Air Pollution Reviews – Vol. 2

Editor

Peter Brimblecombe

The Effects of Air Pollution on the Built Environment

Imperial College Press

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PREFACE

Air Pollution and Our Cultural Heritage

The effects of air pollution on building materials became linked to a wider debate about the protection of cultural heritage. We find ourselves in an age where the links between environment, its pollution and culture seem more obvious than ever. Pollution has become a feature of artistic expression broadening the public interest. The century, just complete, began with the paintings of Monet that rendered impressions of the smoke pollution of London and the novels of Arthur Conan Doyle, had his hero Sherlock Holmes pacing the fog-bound streets of London. In the United States, fictional detectives, such as Raymond Chandler's Philip Marlowe, were driving around Los Angeles in the 1940s when photochemical smog was born. Hardly surprising that Hollywood's detective *film-noir*, ultimately encapsulated a vision of smog, perhaps most intensely seen in the futuristic *Blade Runner* (1982). Here it is always as dark as night, because the orange sun can only cut through the pollution at the tops of buildings. As the century ended, the Ken Saro-Wiwa's literary visions of the environment impelled him to an activism, that became a justification for Nigerian government to order his execution.

The destructive effect of air pollution on our built heritage has long been apparent. Recent interest seems particularly driven by the concerns over the widening effects of acid rain in the 1970s and 1980s. The damage from deposition of sulphur dioxide, often accumulated over centuries, at last found voice. The Convention on Long Range

Transboundary Air Pollution fostered a number of international cooperative programmes in the late 1970s. Among these the international cooperative programme for the effects of air pollution on materials gave rise to a long series of studies at the behest of the United Nations Economic Commission for Europe.

Across the Atlantic, 1980 saw the US Congress authorise the National Acid Precipitation Assessment Program (NAPAP), an interagency task force under the auspices of the Council on Environmental Quality. By the early 1990s, NAPAP had produced a series of reports: *Acidic Deposition: State of Science and Technology*. The program was re-authorised through the 1990 Clean Air Act Amendments and examined trends in emissions, deposition and effects, to evaluate the expected benefits of the 1990 legislation. It looked at important construction materials such as metals, paint systems and concrete, and the culturally important materials such as marble, limestone and bronze.

Within Europe, the European Commission promoted studies of the effects of air pollution on cultural heritage, most particularly under the European Union's STEP and Framework programmes from the 1980s. This policy-driven research developed through a period of increasing interest in the concept of sustainability. Sustainability was set to be a central consideration of policy development in the 21st century. Cultural heritage was not explicitly recognised, as a strategic imperative, within seminal documents such as the *Brundtland Report*. Nevertheless, it appeared in official European publications relating to our cultural heritage. The Council of Europe prepared a document about *Sustained Care of Cultural Heritage* and the European Commission's Framework 5 Programme sought tools for the sustainable management of cultural heritage. The move to link sustainability and heritage was motivated by an admirable desire to preserve so much of what we value, although sustainability was not well defined within the heritage context.

Research often focused on dose-response function research and concerns about the mechanisms of damage under laboratory and field conditions. There was much interest in investing decay of well-characterised ambient exposures for standard size samples, as well as for individual structures. The STEP and Framework Programmes in Europe initially focussed on stone, but as with the NAPAP research widened to take an interest in many other materials, e.g. wood, glass and metals. More recently, European research paid greater attention to indoor materials, such as paper, leather and silver.

This research area gave value that went well beyond the field of materials research. There were important spin-offs into other fields, which characterise the research as innovative and show it had escaped the bound imposed by traditional disciplines. One example of this is the use of research on the behaviour of salts on monuments to gain an understanding the moisture requirements of the house-dust mite, implicated in childhood asthma.

The work that contributes to this volume comes from a period when research on damage to cultural heritage was especially active. Times have changed and the future directions of such research is not necessarily clear. The shifting focus of European research under Framework Programme VI seems likely to foster very different projects. In the U.S., similar changes are felt perhaps with less interest in the outdoor dose-response function and increasing attention on the indoor environment.

Nevertheless, buildings remain a most permanent feature of our culture. Whatever the direction of future research, it is clear that an understanding of the way air pollutants affect materials are of practical concern to many involved in the regulation and control of air pollutants. It is hoped that this volume will be of use to the increasing number of scientists, students, conservators and practitioners whose concerns lie at the interface between research and its application.

CHAPTER 1

LONG TERM DAMAGE TO THE BUILT ENVIRONMENT

P. Brimblecombe and D. Camuffo

1. Introduction

Our cultural property is meant to last. We build in stone. Memorials of our heritage are constructed of the most durable materials. It has become common to talk of our crumbling heritage as the victim of air pollution, sea-level rise, urban development, poor taste, etc. At such times, it is easy to see these processes as recent and to forget that the buildings we are so anxious to preserve are a product of continued environmental and social change. These buildings are records both of the forces that created them and those which have altered them. The patina they accrete is part of the heritage they represent. It is part of our attraction to ruins.

This is not to welcome the destruction of our buildings, but to recognise its inevitability. It is wanton or rapid damage, falsification, disrespect, insensibility that characterises true destruction.

It is important to see buildings in their historical context. This is true of their artistic and social history, but here we will be primarily concerned with the environmental history. As with social history, this is partly to help us interpret the current form of the building, but also to aid with an understanding of the physical changes that have taken place. It further offers the opportunity to gain insight into the long term mechanisms of damage. This historical context may need to be several millenia long to cover the span of our built heritage, although a particular focus on the last few centuries can often be appropriate because of the large number of important buildings from this period.

Architects have long recognised environmental considerations in building structures to survive long periods. In the early modern period, they began to believe that damage was caused by time, weather and smoke. Sir Christopher Wren and his colleagues recognised the interaction of sulphur dioxide with stone as there had been recognition of the problems of sulphation through much of the 17th century London where coal was burnt (Brimblecombe, 1992).

This chapter will look at the effects of long term changes in climate and air pollution on damage to materials in the built environment.

2. Changes in Climate

Substantial direct or indirect evidence of climate changes can be found in ancient literature. The oldest climatic scenario, referring to the rise of temperature in the holocene (the climatic period after the end of the last glaciacion, ca. 10,000 years ago), can be found in the Bible, i.e. book of the Genesis. At the very beginning of the book, God is found engaged in an apparently strange action: to separate between them, waters, earth and sky (Genesis, 1, 6–10), as they were all mixed together. In reality, during the warming period, the glaciers on the mountains Zagros and on the other mountains all around the Fertile Crescent melted, and the waters collected in the plain formed marshes and fog. A clear and permanent distinction between earth, waters and sky was made only when the global warming obliged the glaciers to retreat on the top of the mountains and to feed only a few rivers, and the strong sun dried the marshes forming a fertile plain (Issar, 1990). Again, the earth in the beginning was very fruitful, with all kinds of plants which produced abundant fruits (Genesis, 1, 11–13) in a so fortunate situation that Man in that time had the possibility of living without any need of working. This early period in the Hebrew memory, called the Eden, ended when God sent his angel to punish Adam. The punishment was made with a fire sword (Genesis, 3, 23–24), i.e. a climate change, which dried forever all their country, so that Adam and his sons had to work the earth to live (Camuffo, 1990).

