oxidation products is estimated with parameterizations that assume the flux is equal to the product of the ambient concentration and a deposition velocity. The deposition velocity is usually treated with an approach, developed by Weseley (1989), analogous to Ohm's Law where it is expressed as the product of three resistances in series: aerodynamic resistance above the surface, quasi-laminar resistance to transport through the thin layer of air in contact with surface elements, and resistance to uptake by surface elements.

While some simple approaches have been used to integrate emission and uptake into a unified model to account for BDVOC fluxes (Millet et al. 2010; Stavrakou et al. 2011) these fluxes are typically represented in CTMs as separate emission and deposition models and one or the other may be completely neglected. A uniform approach for modeling BDVOC exchange between terrestrial ecosystems and the atmosphere is needed.

Jardine et al. (2009) proposed a modeling approach based on ambient acetaldehyde concentration, a compensation point that is a function of light and temperature, and stomatal resistance to acetaldehyde but this technique was not implemented in a CTM. A simpler approach described by Millet et al. (2010) was used in a CTM to estimate global distributions of acetaldehyde as a function of LAI, light and temperature. The model simulated maximum acetaldehyde emissions for an LAI of 2 with decreasing emissions for lower or higher LAI. Stavrakou et al. (2011) proposed and implemented a simple CTM algorithm that included both emission and deposition of methanol. However, these algorithms are not used in most CTMs.

Currently, regional scale models do not include detailed in-canopy chemistry and turbulence. In-canopy loss reactions and product formation is usually not considered explicitly. Multilayer simulations indicate that the in-canopy oxidation of the major RVOC usually results in 5–10 % reduction in emission fluxes. In-canopy reactions within CTMs are either handled with the same approach used by the CTM for outside the canopy or parameterized (Guenther et al. 2006).

Gaps and Disadvantages of Current Parameterizations

Surface-atmosphere exchange behavior is typically not considered when categorizing VOC for surface exchange models and yet this could facilitate the development of effective VOC modeling approaches. This is especially important for compounds such as acetaldehyde which have strong bi-directional exchange. The current approach of having one model for emissions of acetaldehyde and a second model for deposition of acetaldehyde is not likely to be able to adequately represent fluxes of acetaldehyde and other compounds with bi-directional exchange. The use of a single model for both emission and deposition may be especially important for accurate representations of feedbacks.

Processes that will need an improved description within most regional models, or that are missing completely, are the effect of humidity and reactions on wet surfaces on deposition or the effect of toxic compounds on BVOC emission and stomatal aperture. However, most of these effects just need to be incorporated into the available deposition schemes rather than requiring a new scheme.

The land cover classification schemes (land use, plant functional type) used in regional and global models are generally inadequate for characterizing VOC fluxes. The schemes suitable for many other processes are not sufficient, especially for characterizing biogenic VOC emission capacities. For example, broad-leaf forests include both low and high isoprene emitting trees.

The Ideal Model

One-Dimensional (1-D) Approach

Ideally, VOC emissions and deposition could be described by simulating the concentration inside the stomata that drives a gradient (Niinemets and Reichstein, 2003), with the in-stomata concentration based on a physiological model of the BVOC formation process within the plant cells. Given a model for the production of these compounds, this model would ideally reproduce the bi-directional behavior observed for some oxidized VOCs and could be easily adapted to reproduce the fluxes of RVOCs and AOVOCs.

An additional consideration is the need to compute within canopy chemistry. The fraction of isoprene and other reactive RVOC emitted by a forest canopy that is taken up before it can escape to the above canopy atmosphere is highly dependent on the oxidizing capacity of the canopy airspace and the canopy residence time. A multi-layer model is needed but this may not require a large number of layers. Model evaluations with canopy vertical profile observations are needed to determine the number of layers required. So far, process based BVOC emission models of different complexity (Monson et al. 2012) within physiologically based plant models are only available for isoprenoid emissions. Despite the value of these models for investigating the processes involved in isoprenoid synthesis, their ability to account for different stress factors and to explicitly simulate the composition of emitted monoterpenes and sesquiterpenes, together with the large number of parameters required for this type of model limits their usefulness, particularly for regional models. In addition to a process based description of the formation of oxidized VOC, which is not yet available, a description of the non-stomatal uptake is necessary for a complete representation of deposition. Finally, it has to be taken into account, that process based descriptions are generally based on leaf or branch level and must be up-scaled to canopy level by a multi-layer model for use in CTMs and climate models.

Given the number and complexity of the processes involved in surface exchange, the development of the “ideal” model, that also includes in-canopy transport and chemistry, could only be considered for sensitivity studies to investigate which degree of detail will significantly improve model estimates of surface-atmosphere exchange of BVOC. For practical applications within CTMs a simple unified emission-deposition model with a variable compensation point for bi-directional VOCs seems to be more appropriate.

Regional/Global Scale Approach

Since observations (Karl and Guenther 2004; Karl et al. 2010) and modeling (Forkel and Knoche 2006) indicate that deposition is underestimated for oxygenated VOCs, improved parameterizations are required. Efforts should also be made to include improved descriptions of non-stomatal uptake (effect of humidity/water films) or feedbacks with gas phase toxic compounds such as MVK.

Up-scaling of sub-grid scale processes is a general key problem for three-dimensional CTMs. A minimum constraint, which is not always fulfilled in existing CTMs, is the application of consistent land use or land cover for meteorology, soil model, emission, and deposition. Deposition could be calculated for sub-grid tiles, similar to the way how emissions are calculated. If bi-directional VOC are to be described by a unified model, this seems necessary anyway.

It is common practice to account for the extinction of solar radiation within the canopy also in single layer BVOC emission models. However, for deposition, this is rarely the case. This issue might need further investigation.

Computed chemical loss rates of between 5 and 10 % within the canopy for the major emitted isoprenoids suggest that explicit in-canopy chemistry is not required in a CTM or climate model. Whether this is required for highly reactive VOC should be a subject of further investigations.

Highly desirable is an improved consideration of emissions resulting from land management. In parallel, a better representation of plant functional types is also urgently required.

Conclusion

The working group concluded that the VOC flux parameterizations used in current models are insufficient. The lack of an integrated approach for characterizing bi-directional exchange, for selected compounds such as acetaldehyde, is a key deficiency. In addition, the lack of parameterizations to account for within canopy transformations (production and loss) is likely to limit current model capabilities to characterize fluxes of at least some VOC. The “ideal” model would use the same framework for all categories of VOC seek to parameterize all of them as bi-directional with parameters set to zero where appropriate for RVOC and AOVOC.

A detailed description of emission, deposition, and in canopy chemistry and turbulence seems premature for every dawy CTMs applications but it should be the subject of specific process models. Such one-dimensional models should then be used to conduct a series of sensitivity studies to determine the conditions under which explicit representations of the individual processes involved in the surface exchange of VOCs are necessary in three-dimensional models and can direct the development of suitable parameterizations.

There was general agreement that the observational database is insufficient for making significant progress on improving model parameterizations of the bi-directional exchange of VOC. However, the development of a community model framework would be useful for driving efforts to improve observational data that could be used for a model test bed, thereby bridging the current gap between models and measurements.

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Aerosol and Acid Gases

D. Simpson, E. Nemitz, J. Burkhardt, D. Famulari, M. Kasik, B. Loubet, I. Rumsey, J. Walker, T. Weidinger and V. Wolff

Introduction

The background for this discussion was the background document in this book entitled: “Surface/atmosphere exchange of atmospheric acids and aerosols, including the effect and model treatment of chemical interactions”.

D. Simpson (✉)
Norwegian Meteorological Institute, Oslo, Norway

D. Simpson
Department Earth and Space Sciences, Chalmers University Technology, Gothenburg, Sweden

E. Nemitz · D. Famulari
Center for Ecology and Hydrology (CEH) Edinburgh, Penicuik, UK

J. Burkhardt
Institute of Crop Science and Resource Conservation, INRES-PE, Plant Nutrition Group, University of Bonn, Karlrobert-Kreiten-Str. 13, 53115 Bonn, Germany

M. Kasik
University of Tartu, Tartu, Estonia

B. Loubet
INRA, AgroParisTech, UMR 1091 EGC, 78850 Thiverval Grignon, France

I. Rumsey · J. Walker
National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA

T. Weidinger
Department of Meteorology, Eotvos Lorand University, Pazmany Peter s. 1/A, Budapest 1117, Hungary

V. Wolff
Air Pollution and Climate Group, Research Station Agroscope, Zurich, Switzerland

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This background document reviewed our understanding of the surface/atmosphere exchange of atmospheric acids and compounds found in the aerosol phase and with some reference to their treatment in current chemical transport models. These are the compounds where it is increasingly becoming evident that the gas-aerosol partitioning of some volatile compounds changes during the deposition process and that the deposition of some compounds cannot be considered without considering the behaviour of the chemically or physico-chemically interacting compounds. This is in particular true for the compounds that take part in the highly dynamic and fast NH_3-HNO_3-NH_4NO_3 equilibrium.

The aerosol and acid gases background document discusses many aspects of acid/aerosol interactions, and these will not be repeated here. This document is a short summary of the discussions which took place within the Working group. These discussions spanned many topics, including deposition processes in general, leaf-level processes (wetting, drying, chemical and morphological changes associated with these), measurement and model needs. Some important questions that came up were:

(i) Can we explain measurements of very high apparent deposition rates for some N-compounds? (For example, see Fig. 1)
(ii) Have observations been interpreted wrongly (not accounting for dissociation or other chemical transformations)?
(iii) Do we know the net exchange of pollutants (e.g. how much of the N associated with such high apparent deposition rates is really being deposited)?
(iv) What kind of modelling approaches are needed to tackle these problems, both at a fundamental level, and in large scale models?

Although nitrogen compounds formed the main topics of the discussion, the subject of aerosol formation issued from biogenic emissions of volatile organic compounds (BVOC, e.g. isoprene, monoterpenes, and sesquiterpenes) was also discussed.

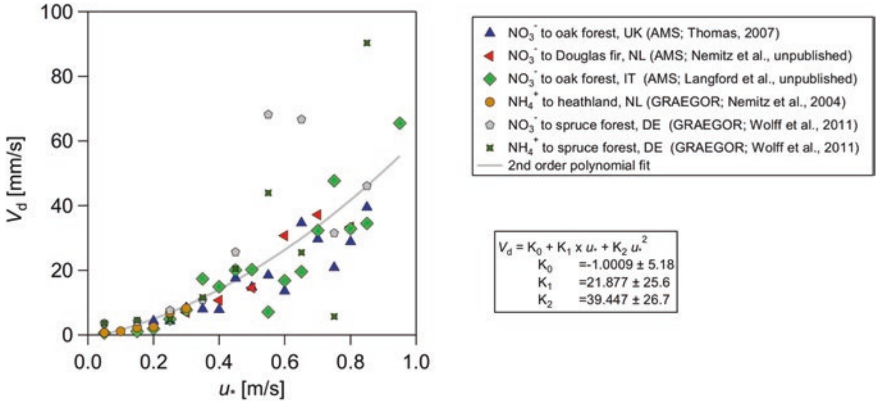

Fig. 1 Apparent nitrate and ammonium deposition velocities, enhanced by ammonium nitrate evaporation. Expanded from Fowler et al. (2009) by aerosol and acid gases background document

Throughout the discussions, a focus was on which kind of modelling tools could be used to interpret the measurements, and how could such understanding be implemented in the larger scale chemical transport models needed for policy formulation.

Products of the Discussion

The issue of chemically induced flux-divergence, which causes the type of high deposition rates shown in Fig. 1, was seen as central to the problem of quantifying fluxes of N-compounds to and from the biosphere. Simple measurement techniques such as gradient measurements have well known weaknesses in this regard, but even state-of-the-art micrometeorological techniques suffer from problems associated with flux divergence. A calculation of the fluxes of N (or other chemically reacting species) requires a calculation of chemical changes, as well as of transport, sink and source terms, inside and above vegetation canopies. Modelling is seen an essential requirement for establishing fluxes in such conditions.

The one-dimensional, multi-layer modelling approach (e.g. the suggested Eclaire Surface eXchange model) to integrating knowledge of surface/atmosphere exchange was seen by the working group as a useful approach. Such a model can incorporate in principle any desired level of detail concerning chemistry, source and sink terms.

A hierarchy of different levels of complexity was foreseen to investigate different aspects. At the most complex levels, such a model would include:

- Detailed chemical calculations in the air within and above the canopy. These calculations should be able to simulate the partitioning of e.g. NH_4NO_3 at different vertical levels, or to account for in-canopy losses of VOC, NO_x, and other gas and aerosol species.
- Simulations of aerosol dynamics. Examples are given in the aerosol and acid gases background document of the process whereby dissociation of ammonium-nitrate (NH_4NO_3) results in a change in the size-distribution of the aerosol population, producing apparent upwards fluxes in some size bins, which actually results from larger particles "shrinking" into that size bin.
- Detailed simulations of the chemistry occurring in wet films on the leaf surface, possibly using the type of wet-chemical modelling approach pioneered by Flechard et al. (1999).
- Accounting for the changes in leaf morphology and characteristics as a result of long-term exposure to aerosols, e.g. salts. J. Burkhardt showed the results of electron-scan analysis, clearly illustrating how leaf-surfaces change after repeated exposure to salts (Burkhardt 2010; Burkhardt et al. 2001).
- Explicit links between stomatal fluxes of trace gases and atmospheric conditions. In principle, a complete energy balance model should be used for each "tile" at the lower boundary condition as an external numerical weather prediction model.

Some caveats associated with such complex models are given below, but some level of complexity is seen as extremely valuable for many reasons, among these:

(i) Interpretation of field data, especially where changes are occurring as a result of several processes, notably chemistry, emissions, deposition, can only be done with such a model.
(ii) A state-of-the-science model acts as an idealised reference, against which simpler models may be tested and developed. With such a model, one can perform many tests to see which simplifications can be made without degrading model results too much.

For regional and global chemical transport models, it is of course desirable to include as much process understanding as possible, but such models cannot make direct use of the complex formulations discussed above. As well as obvious computational power issues, the data required to run detailed models is simply not available on regional and global scales. The aim should be to simulate the most important features of biosphere-atmosphere exchange, using as efficient a modelling scheme as possible. Among the decisions which need to be taken to approach this ideal, we need to decide

- Do we need any near-surface multi-layer modelling at all for CTMs?
- If so, what is the optimal number of layers in and above the canopy?
- How would such a model interact with the larger scale calculations?
- How should the ground-litter and soil interfaces be handled?
- How can we handle leaf-water processes?
- How sensitive are results to details of the canopy structure?
- What are the consequences in terms of computational needs of each choice?

Considering the latter, it is important to point out that typical CTMs use so-called "tile" approaches, in which several different land-cover categories are handled individually for deposition purposes. For example, the EMEP MSC-W model (Simpson et al. 2012) has 16 basic land-cover categories, plus three artificial ones. Typically, such a model would have say 5–10 categories within a given grid call. Allowing a 5-layer model over each tile would require 25–50 extra cells for which chemical calculations are needed, more than are used for the rest of the troposphere (the EMEP model has 20 layers).

Of course, one-dimensional approaches have other important limitations too, even with the most complex formulations. For example they require the assumption of horizontally homogenous canopies, they ignore here-dimensional turbulent structures (which can be important), and in general the prediction of turbulence inside and near vegetation canopies remains one of the hard problems. Such one-dimensional modes are typically not coupled to more regional scale meteorological models, so feedbacks between the vegetation properties (e.g. evapotranspiration, temperature controls) and the larger scale meteorology cannot be tackled. Further, such models will always be under-constrained by observational data.

Although these are serious problems, the group still believed that the sensible application of one-dimensional modelling systems was a better approach than the alternatives in use now, notably big-leaf zero-layer systems in current CTMs and GCMs, or the assumptions of zero chemical divergence in many interpretations of observed concentration profiles.

Areas of Uncertainty

As noted above, and discussed in more detail in the aerosol and acid gases background document and references therein, there are major uncertainty in understanding the observational data that has been collected over the years. This is partly due to the technical difficulties associated with the measurements themselves (fetch, stationarity assumptions, calibrations, filtering, etc.), and partly with the complex nature of vegetation canopies and the many factors that contribute to flux-divergence.

Some other gaps in understanding that we discussed include:

- Measurement of the full range of N-compounds. Measurements typically include only a fraction of the relevant N-compounds, for example sometimes aerosol nitrate is measured, but not NH_3 and HNO_3. Another example is that coarse nitrate compounds are hardly ever measured, leaving open questions about the contributions of species such as $NaNO_3$.
- Many measurement systems have artefacts that are difficult to resolve. Examples include difficulties with N_2O_5 and HNO_3 in MARGA instruments.
- Many processes occurring on the leaf surface are not well understood. As well as the complex chemistry and thermodynamics associated with leaf water films (e.g. how to calculate activity coefficients), issues were raised concerning possible transport of compounds through the water film into the stomata. Such issues are difficult to work with experimentally.
- The contribution of halogen compounds (e.g. HCl) to acidity is often unclear, but may be more important than previously considered.
- Turbulence in and around canopies is a well-known difficult problem. An issue which is often ignored but possibly important is that turbulence inside a canopy may well be very different to that above the canopy. For example, strong radiative cooling of the upper foliage can lead to strong mixing within the canopy. Intermittent turbulence (sweeps) is also an important feature of real canopies, but difficult to incorporate in one-dimensional models.

The issue of wind-tunnel measurements was discussed as one approach to the last problem. The use of large eddy simulation (LES) models or k-ε approaches is also possible in complex models, but combined LES and chemistry modelling is computationally a large challenge. Improvements in this area offer good potential for increased understanding in future.

Conclusions

The basic idea arising from the discussions can be stated: “Understand, then simplify”.

The “understand” phase consists in the application of detailed models alongside comprehensive measurements, in order to clarify the role of emissions, chemistry and deposition processes in controlling biosphere-atmosphere exchange. This phase should use observations to constrain models (and/or sub-models) as far as possible. The result of this understanding should be a reference model (or rather, a set of reference models, since many processes are included).

The simplify phase consists in devising methods to capture the results of the reference model(s), so that CTMs can incorporate good process understanding without excessive computational costs. Simplified methods may range from modifications of the current big-leaf type approaches, modified emissions terms (e.g. accounting for canopy-capture of NO_x, BVOC or secondary organic aerosols or SOA) or simple canopy models (e.g. with 2–5 layers) which allow an explicit accounting for the canopy.

Of course, the simplification phase cannot wait for complete understanding; efforts have to proceed along both lines in parallel. A hierarchy of models is clearly beneficial, bridging the scales between these two extremes, and allowing improvements to be made in particular aspects of the problem even without full understanding. The aim should always be to capture best present-day understanding.

In addition to these modelling approaches, we recognised the need to make better use of large-scale evaluations, using for example satellite data, to establish basic parameters such as leaf-area or biomass, as well as to investigate large-scale fields of for example NOx and NH_3. Satellite data have themselves large uncertainties though; evaluation against ground-level networks and aircraft data is still essential.

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Part III
Synthesis According to Model Component

Gaseous Stomatal Exchange and Relation to Ecosystem Functioning

E. Personne, L. Emberson, L. Balezentiene, J.-F. Castell, A. Kowlaski, A. Tuzet and V. Wolff

Introduction

The Stomatal pathway is a major pathway of exchange of trace gases between the atmosphere and ecosystems. Stomatal exchange is often described using the resistance analogue approach which relates the flux F_s (in mol m^{-2} s^{-1}) to the stomatal resistance (R_s, s m^{-1}) or conductance (g_s, m s^{-1}):

$$\mathrm{F_s} = \frac{\Delta C}{R_s} = \Delta C \times g_s \tag{1}$$

where ΔC (in mol m^{-3}) is the difference between the gaseous concentration inside the sub-stomatal cavity and the concentration immediately above the leaf surface. Equation (1) clearly shows that stomatal exchange is controlled by stomatal opening (which results from many plant and environmental drivers), expressed by the stomatal conductance g_s, and ΔC which is a function of the concentration in

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E. Personne (✉) · J.-F. Castell · A. Tuzet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

L. Emberson
Stockholm Environment Institute, University of York, York YO10 5DD, UK

L. Balezentiene
Institute of Ecology and Environment, Aleksandras Stulginskis University,
53361 Akademija, Kaunas, Lithuania

A. Kowlaski
Department of Applied Physics, University of Granada, 18071, Granada, Spain

V. Wolff
Air Pollution and Climate Group, Research Station Agroscope, Zurich, Switzerland

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the sub-stomatal cavity, called the compensation point C_p (Farquhar et al. 1980). Therefore, quantifying the stomatal exchange of pollutants requires the evaluation of these two terms: g_s, which can usually be derived from water vapour, and the compensation point, specific to each compound.

The stomatal pathway also includes a mesophyll component, leading from the sub-stomatal cavity to the cell. It is through this component that trace gases reach the photosynthetic sites, a key plant physiological process which can be affected by pollutants like ozone (Ashmore 2005).

Several studies have described the stomatal resistances to depend on environmental parameters and plant regulation factors. There are three major modelling methods currently used to determine the stomatal regulation:

1. the multiplicative models of the "Jarvis" type, which are based on species-specific response to key environmental variables (Jarvis 1976),
2. the coupled stomatal conductance and photosynthesis models based on carbon assimilation, also called the "Ball-Berry" approach (Farquhar 1978),
3. the leaf water potential, ABA and hydraulic models, based on more mechanistic approaches that account for both photosynthesis an the soil-plant-atmosphere water continuum (Dewar 2002; Tardieu and Davies 1993; Tuzet et al. 2003).

All these models are leaf scale approaches. At the field or global scales, approaches 1 and 2 are conventionally used (Bonan et al. 2003; Niyogi et al. 2009); although models are now being developed to integrate models of types 3 (Friend and Kiang 2005; Krinner et al. 2005). The transition from the leaf to the field scale is usually based on using the leaf area index (LAI) and its distribution, and associated corrections that account for the radiation attenuation within the canopy.

Key Processes to Account for in Stomatal Trace Gas Exchange Models

Key aspects of stomatal exchange to be considered in a modelling approach irrespective of the trace gas studied are:

Stomatal Exchange Is Essentially Proportional to Transpiration

It is assumed that the resistive approach described by Eq. (1) can be adapted for all gaseous compounds. Stomatal exchange rates should however be modified based on the ratio of the molecular diffusivity of the trace gas with respect to that of water vapour. For a more detailed approach that allows the interaction between the sub-stomatal cavity and cell functioning, the integration of a mesophyll pathway should be included. There is the possibility that the R_{mes} term may be common for all chemical species, although this will be affected by plant physiology. There may be the potential for compounds to directly impair cell functioning (e.g. acid degradation of cell wall complexes) which may cause the plant to loose stomatal control of gas exchange. For stomatal exchanges, during the time of transfer of the pollutant through the stomata, it seems to be reasonable to neglect chemical reactions.

Coupling Energy Balance and Pollutant Exchange Is Essential

The coupling of an energy balance model with pollutant exchange model is essential to get the right leaf and soil surface temperature and humidity which are essential in the thermodynamic equilibrium of pollutants with these surfaces. Moreover it allows validating the water vapour exchange scheme (via the energy balance) and thus give confidence in the predictive capacity of the resistive transfer model and have an estimate of the surface temperature of each canopy component (i.e. ground, air and leaves within the canopy). Unfortunately, the energy balance can only be applied under certain conditions (e.g. when evapotranspiration is high) and therefore there are limits to the time periods for which model validation can be performed.

Accounting for Vertical Variability Is Essential

Within canopy gradients are essential to account for in modelling stomatal exchange response. Those include radiation, wind speed, O_3 and CO_2 concentration, water vapour pressure, and temperatures. Such heterogeneity induces variable stomatal responses at each level of the canopy. A multilayer approach to assess stomatal exchanges is therefore necessary and will require a detailed description of the pollutant concentration gradients.

Some aspects of stomatal exchange are however specific to each compounds. Table 1 gives an overview of the characteristics of stomatal exchange of four different compound groups (NH_3, NO_x/O_3, VOC's and aerosols and acid gases).

Table 1 Description of the stomatal exchange characteristics for the four groups of trace gases considered

NH_3	Bi-directional flux of NH_3 due to $[NH_x]$ in the apoplast, modified by apoplastic pH, N deposition and phenology, currently modelled with of canopy compensation type of model
NO_x and O_3	NO_x has a bi-directional flux largely due to soil NO emissions, stomatal exchange of NO_2 and NO including R_{mes} has been reported, A mesophyll resistance R_{mes} for O_3 is generally not assumed, O_3 can directly damage guard cells at high concentrations causing 'leaky' stomates
Aerosols and acid gases	Aerosols could block stomatal pores; and affect stomatal conductance, acid gases may cause cell damage
VOCs	Production in leaf affected by ambient CO_2 concentrations, drought and intercellular carbon fluxes (between cytosol and chloroplasts) leading to efflux from stomates
	Bi-directional exchange reported but not well understood due to heterogeneity of VOC species

Framework of a Common Conceptual Model Adapted to Different Compounds: Stomatal Exchange

As stated earlier, the resistance framework should be able to accommodate within canopy 'stomatal heterogeneity' and 'pollutant concentration profiles'. Therefore a multilayer model is necessary (Fig. 1).