Several meteorological observations and the mention of climate changes can be found in the Sumerian, Assyran, Babylonian and Hittite cuneiform tablets and other Far Eastern texts (Camuffo, 1990). The Sumer kingdom ended under the pressure of climatic hazards scouged by storms transporting desert sand and then invaded by other people (Babylonian and Assyran) under pressure of the same climate deterioration. Descriptions of the climatic situation in 2000 BC, characterised by famine, dryness, tornadoes and sandstorms are often found in the collection of tablets edited by Pritchard (1969), e.g. "*the afflicting storm by tears is not adjured; the destructive storm makes the land tremble and quake; like the flood storm it destroys the cities. The land-annihilating storm set up (its) ordinances in the city; the all-destroying storm came doing evil*" (A Sumeran lamentation: lamentation over the destruction of Ur, verses 197–201, in Pritchard (1969); see also item v. 111, v. 173–174, v. 190–192; Hymnal prayer of Enheduanna: the adoration of Inanna in Ur, v. 71; Lamentation over the destruction of Sumer and Ur, v. 61; v. 130–132; v. 391–394; v. 491–493; The curse of Agade, v. 120, v. 123; v. 171–174; The Myth of Zu, v. 31–32; Dumuzi and Inanna: prayer for water and bread). The Hyttite kingdom declined in 1200 BC in a similar climatic context, affected by dryness and storms and in short arrived at its end. In the same period, the war of Troy and the travels of Odysseus occurred in the context of peoples migrations for increasing dryness in the 12th century.

The Bible also mentions a number of climatic events (Camuffo, 1990): e.g. severe drynesses and famines occurred between 1200 and 1025 BC (Ruth, 1, 1); for three years during the David's kingdom (1010–970 BC) (II Samuel, 21, 1–10); for three years again starting in 858 BC (I Kings, 17, 1; 17, 7; 18, 1; II Kings 4, 38); at mid-700s BC with scarce and irregular rain before the harvest time (Amos, 4, 7); in 735 BC when Isaiah complains the scarcity of breads and water (Isaiah 3,1) and slightly later when the Nimrun was dried, the grass and all the green disappeared (Isaiah 15, 6 and Jeremy, 48, 34) and this dryness continued to extend to Lebanon and the mountain highlands (Isaiah, 33, 9). The spring rainfall ceased during the Joiakim kingdom between 609 and 597 so that soon the wells dried and the dry earth cracked (Jeremy 3, 3; 38, 6 and 48, 43); another famine followed in 787 to which contributed the dryness and the siege of Jerusalem

(II Kings, 25, 3); dryness again was found in 520 when the crops were lost, also those cultivated with help of the nocturnal dew (Aggeo 1, 11); another terrible dryness is mentioned in which the hot sun fired grass and trees, and dried up rivers (Joel, 1, 19–20): this is probably the same mentioned by Thucydides (*Pelop. Wars*, 1, 23) during the Peloponnesian wars (431–404 BC) and by Strabo (*Geographia*, I, 3, 2) and Herodotus (*Histories*, 1, 94); a long dryness and famine was found between 45 and 50 AD, which culminated in 48–49 AD (*Acts Apostles* 11, 28) and interested Palestine, Mesopotamia, Greece, Egypt and most of the Roman empire (Joseph Flavius, *Antiquitates Judaicae*, 19, 201 and 20, 101; *Bellum Judaicum*, 2, 204; Svetony, *Vita Claudii*, 18; Cassius Dion, *Historia Romana*, 60, 11; Tacitus, *Annales*, 13, 43).

A history of climate that covers the period of our architectural heritage can be constructed from such descriptive documentary records along with some instrumental records for the most recent centuries. Although other sources of data (e.g. varves, ice cores, tree rings are also important to climatologists), the particular focus of our interest in areas of human occupation makes documentary observations especially important. While excellent records exist in Asia, the climate record has been most extensively studied in Europe.

Climate change was ignored during the 19th century development of scientific meteorology. The late Hubert Lamb argued that these meteorologists had been imbued with classical writers. The climate of the classical Mediterranean was superficially like our own, so Victorian meteorologists found it hard to develop ideas of long term climate change. Although if they read Aristotle's *Meteorologica* more closely they would soon discover that Egypt was seen as becoming continually drier. As for ancient Greece, it was argued the Argive was marshy at the time of the Trojan war, supporting only a small population with Mycenae in excellent condition. By Aristotle's time, Mycenae had become dry and Argos fertile.

Despite the difficulty in accepting long term climatic change and a departure from climatic norms, the gradual increase in temperature became persistent enough to provoke a real interest in long term climatic change by the middle of the 20th century.

2.1. History of Climate

It is simplest to examine some of the broad regional changes that have featured in our views of climate history. The interest in historical climatology fostered by work of men such as Lamb, Flohn, Alexandre, etc. had led to a view that the High Middle ages of Europe were characterised by the Medieval Warm Period. The late medieval period saw a pronounced deterioration of weather. The climate became colder, and led to the early modern period being effectively a *Little Ice Age* (Grove, 1998).

As more reliable evidence is gathered, this simple picture has become less acceptable. It may be that the basis of the Medieval Warm Period is largely biological and phenological and if it existed in a climatological sense it was probably more complex than popularly believed (Ogilvie and Farmer, 1997). A widespread expansion of glaciers was apparant in the *Little Ice Age,* but this event covers different periods in different parts of the world and locations (Bradley and Jones, 1992). There were also times of relative warmth. It may be that rather than regarding this as a period of cold in Europe that stretched from the 16th to 19th centuries, to see it broken into shorter periods of colder weather.

In the middle of the 17th century, a new, growing interest for observing Nature developed in Italy with Galileo Galilei and the Academy of Cimento. This was created and supported by the Granduke of Tuscany Ferdinando II de' Medici and his brother Leopold. They played a leading role in creating the modern science which substituted the Aristotelic dogmas. In this context, the thermometer, the barometer and a hygrometer were invented and applied, creating the first meteorological network, called *Rete Medicea* (1654–1667), composed of six stations in Italy, plus Paris, Innsbruck, Osnabrück and Warsaw. In order to get comparable observations, the instruments were made by the same manufacturer in Forence, and then sent to the ten observing stations. The aim of this network, was to start with an international cooperation to gather climatic data that would have been useful for the future generations. When the meteorological instruments and practice became more mature, in 1723 a new meteorological network, with some medical interest, was proposed by

James Jurin, secretary of the *Royal Society, London* and the gathered data were published in the *Philosophical Transactions* from 1724 to 1735. A third international network (1776–1786) was proposed by Louis Cotte under the auspices of the *Societé Royale de Medicine, Paris.* This network had a brilliant start with 22 observing stations, but terminated under the pressure of the French Revolution. More successful was the fourth international network, proposed in the meantime by the *Societas Meteorologica Palatina* (SMP), Mannheim, and led by the Prince Karl Theodor von Pfalz and his secretary John Jacob Hammer. The SMP network was active in the period 1781–1792 and was composed of 39 stations: 35 in Europe (except the Iberian peninsula and the British islands), one in Russia, one in Greenland and two in the Massachussetts. The observations were published in the *Meteorologischen Ephemeriden* from 1783 to 1795. Giuseppe Toaldo was a contributor from Padova, who funded the *Giornale Astrometeorologico,* in which he published meteorological comments and statistical forecasts, especially aimed to the agriculture. The next milestone was an international agreement between France and Britain, signed in 1860 at Airy, followed by the international Congresses in Leipzig (1872), Vienna (1873) and Rome (1879), in which the basis were established for the birth of the World Meteorological Organisation.

Lamb (1966) suggested that alarms at sudden climate change in Europe at the end of the 18th century may have been a catalyst for the development of early observational networks, in France (1776) and Prussia (1817). However, there were other scientific pressures, and in Britain, a particular interest in climate change over the later part of the 18th century was driven by the effects of climate on agriculture. By the mid-19th century, Koppen attempted to use the instrumental data gathered by H.W. Dove to assess likely global temperature variation since 1750, while in England, Mossman (1897) undertook an analysis of the London's long term climate record.

The late 19th century also marked the beginning of widespread meteorological observations and an increase in northern hemisphere temperature still continuing today (see Fig. 1). The instrumental record suggests some very warm summers at the beginning of World War II. From that point, there was a short cooling and then a continuing rise since the 1970s that is attributed to global warming from increased

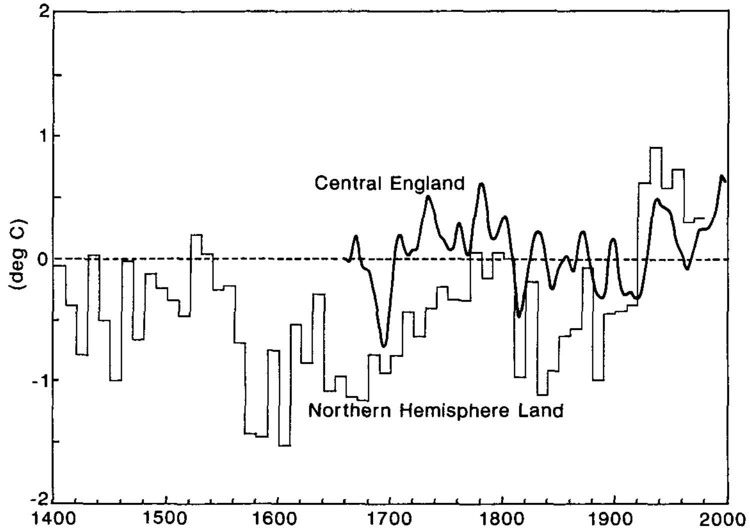

Fig. 1. Northern hemisphere temperature anomalies for the period 1400–1969 compared with the Central England Temperature Record (1660–1989). Anomalies calculated with respect to the period 1861–1960 (Jones and Hulme, 1997).

CO_2 and other greenhouse gases. The changes have been rather subtle and certainly the shifts in annual temperature have been just a few degrees, which would at first suggest only the slightest effect on building materials, but the mechanisms are such that even slight changes can have profound effects. However, we should note that specific locations show different historic changes (Fig. 1).

At a very local level, it is possible to examine climate change at specific buildings, e.g. the Trajan Column after the architect Apollodorus of Damascus built it in Rome in AD 105. The flooding of the River Tiber could be regarded as a climatic indicator of the dominant meteorological features of Rome, at least as a first approximation, and constitutes one of the longest series in the word. In fact, the documentary sources cover an uninterrupted period of 24 centuries because the flooding waters caused severe damage in Rome, so that the number of people killed, the most important damage, the interventions, and the level reached by the waters were carefully recorded. In the cold season, the Tiber floods may be considered as an index of

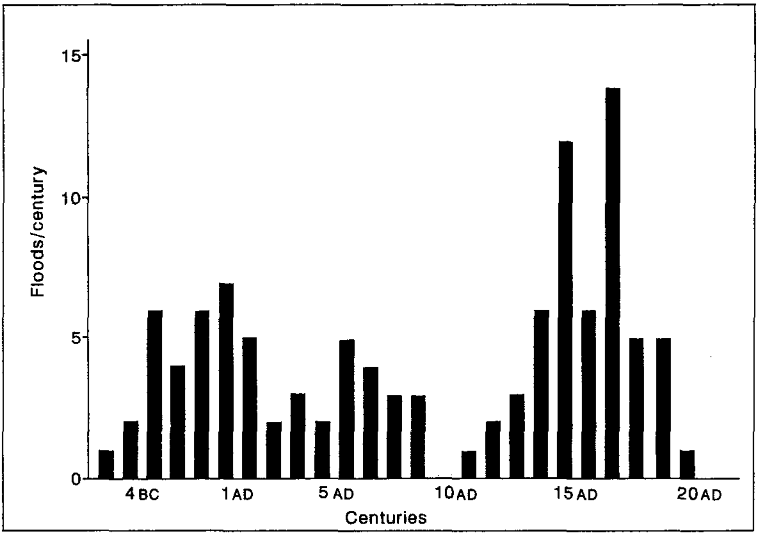

Fig. 2. Secular frequency distribution of major floods in the Tiber.

heavy rainfall, associated with cold inflows over the relatively warm Mediterranean waters. Floods occurred as shown in Fig. 2, with particular severity during some periods: at the beginning of the 2nd century BC, in the 1st century BC, in the 2nd AD, between the years 371 and 860 AD, at the end of the 15th century and in the 17th one. The worst periods were certainly the second half of the 1400s and the whole of the 1600s, two periods when there were various climatic perturbations. Although heavy floodings occurred during the Spörer Minimum of solar activity (AD 1416–1534) all of these anomalies cannot be attributed to the solar forcing, because in other cases the floodings (i.e. the "hydrological effect") occurred for example, before the solar minimum, as for the Maunder Minimum (AD 1645–1714) (Camuffo and Enzi, 1996).

2.2. *Freeze-Thaw Cycles*

Frost damage is a familiar form of stone weathering in temperate and polar climates. It leads to delamination of material from porous stone which becomes wet. The process can be treated as follows.

Water vapour becomes saturated when its temperature reaches the dew point. However, in micropores, the vapour tension in equilibrium with a curved liquid surface becomes lower and lower with increasing the concavity of the meniscus at the interface between the liquid water and the air. This effect is described by the Kelvin equation which states that the saturation pressure and therefore the relative humidity (RH) in equilibrium with a meniscus is calculated by means of the equation

$$\mathrm{RH}(r) = 100 \exp(2\sigma V_m / rRT)$$

where σ is the surface tension of water, V_m is the molar volume of the liquid sorbate (i.e. $V_m = 18\ \mathrm{cm}^3$ for pure water), r is the radius of curvature of the meniscus ($r < 0$ for concave meniscus, as in the micropores), and R is the gas constant. As the radius of curvature r is the main parameter, the Kelvin formula states that the logarithm of the RH in equilibrium with the meniscus is inversely proportional to the radius of curvature of the water surface. RH levels greater than the above equilibrium value cause condensation, and lower RH evaporation. The effect is important only for very small r, i.e. $r < 0.1\ \mu\mathrm{m}$. The problem of surface moisture and condensation is very complex, and depends on the chemico-physical characteristics of both the atmosphere and surface. Total porosity, total pore surface, spatial association of pores that may form pockets and necks, pore size, pore form, pore radii distribution are important variables in the weathering of stones. Stones are characterised by a wide variety of pores and necks, with different shapes and sizes, which range from angstroms to millimetres. The porosity may change with time, especially in the subsurface layer for migration of salts, leaching, dissolution, erosion, and other physical, chemical and biological actions.

When the temperature drops below zero, freezing-thawing cycles can develop, and the pressure exerted by the ice crystals in the pores of materials may have disruptive effects. However, the curvature of the meniscus exerts an important effect between all the phases: the solid, the liquid and the gaseous phase, so that the Kelvin effect in lowering the freezing point in micropores can be calculated. Although a number of equations exist with small empirical corrections (Fagerlund, 1975; Clifford, 1981; Iribarne and Godson, 1986), the chief equation for the Kelvin freezing point depression ΔT_f is

$$\Delta T_f = T_f\ (2\ M\ \sigma_{sl})\ /\ (r\ \rho_s\ \Delta H)$$

where the labels s, l refer to the solid and liquid phases, σ_{sl} = 17.2 erg/cm^2, M is the molar mass of the substance, ρ_s is the solid density, ΔH is the molar heat of fusion, and $L_f = \Delta H/M$ is the latent heat of fusion. For water, $\Delta H = 18\ (80 - 0.5\ \Delta T_f)$ cal/mole and $0.5\ \Delta T_f = \Delta(c_w - c_i)\ dT$, where c_w and c_i are the specific heats of water and ice at p = const. Experimental observations lie between the data computed with the two surface tensions, i.e. s_{sl} for the solid-liquid interface and σ_{sg} for the solid-gas interface, showing that often the ice is covered with a water film.

The formula derived from the Kelvin equation has some important consequences (for a derivation and further discussion, see Camuffo, 1998). (1) Many micropores are filled with water although the relative humidity in the air is far from saturation. The smaller the pore, the higher the probability of being filled. (2) Condensation first occurs in the finest pores and then in the larger ones. (3) In micropores, the freezing point is lowered by the Kelvin effect and the ambient temperature must fall below zero in order to reach freezing. (4) Freezing occurs first in larger pores and then in the finer ones. However, if the pores are at least partially filled with water and the connections between the largest and finest pores are filled, the ice crystals will start to form in the largest pores; when all the liquid water has changed phase, it is transferred from the smallest pores to feed the growth of the ice crystals in the largest pores, so that the finest pores act as a reservoir of water and are emptied. Should this happen, the freezing-thawing damage preferably occurs in largest pores, especially in the case of stones characterised by the presence of both large and fine pores.