Within such a framework, stomatal exchanges could be modelled, either by a multiplicative approach or gs-photosynthesis approach. The advantages and shortcomings of each approach are examined in Table 2.

We suggest using a hybrid version (combination of gs-photosynthesis and multiplicative model) since it would have the advantage of: (1) linking plant growth through carbon cycling and allocation (which may allow investigation of multiple-stress interactions and ecosystem-atmosphere feedback modelling); (2) accounting for the influence of soil water content and plant phenology on stomatal exchange, the former according to an internally consistent multiplicative scheme, and (3) be coupled with an energy balance model to constrain soil water transfer within the soil-plant-atmosphere system and to provide leaf temperature and within canopy direct and diffuse radiation.

A drawback is that currently this approach is not yet 'consistently' parameterised or evaluated, but this could be overcome with time.

In addition to the above and to be able to reproduce stomatal exchange over growing seasons and leaf and plant life-spans and to simulate feedbacks between plant functioning and the micro-environment, the model should take into account plant development/phenology. This would be necessary for estimating: (1) start and end of growing season, (2) within growing season evolution of leaf area index (LAI) and phenology related parameters and (3) senescence. This would also allow identification of periods when plants are particularly sensitive to pollutants

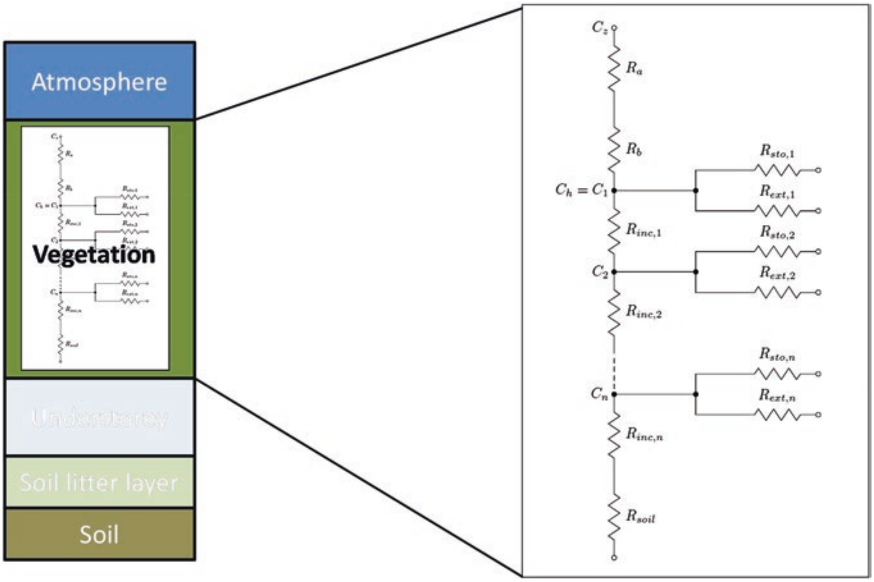

Fig. 1 Proposed framework for a conceptual model for water, CO_2 and pollutant exchange between terrestrial ecosystems and the atmosphere. The exchange between the air and the top of the canopy includes the aerodynamic (R_a) and boundary layer (R_b) resistances. The stomatal and cuticular exchanges are expressed in each layer ($R_{\mathrm{sto,i}}$ and $R_{\mathrm{ext,i}}$). In-canopy turbulent exchange is controlled by in-canopt resistances $R_{\mathrm{inc,i}}$. while soil exchange has a resistance R_{soil}. Each *open circle* represents a potential which is driven by other processes (ecosystem functioning)

or periods when conditions may be particularly favourable for emissions (e.g. VOCs). Such sensitivity also gives the possibility of having prediction tools that are more relevant for application in the context of climate change (since they can be modified to assess plant sensitivity changes that may depend on acceleration or reduction of the timing or length of certain stages of plant development).

Research Needs for Future Developments

Detailed and Consistent Experimental Databases

Model development and testing will benefit hugely from the availability of key ‘stomatal exchange’ related measurements. Ideally these would be collected according to a common protocol to ensure data representing a range of species/ ecosystems types and prevailing climatic conditions are comparable. The following measurements would be required, all collected with simultaneous, meteorological data, ideally at an hourly time step:

Table 2 Synthesis of the advantages and disadvantages for the “Jarvis” approach (named multiplicative approach) and “Ball-Berry” approach (named gs-photosynthesis) concerning the evaluation of stomatal conductance

	Advantages	Disadvantages
Multiplicative	Incorporates species-specific and phenology effects on gs	Unable to incorporate [CO_2] through plant physiology
	Incorporates key meteorological drivers (PAR, T, VPD and SWC)	Unable to incorporate [O_3] effects
	Embedded within EMEP model	No connection to plant growth and therefore feedback effects of pollutant deposition
	Parameterised for 10 deposition cover types (2 coniferous, 4 deciduous, 2 Mediterranean forest species; 6 crops; and 2 productive grasslands species)	
	Extensively evaluated across Europe	
gs-phtosynthesis	Incorporates key meteorological drivers (PAR, T, VPD or RH, [CO_2])	Needs modelled estimates of Photosynthesis adding another level of complexity
	Connections between plant growth and therefore could be used to develop feedback effects of pollutant deposition	Unable to incorporate effects of phenology on gs Unable to incorporate effects of soil water status (aside from using multiplicative type approaches) Unable to incorporate [O_3] effects Parameterised consistently for 5 plant functional types but no consistent parameterisation for other species Not extensively evaluated within deposition model schemes

PAR Photosynthetically active radiation; *T* Temperature; *VPD* Vapour pressure deficit; *SWC* Soil water content

- Leaf stomatal conductivity and photosynthesis (at different canopy positions and times within growing season)
- Canopy stomatal conductivity (estimated using the inverse Penman-Monteith algorithm)
- Canopy photosynthesis (or CO_2 flux)
- Soil water measurements at different soil depths across the rooting zone, taken at frequent intervals over the year
- Leaf/canopy temperatures
- Leaf area index evolution and start and end of physiologically active growth period.

These measurements would ideally be taken with observations of total trace gases deposition or trace gases exchange (for bi-directional pollutants).

Integrating Stomatal Exchange in Deposition Models

The 'multi-layer' stomatal exchange scheme set out in this document would ideally sit within a pollutant exchange model that incorporated all of the most important factors identified in other sections of this book.

The scheme in Fig. 1 provides a broad indication of what such a framework should look like and should include:

1. a connection to the atmosphere (e.g. mechanism to describe how pollutants transfer to or from a height within the atmosphere at which they are provided);
2. a multi-layer canopy model capable of estimating differential stomatal exchange according to gs and flux profiles that will vary within the growing season and may be affected by pollutant impacts;
3. an understorey to allow for within canopy chemical interactions that may be important in determining within canopy pollutant gradients;
4. a soil litter layer that may influence bio-geochemical cycling and therefore the environment within which the plant grows which in turn may affect plant physiology and stomatal exchange and;
5. a soil layer which will also influence the plants environment and physiology, particularly through key factors such as soil water and nutrient supply.

Conclusion

Stomatal conductance is widely studied. Measurements and models exist within different communities. Two key elements to be remembered in developing a stomatal pathway for the exchange of trace gases: (1) the approach should be simple enough with the fewest parameters so that it can be easily integrated in a chemistry and transport model and (2) it should include all the necessary environmental and plant physiological interactions to allow accounting for climate change, different plant species, etc. Ensuring that the measurements and observations described in point 1 above include pollutant exchange and ecosystem impact assessments will help to parameterise and evaluate the full framework model and can be used to estimate the sensitivity, and hence importance, of each model component under different climatic conditions and for different ecosystem types.

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Impact of Leaf Surface and In-canopy Air Chemistry on the Ecosystem/Atmosphere Exchange of Atmospheric Pollutants

J. Lathière, L. Zhang, M. Adon, K. Ashworth, J. Burkhardt, C. Flechard, R. Forkel, A. Guenther, J. Walker, E. Nemitz, E. Potier and I. Rumsey

Introduction

Chemical processes occurring on leaf surface and in air inside vegetation canopies play significant and sometimes dominant roles on pollutant dry deposition budgets. Yet, these processes are seldom explicitly treated in dry deposition parameterizations/models. This report briefly summarizes the current knowledge, outstanding issues, and recommendations for pollutant leaf surface exchange including

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J. Lathière (✉)
Laboratoire des Sciences du Climat et de l'Environnement, IPSL, UVSQ, CEA, CNRS, Gif-sur-Yvette, France
e-mail: Juliette.Lathiere@lsce.ipsl.fr

L. Zhang
Air Quality Research Division, Science and Technology Branch Environment Canada, Toronto, ON, Canada

M. Adon
Laboratoire d'Aérologie, UMR 5560, Université Paul-Sabatier (UPS) and CNRS, Toulouse, France

M. Adon
Laboratoire de Physique de l'Atmosphère, Université Félix Houphouët Boigny, Abidjan, Cote d'Ivoire

K. Ashworth
Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

J. Burkhardt
Institute of Crop Science and Resource Conservation, INRES-PE, Plant Nutrition Group, University of Bonn, Karlrobert-Kreiten-Str. 13, 53115 Bonn, Germany

C. Flechard
INRA, Agrocampus Ouest, UMR1069 Sol Agro-hydrosystème Spatialisation, 35042 Rennes, France

R.-S. Massad and B. Loubet (eds.), *Review and Integration of Biosphere-Atmosphere Modelling of Reactive Trace Gases and Volatile Aerosols*,
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ammonia (NH_3), ozone (O_3) and nitrogen oxides ($NO_x = NO + NO_2$), acidifying pollutants, volatile organic compounds (VOCs), and atmospheric aerosols.

Current Status and Knowledge Gaps

Ammonia

Ammonia is one of the most studied species in terms of dry deposition process. It is a fast depositing species; however, its exchange between the atmosphere and ecosystems is frequently bi-directional. Meteorological (wind speed, temperature, humidity, solar radiation, precipitation), biological (leaf area index, canopy growing stage, leaf wetness, apoplastic NH_4^+), soil (wetness, solution NH_4^+ content), and chemical conditions (ambient SO_2, HNO_3, acid/base ratio, interaction with aerosol phase) all affect its net exchange flux (Chap. 1 in this book). Big-leaf/multilayer dry deposition/bi-directional exchange models have been developed for monitoring networks and for chemical transport model (CTMs) applications. However, few if any of these models include leaf surface or in-canopy chemistry effects. Besides, there is a need to evaluate the few bi-directional models that have recently been developed for CTMs using site-specific flux data and using ambient NH_3 and NH_4^+ data at regional scale.

Some knowledge has been obtained regarding chemistry effects on NH_3 deposition, such as SO_2–NH_3 co-deposition, and the leaf wetness effect which involves aqueous-chemistry. Further knowledge may be obtained through theoretical and field studies. Ammonia-related chemistry mechanisms can be incorporated into a multi-layer vegetation model to quantify the chemistry effect on the surface flux

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R. Forkel
Karlsruhe Institute of Technology (KIT)—Institute for Meteorology and Climate Research, IMK-IFU, Kreuzeckbahnstraße 19, 82467 Garmisch-Partenkirchen, Germany

A. Guenther
National Center for Atmospheric Research, Boulder, CO 80301, USA

A. Guenther
Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA

J. Walker · I. Rumsey
National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA

E. Nemitz
Center for Ecology and Hydrology (CEH) Edinburgh, Penicuik, UK

E. Potier
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France

under various chemical conditions. This type of model can be used for comparing with measurements for research purposes, and, if properly evaluated, can later be used for developing parameterizations for CTMs application. One issue worth mentioning is that a better description of the mechanisms behind the non-stomatal uptake of NH_3 (same situation for any other gaseous pollutants) on leaf surfaces is needed. Is NH_3 temporarily stored in the leaf cuticle? Are chemical reactions on leaf waxes responsible for the non-stomatal uptake? Ammonia is known to dissolve into leaf surface wetness (dew, guttation, rain water) and its solubility and uptake rates are controlled by temperature, pH and the atmospheric acid/base ratio. Non-stomatal uptake is as important as or more important than stomatal uptake.

Ozone and NO_x

Ozone deposition has also been studied extensively and this species is also frequently used as a reference for other reactive but not very soluble species. Stomatal, non-stomatal, wetness effect have all been investigated in numerous studies background document on NO_x and O_3 in this book. The meteorological, biological, and chemical factors mentioned above also play important roles for O_3 deposition. The impact of leaf surface chemistry and in-canopy air chemistry on O_3 flux is likely generally small due to a very large O_3 pool compared with its atmospheric reactants (NO_x, VOC). For example, the NO_x–O_3 chemistry only modifies a small percentage of surface O_3 flux, and leaf wetness only slightly enhances non-stomatal O_3 uptake from its involvement in aqueous-phase chemistry. Dry deposition models with a variety of complexity exist for O_3, including the explicit coupling of gas-phase chemistry (e.g., NO_x–O_3).

The mechanisms controlling O_3 destruction at the leaf surface are not yet elucidated. It is suspected that aqueous-phase chemistry plays a role. O_3 deposition velocity frequently peaks in the early morning, instead of noon to early afternoon, over forest canopies. The phenomena cannot be simulated by existing stomatal models, but may be caused by leaf internal conditions (such as O_3, CO_2 concentrations inside stomata). Interactions of O_3 with deposited aerosols on leaf surfaces (e.g. sea salt, $(NH_4)_2SO_4$) may be involved in the O_3 destruction process, as shown by controlled leaf chamber experiments. The descriptions of O_3 deposition to snow, ice, water, and coastal areas (wave and chemistry) are over simplified in existing models.

NO and NO_2 have also been studied extensively. More emission than deposition cases has been observed for NO; and bi-directional fluxes have been observed frequently for NO_2. Chemistry has significant impacts on NO_x surface fluxes and can sometimes change the flux direction (e.g., from deposition to emission and vice versa). NO_2 is treated similar to, but lower than O_3 in most existing deposition schemes for the non-stomatal uptake.

As a first order approximation, NO can be omitted in the dry deposition budget. To compensate the bi-directional flux of NO_2 in its dry deposition budget, the mesophyll resistance for NO_2 can be increased or a stomatal compensation point can be introduced. A more sophisticated approach would be to adopt the equilibrium NO_x–O_3 chemistry in the air-surface flux scheme (in this case, it is cautioned that the same chemistry should not double-calculated for the surface layer in solving CTM mass continuity equation using time-splitting techniques). On the other hand, a (stand-alone version) surface flux model for research purposes can include many canopy layers, fully coupled chemistry, and other details.

Acidifying Gases

HNO_3 is very sticky on almost every surface, and thus has been widely considered to have a very high deposition velocity. However, the HNO_3 surface flux has also been shown to be reduced by chemistry such as evaporation of ammonium nitrate originally deposited or formed on leaf surfaces or from airborne aerosols. It is, however, difficult to distinguish the contributions from leaf chemistry and in-canopy air chemistry. Very few measurements are available for HONO deposition. It is treated similar to, but slightly lower than, HNO_3 in existing schemes. Upward fluxes have also been detected in recent studies and were likely caused by chemical processes and/or soil emissions, but the underlying mechanisms remain unclear.

SO_2 is frequently used as a reference for soluble species. Co-deposition of SO_2–NH_3 under wet conditions enhances SO_2 surface fluxes. The leaching of (base) cations from leaves are known to reduce leaf surface acidity and thus sustain the SO_2 deposition process. HCl is probably similar to HNO_3, but few CTM treat HCl dry deposition (likely because of its low concentrations and short lifetimes due to other processes).

Many factors affecting NH_3 deposition also apply to the species discussed here. If an approach for handling the chemistry effects on NH_3 deposition is developed, the same approach can be extended to acidifying species in a coupled fashion. Note that a simple approach of enhancing SO_2/NH_3 co-deposition is already included in some deposition models.

Volatile Organic Compounds (VOCs)

Knowledge of VOC dry deposition is very limited. Existing big-leaf schemes give conservative deposition values for some VOC (or grouped) species simulated in air quality models. Recent limited measurements show that some VOCs can have much higher deposition velocities over forests than predicted by existing (stomatal conductance based) models. About a dozen species can be measured using fast online techniques (PTR-MS).

A detailed review of available measurements should be conducted, and relevant physical and chemical properties for major VOC species need to be gathered. It appears that VOCs can be broadly classified into 3 categories (i) mostly depositing species; (ii) mostly emitted species; and (iii) frequently bi-directional species. The existing data can then be used as the basis for constructing model schemes/parameters. The VOCs should be treated in a relatively simple way in CTMs based on the current knowledge (e.g., a simple bi-directional scheme or a big-leaf model). It is possible to include soil emissions if more knowledge is available.

Aerosols

The size-dependence of particle dry deposition velocity is well understood. Several size-resolved deposition models are available and have been validated using bulk and/or segregated flux data. Chemistry modifies aerosol size distribution, thus the measured flux, which might be wrongly interpolated or used for evaluating models. A research-based (stand-alone) model needs to include detailed size distribution, chemical interactions between gases and aerosols, particle growth (or evaporation) under high (or low) RH (note that ammonia nitrate evaporation under high T should be a chemical process instead of a physical one).

Note that CTMs have two approaches for handing aerosols: size bin and modal approach. In CTMs, simple size-resolved or modal based deposition models seem to work well (size dependent, not species dependent). Chemical impacts can be implicitly included by modifying the aerosol's size distributions.

Possibility of a Common Framework

For research-based (stand-alone) version, a common framework for all major chemical species is needed. The model should include detailed canopy structure and chemical reactions including size-resolved aerosols. Different levels of complexity in chemistry may be needed for different group of species (e.g., VOC vs. acidifying species and NH_3).

For CTMs application, a common framework with the option of bi-directional exchange for certain species is the most practical approach. The impact of leaf chemistry and in-canopy chemistry should be parameterized, based on the improved understanding from the detailed 1-D model studies and from more measurement studies.

Existing approaches for modeling interactions between NH_3 air-surface exchange and surface chemistry within resistance-based flux models may provide a foundation for extension to other species. The influence of surface wetness and its chemistry have long been recognized as an important non-stomatal driver of leaf- and canopy-scale NH_3 fluxes. As a component of the cuticular flux, existing approaches for modeling the effects of surface chemistry depend on whether the cuticular exchange is assumed to be bi-directional or deposition only. As reviewed by Massad et al. (2010) parameterization of the cuticular resistance to NH_3 deposition is acknowledged to depend on the degree of surface wetness and the acidity of the surface liquid. Variations in the observed non-linear relationship between the cuticular resistance and degree of surface wetness, modeled as relative humidity, may be related to leaf or needle hygroscopicity, though distinct patterns within similar vegetation types are not obvious. While the physical process is not understood, variability in the influence of RH among ecosystem types is incorporated in the recommended cuticular resistance scheme.

The minimum cuticular resistance is modeled as a function of surface acidity (Nemitz et al. 2001), quantified as the molar ratio of atmospheric concentrations of inorganic acid gases (SO_2, HNO_3, HCl) to NH_3. The cuticular resistance scheme recommended by Massad et al. (2010) can be driven by (relatively) routine meteorological and atmospheric chemistry measurements and is sufficiently mechanistic and computationally manageable for use within CTMs.

Approaches for modeling the cuticular flux as a bi-directional process vary in complexity (Burkhardt et al. 2009; Flechard et al. 1999; Kruit et al. 2010; Sutton et al. 1998). Sutton et al. (1998) implemented a dynamic bi-directional scheme for cuticular exchange in which the uptake of NH_3 by the surface moisture layer is treated as a capacitance. NH_3 can be adsorbed or desorbed from the cuticle depending on the amount of moisture and its Henry's law equilibrium. This approach establishes a non-zero NH_3 concentration χ_d for the cuticle surface. The bi-directional cuticular NH_3 flux is a function of the difference between χ_d and the canopy compensation point χ_c, and cuticular resistance (R_d), which in this case represents the charging resistance of the capacitor. The model assumes a surface moisture pH for initialization. Because the concentration of NH_4^+ in solution is linked to the history of the cuticular NH_3 flux and therefore dynamic, computational requirements of the bi-directional cuticular exchange model are greater than for the deposition only scheme.

The concept of a dynamic cuticular NH_3 flux was extended by Flechard et al. (1999) to include explicit modeling of the H^+ and NH_4^+ concentrations of the surface moisture layer. In their framework, the non-zero equilibrium concentration χ_d of the surface liquid is linked to the bi-directional cuticular flux via χ_c and R_d, which is a function of the ionic strength of the liquid. Aqueous chemistry includes dissolved CO_2, SO_2, O_3, HNO_2, HNO_3, and HCl as well as their air-surface exchange and aqueous reactions including SO_2 oxidation by O_3. Transcuticular exchange of base cations, H^+ and NH_4^+ are also represented. The model is initialized using measurements of the chemistry of dew, guttation, and rainfall (pH, NH_4^+, K^+, Na^+, Ca_2^+, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}).

Burkhardt et al. (2009) implemented the dynamic chemistry model of Flechard et al. (1999) within the resistance-based two-layer (ground + foliage) compensation point model of Nemitz et al. (2001), with the addition of a non-zero equilibrium NH_3 concentration (χ_d) of the cuticular water film linked to a cuticular exchange resistance. Burkhardt et al. (2009) also modeled χ_d over the range of ionic strength rather than switching to a deposition only R_w scheme at ionic strength >0.3 M (Flechard et al. 1999).

The two-layer canopy compensation point model with dynamic cuticular chemistry described by Burkhardt et al. (2009) mechanistically represents the state of the science with respect to NH_3 air surface exchange modeling. This framework acknowledges the contribution of ground and foliage sources and sinks to the net canopy-scale flux and the existence of bi-directional exchange pathways for leaf (cuticle and stomata) and ground (soil and litter) components. With respect to modeling of surface chemistry, one of the primary challenges to further advancement of the work of Flechard et al. (1999) and Burkhardt et al. (2009) is a lack of observational data needed to better understand the chemistry of microscale cuticular water layers present on leaves and needles during the day. Current efforts rely on measurements of the bulk chemistry of relatively large droplets collected at night and early morning or after rain events. The period of canopy drying post-sunrise also appears to be an important period of transition for cuticular chemistry, though again there are no field data with which to characterize the chemical dynamics of the cuticular drying process.

The work of Burkhardt et al. (2012) highlights the usefulness of environmental scanning electron microscopy as a tool for examining the physico-chemical dynamics of wetting and drying leaf surfaces. Experiments examining the physical behavior of salt particles (NaCl, $NaClO_3$, $(NH_4)_2SO_4$) on leaf cuticles over repeated cycles of high and low humidity showed a general pattern of dispersal within a spatially extensive liquid layer at high humidity (deliquescence) and reorganization as a particle (efflorescence) at lower humidity. A similar examination of the behavior of NH_4NO_3 particles would be informative. Deposition of atmospheric NH_4NO_3 affects cuticular chemistry and, within the typical range of atmospheric temperature and RH, may remain as a particle or dissociate to NH_3 and HNO_3. The latter process therefore links the surface behavior of NH_4NO_3 to the in-canopy chemistry and fluxes of HNO_3 and NH_3 directly and through chemical reactions subsequent to deliquescence on the leaf cuticle.

While the task of further characterizing the chemical dynamics of cuticular water layers is daunting, the methods of Burkhardt et al. (2012) represent a path forward. Their recent results suggest that at lower relative humidities the behavior of atmospheric aerosols could perhaps be modeled based on thermodynamic equilibrium, as opposed to aqueous chemistry, which in the case of NH_4NO_3 and NH_4Cl links cuticle surface processes to in-canopy concentrations and fluxes of their gas-phase counterparts. Computationally this represents a simplification relative to the cuticular chemistry model of Flechard et al. (1999), which would still be used for high humidity conditions.

With respect to the development of a common framework for air-surface exchange of VOC, NH_3, acid gases, aerosols, NO_x, and O_3, perhaps the resistance model described by Burkhardt et al. (2012), in which the contributions of M.A. Sutton, C. Flechard, and E. Nemitz should be acknowledged, represents a foundation on which to build. Mechanistically, it is a more complete framework with respect to chemistry and physics than available field-scale models for VOC, NO_x, and O_3. An extension to multiple layers and more detailed incorporation of in-canopy chemistry for an initial field-scale version of such a model represent great challenges. However, this approach represents a possible step forward.

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Soil and Litter Exchange of Reactive Trace Gases

R.-S. Massad, M.A. Sutton, J.O. Bash, C. Bedos, A. Carrara, P. Cellier, C. Delon, D. Famulari, S. Genermont, L. Horvath and L. Merbold

Introduction

The soil and litter play an important role in the exchange of trace gases between terrestrial ecosystems and the atmosphere.