If we make the assumption that frost damage is related to the number of freeze-thaw cycles stone suffers, it is possible to assemble a record of how this stress varies with time. Unbroken instrumental records taken in Rome since 1782 provide good information on the meteorological situation over the last two centuries. The freeze-thaw cycles are not as frequent today as in the past (it reached the maximum frequency in the mid-19th century).

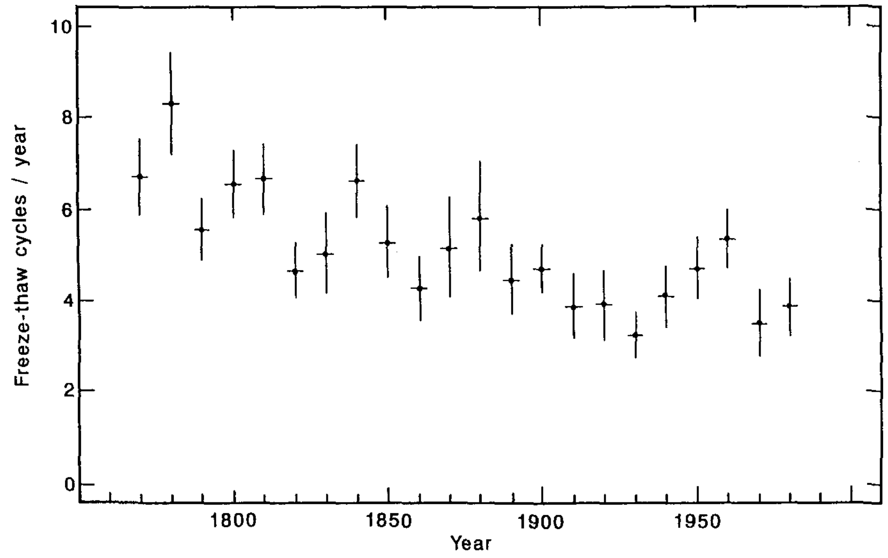

Fig. 3. Decadal means of the freeze-thaw cycles in Central England.

The number of freeze-thaw cycles each year is a sensitive function of average temperature and varies across Europe. At warmer locations, there are no freezing events, while at more moderate climates it increases, although under very cold conditions it is reduced because it remains very cold most of the year. Indeed, under polar conditions there may be no thaw events at all, but such climate regimes have not traditionally been rich in built heritage. The change in freeze-thaw cycles with time is shown for Central England in Fig. 3. We see a substantial increase in events before 1800. Interestingly, this marks an important period or urban development in many European cities and climatic considerations may well have influenced the way in which durable stones were chosen for buildings.

2.3. Storms and Precipitation

Long term trends in precipitation are less well understood than temperature, partly because of the high spatial and interannual variability. Over the long duration, it may have varied only slightly in

Europe although there was a dry period in much of the continent between the 1780s and 1810s (Jones and Bradley, 1992). Given the large degree of interannual variability, it may be best to consider the occurrence of extremely wet or extremely dry years that can impart particular stress on buildings, by lowering or raising the water table.

The time-of-wetness of buildings often emerges as a key factor in likely dissolution of stone surfaces. We have some knowledge of evaporation back to the 17th century which could be used to estimate the potential for changes in time-of-wetness over long periods.

A parameter that may be more important than precipitation amount is the wind-driven rain which drives water into the building fabric. Wind-driven rain is often expressed as the product of precipitation amount and wind speed. This parameter is not measured even in modern period, but can be estimated from other observations. However, in England, it does not appear to have changed very much in the last century or so.

Camuffo *et al.* (1999) have estimated the change in storminess along some Mediterranean coasts from descriptive records. It is well known that in coastal areas, buildings deteriorate more rapidly than at inland sites. The damage is chiefly attributed to the presence of sea salt, which is generated and transported inland by offshore winds, especially when they are strong. Sea spray deposits on buildings, trees and other obstacles, but its concentration decreases rapidly with distance from the coast.

Many million of tons of salt are annually transferred from the oceans to the atmosphere each year. In normal conditions, marine aerosols mainly originate from bubbles in whitecaps, i.e. from the disintegration of the film that forms the cap of the bubble, or from the central jet that forms when the cavity of the bubble collapses and the jet drops seem to be the main source of the so-called giant salt nuclei. During storms, the gale force wind is much more effective in breaking waves, transferring large amounts of seawater to the atmosphere as sea spray. In coastal areas, the deposition rate of sea salt has been evaluated in the range between 21 and 3200 $\mu g\ cm^{-2}\ yr^{-1}$. Extreme events can drive rain deep into building materials or carry salt onto the upper parts of structures in maritime locations. The salt can contribute to salt damage under humidity changes or pollutant deposition.

The wind itself can cause direct damage to structures. Lightning is also capable of damaging buildings. Historical changes in frequency of these are known at a number of locations and there may be hints of increases in frequency at urban locations (e.g. Mossman, 1897). A list of historical buildings hit and ignited by lightning in Venice since 1388 shows the total number of strikes is relatively low [24, although in three cases more than one bell tower was hit during the same thunderstorm (Camuffo *et al.*, 1999)]. In the course of centuries, the S. Marco bell tower was hit 11 times, as it is the tallest bell tower (i.e. 100 metres; all the other bell towers are much lower and were hit only once or so). The first conclusion is that only the taller bell towers were at risk, not the buildings of normal height. In 18 May 1776, a lightning rod was applied to the S. Marco bell tower, and then successively to the other relatively tall buildings as well. After the introduction of lightning roads to the taller towers, this risk practically disappeared. This pinpoints once more the importance of preventive measures.

2.4. Biological Factors

There are secondary effects of climate on buildings via biological interactions. We are unsure of the ways in which temperature and humidity changes may affect the growth of microbiological organisms on the surface of buildings. Although this may be important, it is possible that air pollution is an even more important factor in mediating biological attack on building materials (Urzi *et al.*, 1999).

3. Changes in Air Pollution

The effects of air pollution on buildings have been so important in the 20th century, that there has been much less interest in the effect of long term changes in air pollution on the rate of deterioration of building stone. Nevertheless, European architecture has suffered enormously from centuries of exposure to atmospheric pollution. By the 17th century, there was sufficient understanding of the damaging effects of smoke that sporadic attempts were made to solve the problems it caused.

3.1. History of Air Pollution

Urban air pollution was known from classical times. Rome, with a population in excess of one million, consumed enormous amounts of wood, such that temples were blackened by soot and the health of sensitive individuals affected. Citizens had some redress under Roman law if their property rights suffered interference and legal decisions against the production of smoke are known (Brimblecombe, 1987a).

Patterns of fuel use, and more particularly, changing fuel types seemed to trigger concern about urban air pollution in the past. Especially noticeable was the transition to coal as a fuel. There are important differences in the historical development of fuel use, control policies and the climate of various European cities. The changes to differences in the evolution of air pollution experienced.

It is possible to estimate the changes in pollutant concentration occurring within a city over the centuries by modelling the fuel use. This has been done for London (Brimblecombe, 1977b), York (Hipkins and Watts, 1996) or American cities such as Boston (Sherwood and Bambaru, 1991) or Pittsburgh (Davidson, 1979). Alternatively, there been studies of the exposure of individual monuments such as York Minster (Bowler and Brimblecombe, 1991) or Trajan's Column (Camuffo, 1993). Studies of the long term change in air pollution may be based on the history of fuel use and examine civic and legal records, travellers' descriptions and medical writings. In some cities, scientific measurements of air pollutants began in the late 19th century.