- The exchange of ammonia between vegetation and the atmosphere is highly influenced by soil and litter emissions especially in managed ecosystems (grasslands and croplands) mainly due to the input of mineral and organic forms

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R.-S. Massad (✉) · C. Bedos · P. Cellier · S. Genermont
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France
e-mail: Raia.Massad@grignon.inra.fr

M.A. Sutton · D. Famulari
Center for Ecology and Hydrology (CEH), Edinburgh, Penicuik, UK

J.O. Bash
National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA

A. Carrara
Fundación CEAM, c/Charles R. Darwin 14, Parque Tecnológico, 46980 Paterna, Valencia, Spain

C. Delon
Laboratoire d'Aérologie, Université de Toulouse, Toulouse, France

L. Horvath
MTA-SZIE Plant Ecology Research Group, Szent István University, Páter K. u. 1, Gödöllő 2103, Hungary

L. Horvath
Hungarian Meteorological Service, Gilice 39, Budapest 1181, Hungary

L. Merbold
ETH Zurich, Institute of Agricultural Sciences, 8092 Zurich, Switzerland

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of N, which leads to increases in available N at the soil surface. Apart from fertiliser-induced NH_3 volatilisation, significant emissions may also occur from barren soil and senescent plants and leaf litter (Massad et al. 2010; Sutton et al. 2009). Ammonia emissions from the leaf litter, even if understood in principle, remain very uncertain due to the limited number of studies.

- Soils and litter are sources of several VOCs (furfural, butanoic acid, methanol, etc.), but these sources have not yet been well quantified (Insam and Seewald 2010; Leff and Fierer 2008). Similarly composts and slurry applications may be sources of nitrogen containing VOCs. Recent research on VOC emissions from soil and decomposing litter suggest that microbes may be important sources of VOCs and that such emissions are highly variable across litter types and soils (Gray et al. 2010).
- Soil emission of NO occurs as a by-product of soil nitrification and denitrification processes. The latter are a function of temperature, moisture, and substrate availability (available N, dissolved O_2, and soil moisture). For natural ecosystems, the substrate availability is mainly a function of productivity (input via plant residues) and wet and dry deposition, while for managed ecosystems it depends mainly on fertiliser input (Bouwman et al. 2002; Ganzeveld et al. 2010).
- Concerning NO_2 and O_3, uptake/deposition is considered the main pathway of exchange with the soil. This deposition of O_3 and NO_2 at the soil surface is often masked in the measurements by the activity and the transfer resistance of the vegetation cover and therefore not very well quantified (Gut 2002; Pilegaard 2001).

Products of the Discussion

The discussions in the working group were structured around two main parts. During the first part we discussed the state of the art and already existing models treating soil and/or litter exchange of trace gases. The main focus was around ammonia and some models dealing with CO_2, CH_4 and N_2O. Other trace gases such as NO, NO_x, O_3 and VOCs were addressed very briefly. The second part consisted of elaborating a theoretical scheme for an ideal soil/litter exchange model and establishing a priority list of what are the characteristics of a model that could be immediately feasible (the silver model) and a model that would be ideal but more of a long-term outcome (the golden model).

Existing Modeling Schemes

A lot of recent efforts have gone into developing soil models for greenhouse gas emissions mainly accounting for mineralization, nitrification and denitrification processes (DNDC, CERES-NCSOIL, ACASA, etc.). Those models particularly account for incorporated residues or bare soils. Few mechanistic models exist that account for emissions from soil and litter of reactive trace gases.

- **Volt'air** (Génermont and Cellier 1997) is a mechanistic model that simulates the NH_3 and pesticide volatilization from field applied slurry or pesticides. It accounts for controls by soil, meteorology and slurry/pesticide characteristics on volatilization; it simulates the transfers and equilibria in the topsoil and between the soil and the atmosphere. The model includes an energy balance and advection sub-models, which makes it suitable for field scale applications using simple meteorological data. Sensitivity analysis showed that soil pH has a large influence on volatilization. The model is also sensitive to soil adsorption capacity and some hydraulic characteristics (saturation water conductivity, water content at field capacity) (Garcia et al. 2011). Volt'air has also been extended to simulate emissions by mineral fertilizers.
- **Guano** model (Blackall et al. 2007; Riddick et al. 2012) simulates NH_3 emissions from seabird excreta (guano) on the ground of land-based colonies. The model describes four steps in the processes of NH_3 emission: (i) Excretion of nitrogen rich guano, in the form of uric acid; (ii) conversion of uric acid to total ammoniacal nitrogen (TAN), with a climate- and surface pH-dependent rate; (iii) TAN partition between NH_4^+ and NH_3 on the surface; and (iv) NH_3 volatilization to the atmosphere, controlled by meteorological conditions. Emissions from seabird colonies present similarities to emissions from field excreted dung and their study and modelling proves relevant in this context.
- **EPIC** is a semi-empirical biogeochemical process model developed by the United States Department of Agriculture (USDA) in the early 1980s to assess the effect of wind and water erosion on crop productivity (Williams et al. 1984) and expanded to include soil N and C biogeochemistry (Izaurralde et al. 2006). This model was developed for managed agricultural simulations and includes parameterizations of the crop growth, fertilization management, soil hydrology, N and C biogeochemistry (mineralization, nitrification, and denitrification), and energy balance. Nitrogen losses are modelled for vegetation uptake, NO_3 infiltration and runoff and NH_3 volatilization. Field scale simulations can be made using observed meteorology or regional scale simulations can be made using the output of a regional meteorological model.
- Modeling NO emission from soils with Artificial Neural Network (**ANN**) algorithm. An emission algorithm has been developed for the calculation of NO biogenic emissions (Delon et al. 2007). NO fluxes depend on soil moisture, soil temperature at two depths, wind speed, pH, sand percentage and fertilization rate.
- Several other models were cited that do not explicitly deal with trace gas emissions but that could be useful in terms of modeling the energy and water balance of the top soil layers or of litter and mulch disposed at the surface of the soil. Among those models: (i) **PASTIS** a model that has a top layer of residues and that simulated mineralization and nitrification (Garnier et al. 2003). (ii) an energy balance model for surface mulch (Bussière and Cellier 1994).

Theoretical Ideal Model

A theoretical ideal model scheme was developed, Fig. 1. The scheme depicts the 4 different states of litter decomposition that should be accounted for, their residence time and the different gases exchanged at each state.

- State 1 is the few hours/days following the litter (leaves) detachment from the plant. This state is characterized by the litter being clearly distinguished from the soil. At this stage, NH_3 and probably CO_2 are the main gases being exchanged.
- State 2 lasts a few days to weeks it is characterized by the litter starting to decompose, the leaves are mixed with fungus material but are still clearly distinguished from the soil. At this stage, NO, NH_3, CO_2 and probably VOCs are exchanged.
- State 3 is the litter that has fallen the past year and thus lasts from one to several months. The litter can barely be distinguished from the soil but it is still lying on top of the soil. At this stage, the primarily exchanged gases are NO, N_2O, N_2, CH_4 and CO_2.
- State 4 is the ultimate decomposition state of the litter. At this point it is almost incorporated with the soil and can last decades depending on soil and environmental conditions. At this stage main exchanged gases are N_2O, N_2, CH_4 and $CO_{2.}$

The main requirements for the ideal model were discussed and two options were set as described in Table 1 (gold medal and silver medal options). Whatever the case the model should however be able to generate a pool of $N_2O/NO/NH_3$ that is then transported (by diffusion and advection) into the system, it should have a

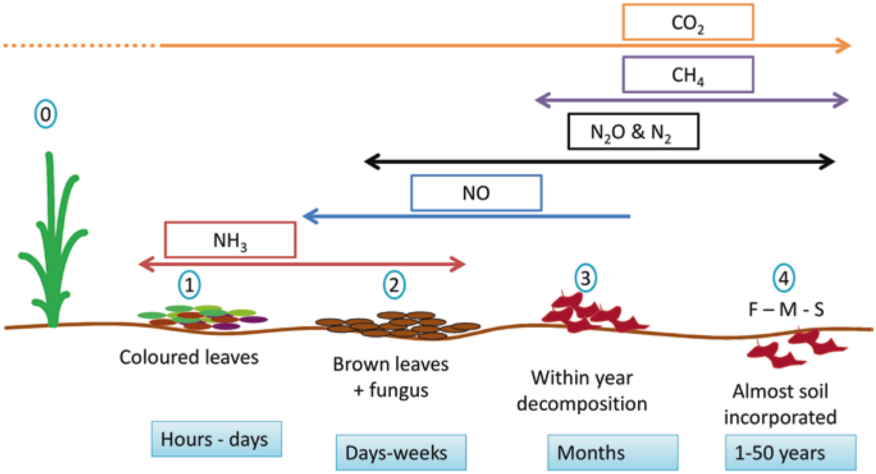

Fig. 1 An ideal soil/litter model scheme for simulating exchange of trace gases with the atmosphere

Table 1 Different variables that should be accounted for in the soil/litter ideal model, together with their purpose and their origin, whether the gold medal or silver medal option is chosen

Variables	Purpose	Gold model	Silver model
Substrate/litter moisture	Process description	Water balance model	External input
Soil moisture	Boundary conditions	Water balance model	External input
Substrate/Soil Temperature	Boundary conditions	Energy balance model	External input
Fertilisation	N condition of soil	Input/parameterisation	Input
Incorporation—discontinuity		Spatial model (horizontal transfer)	1 D spatialized model
Organic inputs (leaves—dung—external OM)		Input at stages 2 or 3	
Soil texture and porosity	Water and energy balance, infiltration	External input	External input
Substrate/soil pH	Thermodynamics, processes (biological, chemical)	Empirical parameterisation	Lookup table
Plant species and litter quality	C & N content and form	Ecosystem/soil model	Lookup tables and/or satellite data
Litter porosity/structure	Litter diffusive resistance	depends on species, management	Lookup table
Litter mass and thickness	Mass balance	Ecosystem model 1 litter layer and multiple soil layers	1 litter and soil layer

OM Organic matter; *C* Carbon and *N* Nitrogen.

litter water and energy balance as well as a litter degradation module and it could be part of a soil model. One major challenge resides in setting the boundary between the different phases of litter decomposition especially between phases 3 and 4.

The major variables that should be accounted for but at different levels of complexity according to the model option chosen (see Table 1) are: substrate moisture to allow reactions as well as determine states of aerobiosis/anaerobiosis, substrate temperature, agricultural practices (fertilization, incorporation, etc.), soil texture, substrate pH, plant species and therefore litter quality and litter structure and porosity.

Areas of Uncertainty

Processes and mechanisms concerning soil/litter NH_3 exchange are well identified and documented. However, a lot of uncertainty remains around the exchange of other trace gases mainly NO_2, NO, O_3 and VOCs all along litter decomposition. One of the major challenges concerns the modelling of organic matter decomposition including N transformation in the litter and to measure the exchange of trace gases between the soil/litter and the atmosphere and their differentiation between exchanges at the whole canopy. Concerning ozone for example the question remains open around what part is deposited to the litter and what part interacts with chemistry. Furthermore, does O_3 impact the litter quality and quantity (C/N ratio in fallen leaves)? Concerning VOCs, we estimate that 10 % of canopy emissions originate from soil/litter. There is a lack of observations to constrain this assumption and it is likely to vary with VOC species. For some compounds this may not be important to emissions or deposition, because uptake occurs before the VOC escapes the canopy. Still a slight shift in the uptake may lead to high emissions and elevated concentrations in the canopy, and because of this cycling, may impact the in-canopy chemistry. Measurements, most likely using cuvettes, are needed to constrain and determine the importance of these processes on net emissions and in-canopy chemistry. Additional uncertainties exist in VOC emissions from wounded plants as well as litter fungus, e.g. methanol.

One major challenge concerning soil/litter trace gases exchange for all compounds is to determine substrate pH. Accurately simulating substrate pH is still problematic while this impacts all major processes involving exchanges of NH_3, other trace gases, microbial decomposition and fermentation processes.

Conclusions

The major conclusion from this working session was that the knowledge we actually have around soil/litter exchange of trace gases is sufficient to build a mechanistic model whose purpose would be simulating exchanges with the atmosphere. The degree of complexity of the model could be determined around each case and/or gas studied. The model could be directly coupled to a soil model and/or be part of a canopy/plant model. Several initiatives are envisaged within the different groups that go in this sense. A simplified version of the Guano model applied to cattle dung is being developed. A litter layer is also being introduced in the Volt'air model to account for pesticide and NH_3 exchange. EPIC is being developed to explicitly model soil NO and N_2O emissions in addition to NH_3 emissions and is being coupled to a regional air-quality model.

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In-Canopy Turbulence—State of the Art and Potential Improvements

**M. Theobald, B. Loubet, C. Ammann, L. Branislava, B. Chojnicki,
L. Ganzeveld, B. Grosz, M. Kaasik, S. Noe, J. Olejnik, J. Rinne,
M. Shapkalijevski, D. Simpson, O. Tchepel, J.-P. Tuovinen,
T. Weidinger and R. Wichink Kruit**

Introduction

The turbulence within and immediately above a vegetation canopy is the driver of the exchange processes of heat, trace gases and particles between the soil, the plants and the atmosphere above. As a dynamical source and sink of momentum, heat, water vapor and gases (Tóta et al. 2009), plant canopies (especially forests) play a crucial role in land-atmosphere-interactions. However the turbulence in a

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M. Theobald (✉)
Higher Technical School of Agricultural Engineering, Technical University of Madrid
(UPM), 28040 Madrid, Spain
e-mail: mark.theobald@ciemat.es

B. Loubet
INRA, AgroParisTech, UMR 1402 ECOSYS, F-78850 Thiverval-Grignon, France

C. Ammann
Air Pollution and Climate Group, Research Station Agroscope, Zurich, Switzerland

L. Branislava
Faculty of Agriculture, University of Novi Sad, D. Obradovica Sq 8, 21000 Novi Sad, Serbia

B. Chojnicki · J. Olejnik
Meterology Department, Poznan University of Life Sciences, Piątkowska 94, 60-649 Poznan,
Poland

L. Ganzeveld · M. Shapkalijevski
Max Planck Institute for Chemistry, Mainz, Germany

B. Grosz · T. Weidinger
Department of Meteorology, Eotvos Lorand University, Pazmany Peter s. 1/a, Budapest
1117, Hungary

M. Kaasik
University of Tartu, Tartu, Estonia

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canopy is intermittent, especially at night (Acevedo and Fitzjarrald 2001, 2003). During the day, heating at the canopy top can produce thermal transport, limiting the validity of classical "K-theory" or gradient-flux theory in many situations (Acevedo and Fitzjarrald 2003; Denmead and Bradley 1985; Fitzjarrald and Moore 1995; Lalic and Mihailovic 2008; Lalic et al. 2003a).

In addition, large-scale turbulent structures transport the mass and energy "fractionally" during short periods (sweeps) while the average concentration gradient is determined by longer quieter periods (ejection) (Kaimal and Finnigan 1994). The apparent diffusivity is also influenced by the distribution of sources and sinks within the canopy (Raupach 1988), its architecture, thermal characteristics and the significant drag of foliage (Fitzjarrald and Moore 1995; Lalic and Mihailovic 2004; Lalic et al. 2010; Staebler and Fitzjarrald 2004).

Moreover, under closed canopies, temperature gradients, which result from the energy balance of the canopy and soil, can lead to stable or unstable stratification, which in turn affects the turbulence (Acevedo et al. 2007, 2008; Staebler and Fitzjarrald 2004, 2005). This phenomenon is well known and parameterised in the atmospheric boundary layer (Ryall et al. 1998) but generally not included in surface exchange models.

However, although the turbulence in the canopy is complex and often non-diffusive, K-theory, which includes resistance analogue approaches, is often applied with some success. The use of K-theory also has the advantage of being computationally quick, which is important when considering surface models for use in chemical transport models (CTMs). The objective of this working group was to discuss the development of a conceptual in-canopy turbulence model that can be integrated into a CTM.

S. Noe
Department of Plant Physiology, Institute of Agricultural and Environmental Sciences,
Estonian University of Life Sciences, Tartu, Estonia

J. Olejnik
Department of Matter and Energy Fluxes, Global Change Research Center, AS CR, v.v.i.
Belidla 986/4a, 603 00 Brno, Czech Republic

J. Rinne
Department of Physics, University of Helsinki, Helsinki, Finland

D. Simpson
Norwegian Meteorological Institute, Oslo, Norway

D. Simpson
Department Earth and Space Sciences, Chalmers University Technology, Gothenburg,
Sweden

O. Tchepel
CESAM and Department of Environment and Planning, University of Aveiro, 3810-193
Aveiro, Portugal

J.-P. Tuovinen
Finnish Meteorological Institute, 503, FI 00101 Helsinki, Finland

R. Wichink Kruit
TNO, Climate, Air and Sustainability, P.O. Box 80015, 3508 TA Utrecht, The Netherlands

Current Parameterisations of in-Canopy Turbulence

Meterological Models and Chemical Transport Models (CTM)

In current meteorological models and CTMs, the canopy turbulence is modelled as a two layer resistance analogue model with one layer of transpirable vegetation and the soil surface. Many models include above and within canopy aerodynamic resistances, leaf and soil boundary resistances and sometimes dry soil resistances. The main assumption is that above the canopy (i.e. above the roughness length z_0) the Monin-Obukhov similarity theory holds, while in the canopy an exponential (Raupach et al. 1996) or hyperbolic (Lalic and Mihailovic 2008; Lalic et al. 2003b, 2010; Thom 1971) decrease of the wind speed with height is assumed (Raupach et al. 1996). The soil boundary layer resistance is calculated as above a flat surface with a given roughness and the ground friction velocity is estimated from momentum profile assumptions (Personne et al. 2009). The models differ in their parameterisation of the resistances and their locations in the vertical profile, but none of them take instability and intermittency into account. In general, CTMs such as CMAQ (Byun and Schere 2006) or the EMEP MSC-W model (Simpson et al. 2012) do not currently include in-canopy parameterisations although potential schemes have been developed (Wu et al. 2003).

Meso-scale meteorological models such as MM5 and WRF provide only a very basic description of vegetation canopies in order to calculate heat and moisture fluxes between the soil surface and the atmosphere. This is done through land-cover-dependent values of roughness length etc. and calculations of exchange coefficients of heat and moisture (Grell et al. 1994; Skamarock et al. 2005). However, in-canopy parameterisations have been developed for these models in order to simulate in-canopy processes. For example, Dupont (Dupont et al. 2004) incorporated a 'drag-force' approach in the MM5 model in order to simulate vertical profiles of turbulent kinetic energy, potential air temperature and eddy diffusivity for both urban and rural canopies.

More Advanced Parameterisations

More complex approaches of in-canopy turbulent transfer are also found in the literature. They can be categorised into Eulerian and Lagrangian approaches. Lagrangian models include those based on the near field theory of Raupach (1988) (Ogée et al. 2004), or random walk or Lagrangian stochastic models (Loubet et al. 2006). All these models rely on a parameterisation of the standard deviation of the vertical wind speed (σ_w) and of the dissipation of turbulent kinetic energy (ε) in the canopy (Loubet et al. 2006). Sometimes the Lagrangian time scale is parameterised in place of ε. Although Lagrangian models can reproduce non-diffusive fluxes, Wilson (Wilson et al. 2004) have shown that Lagrangian near-field theory has a similar performance to K-theory in describing heat and trace gas fluxes in a corn and a potato canopy. Additionally, Lagrangian Stochastic models are computationally demanding.

Eulerian approaches can be of first order (K-theory) (Walton et al. 1997) of higher order (Foudhil et al. 2005), or of the type 'Large Eddy Simulation' (LES) (Edburg et al. 2012; Hanna et al. 2002). K-theory is simple but lacks the representation of non-diffusive fluxes. Higher order models can overcome these limitations but at a cost of computational time. LES models have started to be used in canopies, but are still not strongly coupled with energy balance models and are even more computationally demanding.

Disadvantages of Current Parameterisations

The simple treatment of in-canopy turbulence may be sufficient to describe the general interactions between the canopy and the atmosphere above it for most atmospheric conditions. However, for processes that are very sensitive to concentrations and residence times within the canopy (e.g. fast chemical reactions between compounds or internal re-deposition of emitted compounds), the turbulent exchange between different canopy layers can have a large influence on the net canopy exchange and should be described in a more detailed and adequate way.

For example, under certain conditions, the in-canopy stability can be very different to the stability above the canopy, especially for closed canopies (e.g. stable during the day and unstable at night in the canopy, while it can be the opposite above the canopy) (Jacobs et al. 1996; Kruijt et al. 2000). Current parameterisations that derive the within-canopy turbulence from the above-canopy turbulence do not reproduce these phenomena and, therefore, may inaccurately estimate mass exchange rates, as well as the in-canopy transfers of heat, momentum and water vapor transfer (Dupont and Patton 2012; Lee et al. 2012; Patton et al. 1998). Transients such as gravity waves within the canopy (Fitzjarrald and Moore 1995; van Gorsel et al. 2011) are still poorly understood. The importance of in-canopy stability is demonstrated in Fig. 1, which shows the influence of the inclusion of in-canopy stability on ozone concentrations in the canopy crown layer.

Another experimentally observed phenomenon is nocturnal emission fluxes from the canopy during periods of stable conditions above the canopy. Current parameterisations cannot simulate this process since they assume zero or very low air flows within the canopy during these apparently stable periods, even though the quantity transported may be important (Ganzeveld et al. 2002a).

Ways to Improve Parameterisations of in-Canopy Turbulence

It is essential that the importance of the aforementioned (and other) in-canopy turbulence-related processes is assessed with respect to their contribution to the net exchange in order to conclude whether they should be incorporated into CTMs and other modelling systems. One initial step would be to compile the existing

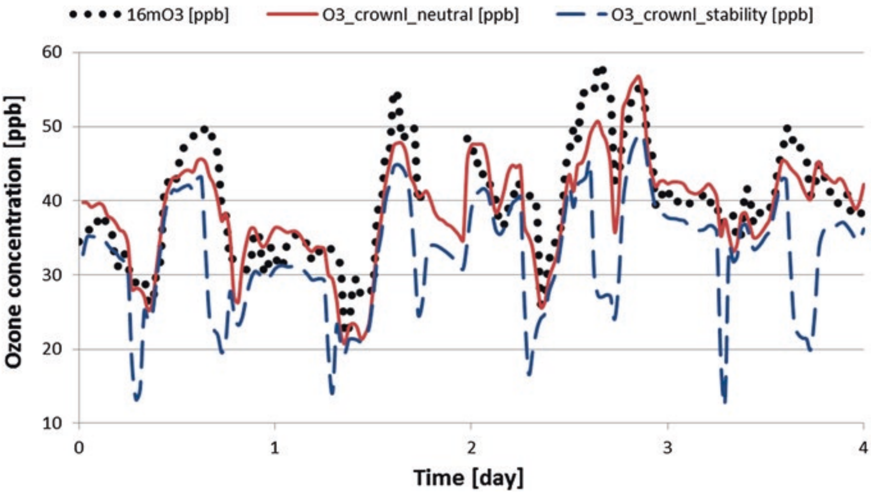

Fig. 1 Role of the atmospheric stability on ozone concentrations in the canopy crown layer using the observations from the EGER campaign (*black dots*) and simulations with MLC-CHEM (*red solid line* $\mathrm{Ri} = 0$: neutral-only regime, *green dashed line* stability corrections applied for stable and unstable regimes). The simulation with neutral-only conditions fits the observed data quite well whereas the simulation using the stability corrections underestimates the observed data (Shapkalijevski, unpublished data)

experimental evidence for these processes, e.g. in the form of a review paper. The following step would be to try to recreate these processes with an in-canopy turbulence model that includes a detailed parameterisation of canopy architecture using, for example, empirical relations for leaf area density (LAD) profiles (Lalic and Mihailovic 2004). This could be done using large eddy simulation (LES). At this stage it wouldn't be necessary to include in-canopy chemistry, which would be complicated to implement. LES models are usually used for steady-state conditions although they are now also applicable to dynamic situations. These simulations should include, at least:

- Relationships between canopy structure and turbulence;
- The coupling/decoupling of in-canopy and above canopy stability;
- Full in-canopy energy balance.

If certain processes are demonstrated to be significant for net exchange, the LES models could be used to derive simple relationships that could be included in other, simpler, in-canopy models.

Another way to assess the importance of these in-canopy processes is through the experimental estimation of in-canopy residence times, e.g. by Radon tracer experiments (Martens et al. 2004). It would be a good idea to carry out more experiments of this type for different canopy structures. Isotopic methods (e.g. with CO_2) could be also used, although they are expensive.