London has an interesting air pollution history because the shift from wood to coal, as a fuel, began so early. While the transition there began in the 13th century, it was as late as the 20th century in some parts of Europe. When fuel is changed, it may be accompanied by a noticeable change in the quality of the smoke. The unfamiliar smell of coal smoke led to early fears about the health risk, through the belief that disease was carried in malodorous air (miasmas). Coal in 13th century London was mostly used for industrial processes such as lime-mortar production and it was not until the late 16th century, with the widespread construction of household chimneys, that the fuel began to be used domestically (Brimblecombe, 1987b). At this time, we can find early observations of damage. John Thornbrough, the Dean of York Minster, suggested that coal should be desulphurised to make it less offensive. In the early years of the 17th century, King James I complained of the terrible damage done to the fabric of St. Paul's cathedral and Archbishop Laud fined the brewers upwind for damaging the same building. The diarist John Evelyn described the effects of smoke in his book Fumifugium of 1661, which told how air pollution made churches and palaces look old, clothes and furnishings foul, and paintings yellow.

3.2. Early Acid Rain and Dry Fogs

Lucius Annaeus Seneca (4 BC?–AD 65) gives us a clear evidence about air pollution and acid rain, discussing the reasons why water has a different taste in different places: "The first is the type of soil from where it comes. The second depends on the soil, whether it arises from its transformation. [He believed that the springs were the result of a direct transformation of the soil into water.] The third from the air which is transformed into water. The fourth due to the corruption of the water when it is contaminated by polluting agents" (*Nat. Quaest.* III, 20, 1). The observation that dripping droplets or running water eroded stones (Lucretius, *De Rerum Natura* 1, 314; Ovid, *Ars Amatoria* 1, 475–476) was another indirect mention of acid water in ancient Roman times.

However, the early scientific observations of atmospheric acidity (Camuffo, 1992) can be found only after the development of the science in the 1600s which followed the example by Galileo and the *Accademia del Cimento.* The physicist Honoratus Fabri published in 1670, an extensive treatise of physical and meteorological sciences in which he devoted a whole chapter to the problem of impure water. Of course, several types of impure rainfall are considered, from the rain which seems like blood from the inclusion of reddish lime, to a type of corrosive rain that damages the agriculture: "A certain type of rain causes spot damage to the fruit, and sometimes the whole fruit is burned, e.g. the rain that falls during the hottest hours in the middle of the day, with rarer but larger drops; as it evaporates rapidly leaves some acid particles on the fruit. Due to their great capacity to acidify, the fruit is burned, dessiccated, or undergoes spot lesions, or some other damage" (Fabri, 1670). Of course, at that time, and in the hot season, when domestic heating was absent, we cannot attribute this atmospheric acidity to anthropogenic activity (Camuffo and Daffara, 1999). The only possible cause for background or widespread pollution was attributable to natural factors, and volcanoes were the only possible source of powerful emissions. In fact, a major eruption of the volcano Etna (38°N, 14°E) occurred in 1669, the year preceding the publication of the treatise by Fabri.

Sixty years later, Hermannus Boerhaave, wrote in 1731, and published in Venice in 1749, an important treatise containing the basic ideas concerning air pollution, atmospheric scavenging and acid rain. A sample from the text, dating more than two and half centuries ago, reads as: "The soot deposited by the smoke at the top of very high chimneys by the combustion of plants, and in chemical distillation it is transformed.... These fossil compounds called sulphurs each time they are burnt, are so completely dispersed in the air that they disappear: the saline and acid parts are transformed into suffocating emanations.... The same sulphur, if it is alone, is transported away by the air, once it has been transformed by heat into minute particles.... Also the winds themselves, when they transport the air with all it contains from place to place, always move materials from the places where they originated, and gradually change the composition of the air, continually removing substances belonging to one place and giving back always those which have been taken up a short time before.... The rain could be called a real and proper agent that washes the atmosphere, and that collects all types of substances that are suspended in the air. However, the rain that falls after long periods of dryness is very different from that which falls during the rainy period. The water of storms is different from other waters, without speaking of the effects of the winds, which carry atmospheric water from place to place; for this reason, with persistent winds which always blow violently from one zone only, the rain is full of emissions belonging to that remote zone. The winds perturb these substances, they mix them with the rains, they disperse them, carrying them from distant places and sometimes form a mixture which is so wonderful that it is a joy when such rains irrigate the plants and the fields. The frequent observations of the rains falling from the sky during the hot season, and collected in vases which have been carefully cleaned and then observed for a long time, shows that it putrifies spontaneously being transformed into a fetid and putrid lattice.... The rain which falls in the hot seasons, with strong winds, in urban areas, in low lying [or humble] places consists of very impure water, where putrification occurs, where animal and vegetable products, and products of any other nature are dispersed in the air by man in great quantities and in various ways. And the rain coming from such places will be even more impure if the air has been very nebulous, dense and fetid, such as to carry a horrendous odour to the nostrils, air and emissions that are harmful to the lungs" (Boerhaave, 1749). The same author also had a clear idea about the role of the volcanoes as agents of acidification, and of the long-range transport of volcanic aerosols: "We should remember that the winds carry in the air, like waves, the sand from Egypt and Lybia, and transport the ashes of Etna over long distances. The dusts of Vesuvius were dispersed in the air for over one hundred miles.... The ashes erupting from the volcano (Vesuvius, 41°N, 14°E) were found to have been transported over one hundred miles away" (Boerhaave, 1749).

Besides acidic rain, volcanic emissions also caused *dry fogs* (Stothers and Rampino, 1983) which consist of a mist composed of gases and aerosols, foul smelling, and characterised by a reddish colour. These reddish, maloderous fogs which do not wet surfaces (for this reason they are called "dry"), appeared at dawn and sunset, sometimes persisting even into the middle of the day. They appeared especially in the summer (instead of the cold season) and were often accompanied by red dusks, weak sun, solar and lunar haloes, which caused damage to the vegetation and brought in their wake, epidemics. The most famous event, which affected for months the whole of Europe, occurred in 1783 for the eruption of the Laki volcano, Iceland (Thodarson and Self, 1993; Grattan and Charman, 1994; Grattan and Brayshay, 1995).

The damage caused by these fogs on vegetation were so important that they were described in treatises on agricultural meteorology: "There are 'fogs which wet' bodies they touch and they are in the majority; but there are also dry fogs, whereby the hygrometer moves towards 'dry'.... Among the different species of fogs we can, for agricultural purposes, reduce them to two only — the damp fogs and the dry fogs. The damp fogs favour agriculture, as long as the plants are not near maturation. They bring, like the dew, humidity and substances in solution.... The dry fogs, form a haze through which the sun appears to be a bright red, not a real fog. These hazes.... spread over Europe in 1783, where they lasted for months" (Orlandini, 1853). In Italy, the most important dry fogs occurred in the years: 1374, 1465, 1499, 1587, 1592, 1648, 1682, 1710, 1734, 1735, 1775, 1780, 1783, 1785, 1786, 1791, 1794, 1802, 1803, 1805, 1812, 1814, 1816, 1819, 1821, 1824, 1831, 1866, 1869, 1883/4, 1886 when chroniclers and scientists described fouling, reddish fog, leading to damage to vegetation, people illness, weather anomalies, and other unpleasant effects (Camuffo and Enzi, 1995).

3.3. Early Descriptions of Damage

Damage to buildings in the past can be established from descriptions of the state of the exterior, most particularly those of architects from the beginning of the early modern period. Nevertheless, classical descriptions survive and Horace complained of smoke blackening to the temples in Rome. In religious buildings, smoke encrustations might be seen as desecration, but secular buildings seem to require an appreciation of architecture as an art form. In 17th century England, there was a predominance of interest in the damage to religious buildings, but this should not be taken to mean that it was primarily a religious concern. The complaints of King James I about smoke damage to St. Paul's Cathedral came from someone who also complained about the besooted state of English kitchens.