The Development of a Conceptual in-Canopy Turbulence Model that Can Be Integrated into a Chemical Transport Model (CTM)

One of the problems of incorporating in-canopy turbulence into CTMs is the inconsistencies between the treatment of vegetation canopies in meteorological models and the CTMs that are driven by their data. If a multi-layer in-canopy turbulence model is incorporated into a CTM, there is a risk that the parameterisation (e.g. energy budgets) is inconsistent with that of the meteorological model, which has a more basic treatment of plant canopy processes. The ideal solution, therefore, would be to incorporate a multi-layer in-canopy model into the meteorological model so that consistency is maintained between it and the CTM. However, it was recognised that such an ideal system may have a long development time, although in-canopy processes are already being considered in meso-scale meteorological models such as WRF and MM5 (Dupont et al. 2004).

However, it is important to bear in mind that canopy-related processes, in numerical weather prediction models (NWP), are already treated within, so called, surface schemes. These schemes are part of the soil-vegetation-atmosphere-transfer (SVAT) modelling family. All NWP models have several surface schemes that can be selected before the model run. This means that the problem mentioned above can also be solved in the following way.

Firstly, the number of canopy layers to include in the surface scheme needs to be defined, depending on the CTM model to be driven by the NWP model. Secondly, chemical sub-models need to be fully coupled with the surface scheme. This implies that for each height z, within the canopy, the surface scheme calculates e.g. leaf area and micrometeorological processes, which can be used by chemical sub-models which, in turn can be used to calculate gas transfer at that level. In this way the NWP can estimate the gas exchange between the canopy and the atmosphere.

In the shorter-term, there is a need to include in-canopy turbulence directly into CTMs. Two promising approaches to do this were presented at the workshop by Tuovinen and Simpson (ESX; ECLAIRE Surface Exchange model) and Ganzeveld (MLC_CHEM). In fact an earlier version of MLC_CHEM has already been coupled to the global CTM ECHAM to assess the influence of incorporating a two-layer canopy model on NO_x emissions to the atmosphere (Ganzeveld et al. 2002b).

In fact the development of both approaches should be encouraged, so that the current simple parameterisations can be improved to simulate those phenomena considered important with regards to net exchange processes of gases and particles (e.g. through assessment by LES models). In a wider context, atmospheric boundary layer parameterisations in NWP models are often not consistent or compatible with those of CTMs (e.g. through spatial or temporal mismatches or missing parameterisations of important variables) (Sofiev et al. 2010). A way to overcome this problem would be to re-state the atmospheric boundary layer parameterisation in the CTM based on scaling parameters such as Monin-Obukhov length (*L*), friction velocity (u_*) and the temperature scale (T_*), as is done in the SILAM model (Sofiev et al. 2010), with the inclusion of new in-canopy schemes.

Although a two-layer canopy model has a simple analytical solution, it is probably necessary to have more than two layers for a realistic simulation of in-canopy processes. Such a parameterisation should be flexible enough, so that the user can add or remove canopy layers, if necessary. This option is planned for the next version of MLC_CHEM.

Interactions of different gases and particles with in-canopy turbulence should be similar, although processes such as segregation (turbulence affecting efficiency of chemical reactions) and turbophoresis (tendency for particles to migrate in the direction of decreasing turbulence) may be important. However, these interactions are not considered a priority at the current time. The turbulent parameters required to model these processes would need to be provided by the CTM turbulence models.

Conclusions

It is widely recognised that the current treatment of in-canopy turbulence in chemical transport models (CTMs) is insufficient to properly explain net exchange processes. Many phenomena have been identified in the field that cannot be simulated using the existing simple parameterisations, although the importance of these phenomena for net exchange processes is not clear. More work is therefore needed to develop models that can simulate these processes (e.g. Large Eddy Simulation models coupled with energy balance models) in order to assess their importance.

In order to incorporate in-canopy turbulence into CTMs, the ideal situation would be to include a multi-layer canopy model into the driving meteorological model in order to maintain consistency with the CTM. However, in the short-term, it was agreed that the two approaches presented at the workshop (ESX model and MLC_CHEM) are a good step forward.

These simple approaches should be developed further to include a user-defined canopy structure with realistic turbulence, temperature and energy gradients that are consistent with the other conceptual models developed at this workshop (i.e. chemically reactive multi-compound soil, litter and leaf exchange processes).

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A Common Conceptual Modelling Framework for Reactive Trace Gases and Volatile Aerosols Atmosphere-Biosphere Exchange in Chemical Transport Models

R.-S. Massad and B. Loubet

Conclusions of the background documents as well as discussions prior to the workshop highlight the model requirements that are needed today to advance our knowledge on biosphere—atmosphere exchange of trace gases and volatile aerosols. We present here the model requirements, to address the needs in model improvement, the conclusions of the working group sessions highlighting the ideal model per compound and a synthesis presenting the necessary features for a common conceptual modelling framework.

General Model Requirements

In order to better couple the atmosphere, biosphere and hydrosphere and better account for the exchange of chemical compounds between these compartments, the surface exchange model should follow some requirements exposed here:

1. **Generic**: the framework should be applicable to different compounds and chemical species. Most of the models that exist today are species specific and in their conception do not allow exchanging a compound by another and even less combining several compounds. This is partly caused by different research communities working on different compounds.
2. **Multiple scales**: the common model should be functional at different scales. One should be able to use it online with a chemistry and transport model

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R.-S. Massad (✉) · B. Loubet
INRA, AgroParisTech, UMR1402 ECOSYS, F-78850 Thiverval-Grignon, France
e-mail: Raia.Massad@grignon.inra.fr

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(CTM) at the regional scale but should also be able to use a 1-D version of it independently of the CTM. This would allow integrating detailed process modules and "research" versions in the model for testing at the CTM scale as well as using the model to understand, test and interpret field scale data.

3. **Bi-directional exchange**: the model should integrate bi-directional exchange of compounds when this is relevant. This requires replacing the existing deposition schemes and emission databases by a more integrated approach. This will also require a change in the way CTM link sources and sinks together and will need developing approaches to scale-up bi-directional fluxes.
4. **Compounds interactions**: the model should not only allow the modelling of different compounds but should account for chemical interactions between those compounds. This means including within-canopy chemistry schemes in the gas phase and at the leaf and soil surfaces. This also requires linking with in-canopy turbulent transfer and accounting for most sources and sinks within the canopy.
5. **Link to Climate and external drivers**: One of the main objectives is to be able to simulate the effect of global change (climate, air pollution, land-use change) on the exchange of trace gases and volatile aerosols between the biosphere and the atmosphere. These factors should therefore be explicitly linked and/or modelled within the framework. How these exchanges will modify the ecosystem functioning should also be considered through coupling with ecosystem models, to account for possible feedback mechanisms.

The Ideal Model for Each Compound

Based on the background documents each working group has proposed two ideal models for each category of compounds considered: a **"gold" model** which consists in the most process-based approach to depict advanced surface exchange, and a **"silver" model** which consists of a compromise approach, yet constituting a clear outbreak when compared to the actual models.

For each category of compounds, a number of processes are needed for describing surface-atmosphere exchange. Six critical processes have been identified based on the background documents and the working group discussions. These are (1) litter and soil exchange; stomatal exchange which can be separated in (2) stomatal aperture and (3) leaf compensation point; (4) leaf surface exchange; (5) in-canopy chemistry; and (6) turbulent transfer (Fig. 1). For each of these components the requirements for silver and gold models are summarized in Table 1 and discussed.

Ammonia

- The main ammonia source in a canopy is clearly the soil and the litter, which hence constitute the main priority for model developments, mainly limited by data availability on management practices and especially organic fertilization.

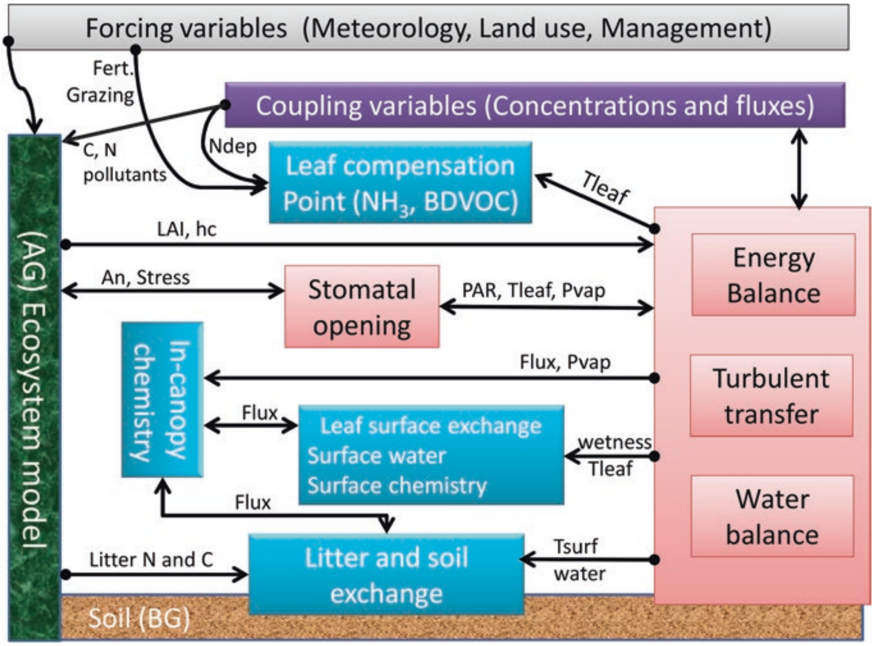

Fig. 1 Modules to be included in the conceptual modelling framework and links to be made between different modules. *AG* and *BG* stand for above and below ground. *Tsurf* and *Tleag* are the ground surface and leaf temperature. *Pvap* is th vapour pressure. *An* is the net assimilatoin of carbon. *LAI* is the leaf area index. *hc* is the canopy height. *PAR* is the photosynthetically active radiation.*BDVOC* stands for bi-directionnal volatile organic compounds. *Ndep* stands for nitrogen deposition

Modelling grazing dynamically was also identified as an essential development for better assessing NH_3 emissions. In terms of processes understanding, the dynamics of the soil and litter pH and litter decomposition were pointed out as critical gaps in knowledge which will require further research. Bearing in mind these limitations, a parameterization of the emission potential of litter and soil (Γ_{litter} and Γ_{soil}) as a function of time, nitrogen load and ecosystem type was considered as an improvement for a silver model.

- Although the soil/litter source is a major component, biosphere-atmosphere exchange of NH_3 is also driven by leaf exchange which includes a stomatal and a cuticular component, both critical in driving the flux. These two pathways would require significant improvements on: (1) a dynamic stomatal emission potential (Γ_{stom}) model as a function of the nitrogen status and plant developmental stage; and (2) a dynamic leaf surface exchange model including leaf-surface wetness and leaf surface chemistry. This will require a coupling with the exchange of atmospheric acids and aerosols. Ideally chemical interaction with atmospheric acids and aerosols would also be desirable, but may be neglected in a silver approach. An improved parameterisation of the cuticular resistance, accounting for humidity, temperature and the deposition of acid compounds and aerosols would be an attainable step forward.