There was a clear recognition that coal smoke was a most important cause of damage. Keepe (1683) tells us that at Westminster Abbey you see "the skeleton of a church than any great comeliness in her appearance, being so shrivelled and parcht by the continual blasts of the northern winds, to which she stands exposed, as also the continual smoke of the sea-coal which are of a corroding and fretting quality...."

At York Minster, many houses whose smoke damaged the fabric, were demolished under the guidance of the Dean during the early 1700s. At the same time, smoke and scurff [an archaic word for a saline or sulphurous encrustation] were removed from the stonework during cleaning operations (Drake, 1736). The aim of the repair work was to "stop up all the Cracks, Flaws and Perishing of the Stones, with excellent Cement and Mortar, that.... this Fabrick might yet bid Defiance to Time and Weather for many succeeding Generations". In a similar vein, Nicholas Hawksmoor concluded his repairs at Westminster "will stand 1000 years" (Westlake, 1863). Architects involved in such large scale restorations had yet to realised the impermanence of their repairs. Interest gradually spread to dwellings, and in London of the 18th century, the rate of darkening to the paintwork of some houses was so rapid that repainting needed to be frequent (Malcolm, 1770).

3.4. Industrial Development and Pollution

The late 18th and 19th centuries saw an enormous amount of industrialisation across Europe. The development of the steam engine and the intense urbanisation created very special problems. In England, civic administrators soon became aware that their old legislative frameworks were inadequate to cope with pollution on this much enlarged scale (see Manchester's problems in Bowler and Brimblecombe, 2000a). The problems continued throughout the 19th century with the development of much sanitary legislation concerned with the health of urban populations. These beginnings to modern pollution environmental legislation reflect a desire for cleaner air, but it was often thwarted by weak laws that were erratically applied and poor control technology. The regulations usually failed to achieve substantial abatement of smoke in the 19th century. However, the framework initiated pressure on industry, either their workers had to be trained or they had to be replaced by automated stoking. Gradually, the pall of smoke over cities lessened, though it was soon to be replaced by different pollutants originating from mobile sources.

3.5. Victorian Approaches to Damage

The cities of the Victorian period were so badly polluted that there was much awareness of the need to choose building stones carefully for new structures. Major building works often began with the formation of a select committee of "experts" — architects, chemists and stonemasons, who could then deliberate over the right choice of stone to resist the polluted atmosphere. The Palace of Westminster (1837–1870), constructed after much thought on the ideal stone, began to manifest signs of stone decay in 1847. This showed that "expert" opinion on such matters did not always guarantee that buildings would not succumb to the enhanced weathering (Scott, 1861). At Westminster Abbey, a committee of architects and chemists reported on the best means of preserving the stonework (Carpenter, 1966). They used a scientific approach and concluded that disintegration resulted from acid vapours, particularly sulphuric acids, although they also saw hydrochloric acid as a contributor.

Where thoughtful choice of stone failed to provide adequate protection against the polluted atmospheres, there was some enthusiasm with induratating the stone with protective solutions. Materials such as linseed oil, beeswax, paraffin, gums and resins were all tried, but these techniques were ultimately discredited. Inorganic materials were also applied to the stone. Baryta-water (barium hydroxide) was thought to prevent damage (Jackson, 1901; Church, 1901). Professor Desch also recommended "magnesium silicofluoride", and for the more porous sections of the stonework, "double silicofluoride which contains zinc" to prevent the growth of vegetation at the Abbey (Desch, 1921). These techniques also failed and the early 20th century applications of silicates had produced grey patchy discolouration pitted with small spalls.

On hindsight, it is now accepted that the stone indurators of the period 1850s–1920s had often wreaked more havoc than centuries of decay and weathering (Ashurst, 1985). Writers of the Victorian period had many theories to explain stone decay so prevalent in their cities. The erratic classical scholar Paley (1878) argued that the blackening of St. Paul's cathedral was really due to the presence of lichens and should be treated with the biocide copper sulphate. While at York, the vulcanologist, Tempest Anderson, wrote that stone decayed from both air pollution and biological attack (Anderson, 1910). However, increasingly smoke abatement was seen as the most appropriate solution, and was strongly advocated by ecclesiastical officials and architects alike.

3.6. Architectural Responses

The Victorians wrote that coal smoke was imparting a "new colour" to towns, but aesthetic opinions about this were divided. Some felt *Time* and *Nature* effected a "softening" appearance on urban buildings and accepted the effects of smoke, while others claimed that all that was required to bring colour back to London was to regularly wash buildings with water. Yet others argued that architects should aim at designs that would become "beautifully coloured by Nature charged with smoke" (e.g. Ricardo, 1896).

The problem was deeper than the simple mechanical response hinted at above. By late Victorian times, the issue of air pollution encompassed many aspects of the design of urban buildings. Architects recognised that within cities there were problems of overcrowding, access to light, air pollution, stone discolouration, indoor pollution and inappropriate building styles. The urban environment needed to be an aspect of their designs. At the end of the 19th century, the range of responses included (Bowler and Brimblecombe, 2000b):

(1) abandonment of gothic and the promotion of less detailed classical styles not so suceptible to air pollutants,
(2) careful choice of pollution-resistant stone and glazed materials,
(3) extensive provision of clear window glass to let in more light,
(4) adoption of electric light and air filtration to lower pollution indoors, and
(5) development of dust excluding interior fittings to protect books, etc.

3.7. The Twentieth Century

The present century has seen a gradual decline in the use of coal in cities of Europe and North America. This has been replaced by oil, gas or electricity (often generated outside the urban area). These changes have led to the emergence of an entirely new kind of air pollution — photochemical smog. This arises when volatile organic compounds (primarily from liquid fuels), sunlight and nitrogen oxides interact. Ozone is the most characteristic compound found in these smogs. Photochemical smog first began to be noticed in Los Angeles during the Second World War and was actively studied in the 1950s when the mechanism of their formation was finally established. At first, it was assumed that these types of smogs would be restricted to warm sunny climates, but soon they began to be found at most industrialised locations.

Ozone is harmful to organic materials, especially those with double bonds. However the oxidising atmosphere of photochemical smog is also able to oxidise nitrogen oxides to nitric acid, which can damage metals and stone. Ozone may also enhance sulphate formation on building surfaces.

In many cities, the potential for damage by sulphur-derived acidifying substances appears to have lessened in recent decades. Vehicle fuels (particularly now low sulphur diesel oils are available) are not as significant a source of sulphur as coal. Many had thought that the improved urban air quality would be matched by proportionately lower rates of degradation to historic buildings. The rates of stone damage may not have declined as much as hoped, although at St. Paul's in London, limestone weathering seems to occur at a fairly constant rate (Trudgill *et al.*, 1991). In Britain, ferrous metals appear to be less rapidly corroded than in the earlier part of the century (Butlin *et al.*, 1992).

At the end of the century, many cities find that diesel soot is an important source of soiling (see Chapter 10) reflecting yet another fuel change of the 20th century.

3.8. Economic Analysis

Economic materials provide a further potential source of evidence regarding historical changes in building damage and are especially relevant as we are very much concerned about the costs that air pollution imposes on contemporary buildings. Many cathedrals have kept detailed accounts of their expenditure for many centuries. Their fabric accounts record money spent in both construction and repair of cathedral property. In some cases, these accounts begin at the foundation of the building and may be detailed enough, in later periods, to preserve all the original vouchers accounting for the expenditure on individual items.

In England, cathedral income was rarely sufficient to undertake all desirable repairs and was often dependent on large gifts from wealthy patrons to restore dilapidated parts of the building. In more recent times, religious authorities have been faced with great structural change. Under an 1840 Act of Parliament, cathedrals lost wealthy benefactors as stipends were abolished. Since then, there was a frequent need to appeal for money from the Ecclesiastical Commission. Currently, cathedrals have a broad approach to funding maintenance. The importance of public involvement was stressed with the formation of societies, such as the Friends of Norwich Cathedral or Friends of York Minster. These have widened the base for support, interest and concern for financial problems. Casual visitors to cathedrals are usually reminded of the great running costs and encouraged to make donations during their visit or attracted to purchase souvenirs in cathedral shops.

The annual expenditures from the fabric fund of four English cathedrals (York Minster, Westminster Abbey, Norwich Cathedral and Exeter Cathedral) illustrate the increases in expenditure across the centuries (Brimblecombe *et al.*, 1992). The amounts have been corrected for inflation using the prices of consumables established by Phelps-Brown and Hopkins. Figure 4 shows expenses corrected to the 1447 value using their indices. We see that at York, there were declines in fabric expenditure from the 14th through to the 16th centuries as the Minster was finished. However, in recent centuries the existing records suggest that the rate of inflation in the price of consumables is insufficient to explain the increasing costs in maintaining the fabric. This observation is similar at other sites. An analysis of this data suggests, rather surprisingly, that the rate of increase was somewhat greater over the period 1700–1850 (especially

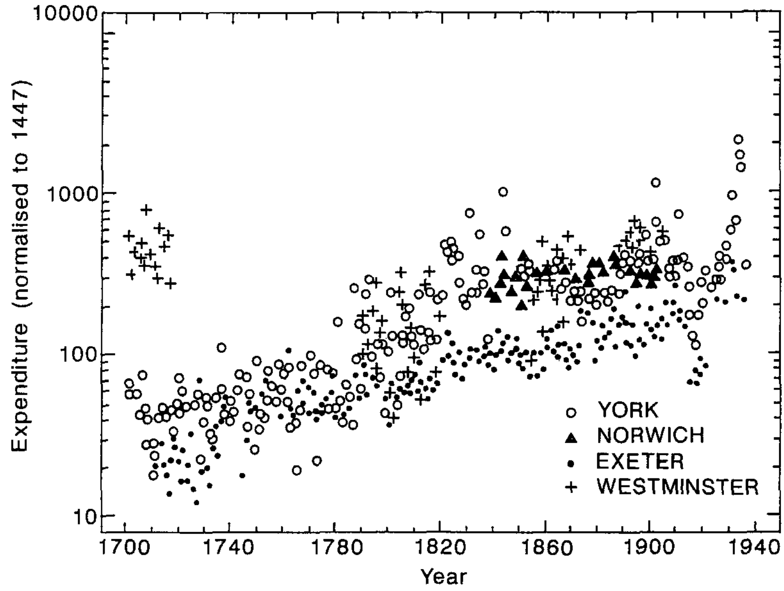

Fig. 4. Annual expenditure from the fabric funds of four English Cathedrals corrected for inflation.

for York Minster) than for 1850–1930. The lack of a rapid rise in expenditure in the late 19th century, a time of rapidly increasing air pollution in UK cities, is rather unexpected.

With the exception of the early data from Westminster, the changes over time show a remarkable similarity in the rise in fabric expenditure at all the sites. The most immediate explanation for this would be to assume that the pressure on fabric expenditure was rather similar across the nation. However, the air pollution histories of these locations are quite different. Westminster, and to a lesser extent York, have been coal-burning cities for many centuries. Norwich and Exeter have been less polluted, so their cathedrals would have been expected to show lower levels of expenditure.

These differences are not evident, so it may be that we cannot attribute the enormous costs in mantaining cathedral fabric simply to air pollution. There are social interactions that make expenditure a good deal more complex than this. Catastrophic costs may be driven by the importance now given to culturally significant buildings. Restoration is no longer work for the local jobbing builder or the mason and now requires specialist skills and expertise far beyond that traditionally expected of local artisans. This is so important that some cathedrals give evidence of a rebirth of local skills in their workshops. Possibly "major restoration programmes", with considerable profile and media interest, have also increased public relations costs, consultant fees and other items not traditionally requiring high expenditure.

We have to remember that "Cathedrals are getting older". Air pollutants clearly cause great damage to materials outdoors. With this few would disagree, but it may be more difficult to relate the catastrophic increase in costs over the last century or so to air pollution alone. If the vast costs are related to factors other than air pollution, it is likely that these buildings will continue to require high expenditure despite the improvements in the corrosive nature of urban air.

As Peter Foster (1985), surveyor to the fabric of Westminster Abbey for many years wrote: "I have endeavoured to take the best advice and to act upon it. To blame everything on acid rain, atomic waste, aerosols or whatever is the latest 'Green' view of the world, is surely 'simplistic'...."

3.9. Archeometric Sources of Information

The historical analysis above has restricted itself to relatively conventional approaches using documentary data to establish changes in air pollution over time. Documents can be supplemented by pictorial sources of information. Roger Lefevre has shown that paintings of buildings can often record the patterns of blackening. Viles in her studies of building damage in Oxford (Viles, 1996) found early photographs useful, and Tang *et al.* (Chapter 11), also used photographic methods.

Modelling is a useful approach to establishing past pollution concentrations (Brimblecombe, 1977b). Where trace gas concentration can be estimated over a long time period, it can be used to estimate the deposition of pollutants to buildings. Figures 5(a) and (b) show

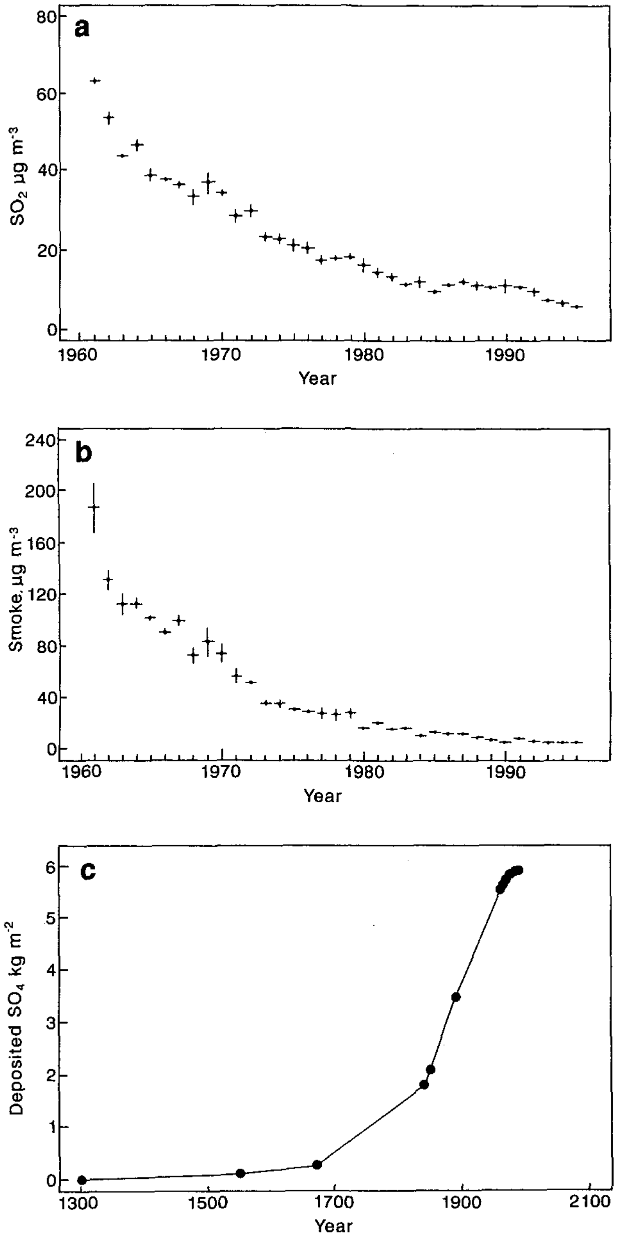

Fig. 5. **(a)** Measured sulphur dioxide concentrations in York (sites 4–9 normalised to site 4) and **(b)** smoke concentrations. **(c)** Cumulative long-term deposition of sulphate to the minster assuming a deposition velocity of 1 cm/s.

measured pollution concentrations in York. Figure 5(c) shows the cumulative deposition of sulphate to a building such as York Minster assuming a deposition velocity of 1 cm/s (using Hipkins and Watts, 1996). These calculations suggest that much of the pollutant deposition had already occurred before the 20th century and that the current rate of accumulation is relatively small.