Table 1 Short description of the model components necessary for a "gold" and a "silver" model for each set of compound considered (NH_3, NO_x–O_3, VOC, aerosols and acid gases)

	Model component	Gold model	Silver model	Critical development required
NH_3	Litter and soil exchange	Dynamic litter decomposition and pH as a function of the water status	Parameterised Γ_{litter} and Γ_{soil} as a function of nitrogen input	Dynamic grazing Management data (organic fertilisation) Soil and litter pH dynamics
	Stomatal aperture	Sunlit and shaded leaves	Standard stomatal functions with water stress parameterisations	Plant functional types definition
	Leaf compensation point	Dynamic NH_3 compensation point linked to plant physiology	Parameterised Γ_{stom} as a function of nitrogen input	Process understanding Datasets for parameterisation
	Leaf surface exchange	Dynamic leaf surface water and multi-pollutants concentration	Parameterised cuticular resistance as a function of humidity, temperature and acid load	Multi-compounds exchange model Leaf wetness modelling
	In-canopy chemistry	Ammonia, aerosol and acid gases chemistry	Not necessary	Multi-compounds exchange model Dynamic aerosol size distribution model
	Turbulent transfer	Multi-layer coupled with in-canopy chemistry	Three layer resistance scheme	Coupling in-canopy chemistry and turbulent transfer
NO_x–O_3	Litter and soil exchange	Dynamic soil NO emission NO_2 and O_3 process-based deposition to ground as function of soil type	Parameterised NO emissions Parameterised NO_2 and O_3 deposition to soils	Organic matter decomposition Management NO_2 and O_3 soil deposition dataset
	Stomatal aperture	Sunlit and shaded leaves O_3 impact on photosynthesis and subsequently on stomatal aperture	Stomatal functions coupled with photosynthesis and including water stress parameterisations Dose-response relationships	Plant functional types definition

(continued)

Table 1 (continued)

	Model component	Gold model	Silver model	Critical development required
	Leaf compensation point	O_3 detoxication module NO_2 compensation point	Compensation point equal to zero for NO_2 and O_3	Ozone detoxification process Demonstration of NO_2 compensation point
	Leaf surface exchange	Dynamic leaf surface water Interaction of O_3 with pollutants including VOC	Parameterised cuticular resistance as a function of humidity	Multi-compounds exchange model Leaf wetness modelling VOC–O_3 interaction at the leaf surface
	In-canopy chemistry	Multi-layer NO_x–O_3 chemistry RVOC–O_3 chemistry	Not necessary for O_3 Analytical NO_x–O_3 chemical model	RVOC–O_3 homogeneous reactions
	Turbulent transfer	Multi-layer	Three layer resistance scheme	Coupling in-canopy chemistry and turbulent transfer
Aerosols and acid gases	Litter and soil exchange	Dynamic litter decomposition as a function of water content	Parameterised as a function of nitrogen content	Dynamic grazing Management data
	Stomatal aperture	Sunlit and shaded leaves Include the phoresis effects	Standard stomatal functions with water stress parameterisations	Plant functional types definition
	Leaf compensation point	Dynamic NH_3 compensation point linked to plant physiology Oxygenated VOC emissions	Parameterised as a function of nitrogen deposition	Process understanding Datasets for parameterisation
	Leaf surface exchange	Dynamic leaf surface water-aerosol thermodynamic model adapted to the leaf surface	Parameterised cuticular resistance as a function of humidity	Multi-compounds coupled exchange model Long term leaf morphology change with exposure Leaf wetness modelling

(continued)

Table 1 (continued)

	Model component	Gold model	Silver model	Critical development required
	In-canopy chemistry	Dynamic aerosol size distribution and speciation, and interaction with acid gases	Parameterised deposition velocity as a function of stability and friction velocity	Multiple-compounds exchange model Dynamic aerosol size distribution model Datasets (field and wind-tunnel studies) Measurements technique avoiding artefacts
	Turbulent transfer	Multi-layer coupled with in-canopy chemistry Include stability effects	Three layer resistance scheme Inside-canopy stability parameterisation	Coupling in-canopy chemistry and turbulent transfer
VOC	Litter and soil exchange	Dynamic RVOC compensation point	Parameterised soil/litter RVOC emissions	Better quantification of soil and litter emissions, especially following land management Agricultural sources of RVOC to be quantified
	Stomatal aperture	Sunlit and shaded leaves Response to stress	Standard stomatal functions with water stress parameterisations	Plant functional types definition
	Leaf compensation point	Dynamic BDVOC compensation point linked to physiology	Parameterised BDVOC and RVOC emissions	Datasets for parameterisation
	Leaf surface exchange	Dynamic leaf surface water coupled to AOVOC deposition	Parameterisation of cuticular AOVOC deposition as a function of humidity	Multi species and ecosystem datasets of AOVOC deposition
	In-canopy chemistry	Not necessary	Not necessary	Multi-compounds exchange model Dynamic aerosol size distribution model
	Turbulent transfer	Multi-layer coupled with in-canopy chemistry	Two layer resistance scheme	Coupling in-canopy chemistry and turbulent transfer

The critical development required to improve the model are also given

- A three layer model (soil, litter, plants) was considered as sufficient for NH_3, although a multilayer model would be needed to couple with aerosol chemistry. Improved parameterisations of the turbulent transfer may be incorporated in such a framework.

Nitrogen Oxides and Ozone

- As for NH_3, the soil and litter layer was acknowledged as a major driver of the NO_x and O_3 biosphere-atmosphere exchanges. Indeed, O_3 deposition to the ground constitutes a significant part of the overall O_3 deposition budget, while NO emissions from agricultural soils and litter are also significant. The underlying processes are yet not well quantified and there is a lack of data for process study or model parameterisation. Experiments designed at producing such data are therefore highly recommended. Improved parameterisations of soil-atmosphere exchange of NO, NO_2 and O_3 as a function of soil texture, moisture and ecosystem type and management would be a desirable step forward.
- A second requirement in modelling O_3–NO_x exchange is the necessity to account for in-canopy chemical interactions between O_3 and NO_x and possibly reactive VOCs yet to be identified. This is a major requirement for NO_x exchange but it can be neglected for O_3 at first. Although a multi-layer approach would be desirable for chemical interactions, an analytical solution may be used with a three layer turbulent resistance model including (soil, litter and plants) and would constitute a significant improvement compared to existing models. For O_3, the inclusion of a cuticular and soil resistance parameterized as a function of humidity and ecosystem type was acknowledged as necessary.
- Finally, the impact of ozone on photosynthesis and the plant detoxication capacity would be essential to include, especially for modelling global change impacts on ecosystem functioning and feedbacks mechanisms. In a first step the use of a photosynthesis based conductance model including water stress parameterisations and empirical ozone dose-response relationships would be highly desirable.

Aerosol and Acid Gases

- For aerosols and acid gases, the major model improvement, which is also a great challenge, resides in the ability to dynamically model the joint aerosol size distribution and speciation and their interactions with acid gases and microclimate in the canopy. This is indeed a prerequisite for modelling and interpreting volatile aerosol exchange between the atmosphere and the biosphere.

This would especially require new datasets based on flux measurement techniques that avoid artefacts. The coupling of in-canopy chemical interactions with the turbulent transfer is necessary, such as is the distribution of sources and sinks of the gaseous compounds and the deposition of aerosols. In a stepwise approach, the development of apparent deposition velocity parameterisations for speciated aerosols as a function of the friction velocity and the surface layer thermal stratification can be envisaged.

- The interaction of aerosols with gaseous acids (including some oxygenated VOCs) and ammonia requires including the sources and sinks of these compounds in the surface exchange model. This means developing an explicit link with the NH_3 exchange module including soil, litter and stomatal compensation point modelling as well as the cuticular exchange model.

Volatile Organic Compounds (VOC)

- Similarly to NH_3 and NO, soil and litter emissions of VOCs resulting from land management are poorly quantified. Improved parameterisations of such emissions including agricultural sources are therefore highly desirable.
- There are evidences that deposition of oxygenated VOCs to the biosphere is underestimated. Improved parameterisation of oxygenated VOC (AOVOC) deposition including cuticular uptake and its dependency on leaf wetness are hence needed.
- Some low molecular weight VOCs have shown to be bi-directionally exchanged. These exchange should hence be modelled with a compensation point approach, where the compensation point could be parameterized to reproduce either reduce VOC emissions (RVOC) or bi-directional VOC exchange (BDVOC).
- It was agreed that in-canopy chemistry of VOCs would not be necessary in the current status of knowledge as it would represent at most 5–10 % loss in the canopy for the major isoprenoids. This should be further investigated for very reactive VOCs.

Emerging Common Features in the Modelling Framework

Merging the needs expressed for each reactive compound listed in Table 1 together with requirements of a CTM, leads to the emergence of a common modelling framework for atmosphere-biosphere exchange of reactive compounds and aerosols (Fig. 1).

A New Paradigm of Bi-directional Dynamic Exchange

The bi-directional exchange of gases and aerosols was a consensus for NH_3, NO_x–O_3, VOC and volatile aerosols. The need for efficient approaches to couple such bi-directional exchange with chemistry and transport models was found essential in future developments. Moreover this bi-directional exchange should be explicitly linked with the ecosystem functioning, and especially the nitrogen cycle for ammonia and NO_x exchange.

Model Components

The model should include explicit soil-litter and leaf surface compartments and allow for bi-directional exchanges.

- The litter-soil interface appears as being essential for NH_3, NO, O_3 and VOCs, and requires an explicit description of water and energy balance in these interfaces as the underlying exchange and decomposition processes are extremely sensitive to water and temperature.
- The cuticular exchange seems to constitute a converging focal point for NH_3, O_3, AOVOCs, acid gases and aerosols exchanges, with respect to the uncertainties in theirs quantifications and a major compartment for interactions among compounds. The chemistry of this compartment is central for acid gases and NH_3, and may play a role in O_3 and NO_2 deposition (yet to be demonstrated). The surface wetness was furthermore demonstrated to be linked to aerosols load hence leading to a coupling of aerosols and gaseous exchange at the leaf surface. The dynamics of the compounds (gases and aerosols) deposited at the leaf surface should be inspired from aerosol thermodynamical modelling. The production of data for validating such model is crucial.
- The in-canopy air-chemistry appears as an essential feature to consider for NO_x–O_3 and aerosols-acid gases exchanges. Its modelling however constitutes a varying degree of difficulty: relatively easy for NO_x–O_3, and difficult for aerosols and acid-gases.

Since temperature and humidity of the soil and leaves surfaces are crucial in determining compensation points and surface exchange of reactive compounds, chemical reaction rates and aerosol condensation/evaporation, a special attention should be paid on the triad energy balance, turbulent transfer and stomatal exchange.

- For all compounds updated modelling features were acknowledge:
  - Stomatal conductance should be linked with plant physiology and ecosystem functioning;
  - Energy and water balance model should include in-canopy stability and surface wetness.

Model Structure and Modularity

- The necessity of a multilayer approach for all discussed compounds was acknowledge with a number of layers ranging from 3 (soil, leaves, atmosphere) for ammonia for example to more layers for microclimate, aerosols and NO_x–O_3. The number of layers would thus be modifiable allowing complex multi-layers models for process understanding and simplified 3 layers models for application in chemistry and transport model.
- The model needs to be as modular as possible, and be at least:
  - adaptable and usable as a 1-dimensional plot scale model for process understanding and data interpretation;
  - Connectable with a regional chemistry and transport model (EMEP for example).

Links with External Drivers and Models

- The link to an "ecosystem" type model is also necessary
  - to determine vegetation growth and soil (water, nitrogen) conditions.
  - to account for global change effects (climate and land use change).
  - to account for feedbacks mechanisms.
- For all compounds, a need for updated databases on land management and updated plant functional type definitions were also identified as a priority.
- Ideally the energy balance modules should be part of meteorological dynamic models to allow for a better coherence between the meteorological drivers and the model.

A First Basis for a Common Framework

A conceptual model structure (the ESX framework for Eclaire Surface eXchange) based on the EMEP model with variable number of layers was already developed and presented in the workshop by David Simpson and Juha-Pekka Tuovinen. The structure, which includes a multi-layer model of turbulent transfer within the canopy, is a basis to incorporate various modules. In a 1 D stand-alone version, this model would be forced by meteorological variables as well as component concentration and simulate the fluxes. In a version coupled with a chemistry and transport model (CTM), the concentrations and fluxes would be tightly coupled to the CTM model. ESX will simulate surface temperature and water content that are necessary for controlling stomatal opening, soil dynamics and litter decomposition as well as leaf surface chemical reactions.

Conclusions and Key Challenges

This book has reported the building up of a new conceptual framework for modelling biosphere atmosphere exchange of reactive trace gases and volatile aerosols. The framework aims at integrating recent advances in research but also tries to be as realistic and feasible as possible within the requirements of modelling air chemistry and transport at the regional and continental scale. The framework is therefore more of a "silver medal" model and one could think of various couplings and modules that could be added allowing it to evolve to a "gold" or even "platinum" model.

Even within a "silver" framework there are still key challenges to face to develop this model, some of which are listed below:

- Concerning the aerosol and VOC components a key challenge is dealing with the complexity and large number of compounds but still being able to propose a simple enough scheme that could be computationally feasible at regional and global scales.
- Validation of a multiple-compounds model requires flux and concentration databases which are sparse with all these compounds and should hence be produced. This may require the development of new instruments and methods and large collaborative experiments.
- Imbedding bi-directional exchanges in chemistry and transport models require new approaches to be implemented that decouple emission and deposition which will need to be tested.
- The large number of processes modelled will require more spatially explicit input data over large scales, such as land use and land cover dynamics, nitrogen and water content of the soil surface, the phenological state of the ecosystem, and the management practices.
- To overcome these limitations in data availability, linking with an ecosystem model could be conceived. This in itself is a challenge due to the complexity of both types of models, but is highly desirable and several initiatives are currently trying to tackle this issue (Landscape-DNDC/EMEP, Orchidee/CHIMERE, EPIC/CMAQ, etc.).
- How to account for sub-grid variability and lateral transfers is also a key challenge. The ecosystem spatial distribution may be crucial for modelling the fluxes and lateral transfers of several compounds, including water and nitrogen (e.g. indirect N_2O emissions). Sub-grid variability of meteorological drivers may also influence the exchange processes.

Finally, once this framework and the key modules are integrated, as all community models, its development and progress will depend on the implication and motivation of the community itself.