Pittaluga (1994) and Cesarino and Pittaluga (1995) studied the past pollution by means of a stratigraphic analysis of the gases which have been absorbed and the particles which are sticking on the several layers of paint coatings found on the historical buildings in Genova. Knowing the date of each painting layer, it was possible to date the intervals of time in which each deposit of pollutants was formed. Ausset *et al.* (1998) have studied the history of air pollution and building damage through a direct examination of old crusts on stone. Ancient crusts of buildings have revealed unburnt wood fragments along side microspherules from wood combustion. Within crusts from the Arch of Constantine is possible to trace a decline in gypsum concentration as one penetrates from the recent crust surface into older layers. This is taken to represent an increase in the sulphur burden on Rome's air with time.

4. Recent Changes in Modern Pollutants and Materials

Our view so far has considered the changes of the past. Although it is often suggested that we study history to learn about the future, we should be cautious in our view of parallels for the future. There has been an enormous change in the types of materials used for buildings. We should not only consider structural elements, but recollect the vast range of polymers now in use as coatings and sealants. Changes in the types of air pollution have been equally large as we have moved to atmospheres that are often controlled by photochemical oxidation. Broader atmospheric changes have also thinned the ozone layer, so ultraviolet fluxes have also increased.

One should note that polymers are often sensitive to ozone. Although the changes in UV flux are small, many polymers are sensitive to light and the photodegradation can be enhanced by some polyaromatic hydrocarbons present in the atmosphere.

We should also reflect on the suitability of modern architecture in relation to the urban environment in which it is found. Its simple lines, limited surface detail and a preoccupation with glass, tile, metal and generally resistant materials may be easy to clean. However, sealants are needed that resist degradation, and the deposits of diesel soot from the contemporary is also particularly visible on the light-coloured surfaces that are much in favour.

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CHAPTER 2

BACKGROUND CONTROLS ON URBAN STONE DECAY: LESSONS FROM NATURAL ROCK WEATHERING

B.J. Smith

1. Introduction

Despite the aspirations of architects, the best intentions of builders and the fervent wishes of building owners, stone is not immutable. Sometimes, as in many dense limestones, the rate of decay may be gradual and, given constant climatic conditions, largely predictable. Even then, solution rates can vary in response to fluctuations in pollution levels and changes in the surface morphology of stonework. However, there are also many commonly used building stones which do not decay gradually, but instead experience episodic and sometimes catastrophic breakdown. This occurs as strength is exceeded by the cumulative effects of internal decay and/or when stones are subjected to extreme environmental stresses associated with, for example, a severe frost. Included in these stone types are the quartz sandstones that are widely used across northwestern Europe. Characteristically, such stones are immune to all but the most limited solutional erosion, but are particularly prone to disruption by the effects of accumulated salts which produce effects such as granular disintegration, contour scaling and flaking (Smith *et al.*, 1994). In view of these observations and a long acceptance of natural rock weathering, why does the search for immutability in building stones persist?

In part, this search is conditioned by a widespread assumption that once stone is placed in a building, it is immunised from natural processes of weathering. An assumption that is compounded by a lack of public awareness and poor understanding of these weathering processes, the controls on them and their consequences. This belief that decay can be switched on or off is reflected in the commonly held view that where rapid decay is observed, it is in some way accidental and attributable to human intervention. Usually, this entails the creation of an atmospheric environment peculiarly aggressive to stone and the corollary that once polluted conditions are removed, decay will cease. This quest for immutability is further fuelled by references to ancient structures that have survived, recognisably intact for thousands of years. Such references conveniently ignore, however, the multitude of other structures that have not survived. Similarly, earlier phases of conservation and replacement can be forgotten or ignored. Thus, for example, we often neglect the fact that many of the great "Medieval" Cathedrals of England underwent major programmes of stone replacement and re-dressing in the 18th and 19th centuries. Finally, underpinning these observations and conclusions is the inevitable, though rarely acknowledged, assumption that processes of urban stone decay are distinct from and only loosely related to those responsible for the weathering of natural rock outcrops.

2. The Origins of Misconceptions

The roots of the relationships between natural weathering and urban stone decay lie in a mixture of the practical, the theoretical and the philosophical. At the heart of this is a *de facto* separation between researchers and practitioners in the two disciplines. There are sufficient points of contact to have established the various problems as being multidisciplinary, but to-date insufficient discourse to promote interdisciplinary solutions.

2.1. Decisions Governing Choice of Materials

Builders and architects are rightly concerned with the practicalities of stone properties and behaviour. Selection of stone is invariably driven by questions of personal preference and experience, availability, cost and aesthetics, whereby building design can drive choice rather than "fitness for purpose". Where "fitness" is a consideration, it is invariably based upon performance in standard durability tests. Unfortunately, these tests need not relate directly to conditions experienced by the stone in use nor long-term exposure to a succession or combination of processes operating at a range of magnitudes and frequencies. Alternatively, selection may be based upon initial, but rapidly changed, properties including strength, porosity, permeability and colour. This is particularly the case for replacement stone where matches are sought for existing stonework and where rapid decisions are often required for the choice of conservation strategy. As a consequence most conservation measures inevitably treat symptoms of decay rather than causes. Rarely, if ever, are time, expertise or resources available to research individual conservation projects. Exceptions can be made for particularly prestigious buildings and stone decay research is dominated by studies of high profile municipal and ecclesiastical structures at the expense of more mundane, but more numerous domestic, secular and industrial buildings. In some areas, this bias against scientific investigation can become almost institutionalised so that, for example, public funding for renovation through schemes such as the European Union Structural Fund and United Kingdom National Lottery is either not directly available for research or specifically excludes it. Inevitably, therefore, what research there is into urban stone decay is dominated by short-term, problem-based case studies. Pure research has been centred mainly in government-funded laboratories. But, especially in Europe, even this is under threat as these facilities are increasingly required to be self-financing and hence to concentrate upon commercial applications of their research.

2.2. Research Bias and Accessibility

Because of the above factors, pure research into urban stone decay, especially into decay processes and the long-term behaviour of stone, has historically been very difficult to pursue. This difficulty is compounded by the tendency for the results of government-funded research to appear as internal documents, government reports (BERG, 1989) and other forms of "grey literature". Rarely are these documents readily available to the wider research community and, if produced as commercial reports, they may be restricted by client confidentiality. As a by-product of this, there is little demand for and hence little provision of international journals dedicated to or even willing to accept, this kind of research. Instead, publication is dominated by professional magazines and conference proceedings. This has two effects: first it tends to reinforce the insularity of the stone decay/ conservation community and, second, it actively discourages participation by university-based researchers. In these days of journal impact factors and subject-based research assessments, few academics can afford to publish outside of international journals or beyond their peer group subject.

There are clearly numerous exceptions to this intellectual isolation and classic texts such as that by Winkler (1973) made a cogent case for a more geological approach to stone decay. More recently, Cooke (1989) and the excellent review of salt weathering processes and products by Goudie and Viles (1998) have successfully brought together a wealth of information from across a wide number of disciplines. Similarly, earlier forays into stone decay by geologists/geographers such as Cooke and Gibbs (1993) produced many perceptive analogies between natural and urban environments, but even this was published in a format largely inaccessible to both research communities, let alone the wider public.

Despite these points of contact, geomorphological and geological research has continued to concentrate on rock weathering in natural environments and has been separated from urban stone decay by its journal and book base, separate terminologies and an absence of funding opportunities. This is exemplified in the UK by the support of environmental and geological research through the Natural Environment Research Council. Thus, for example, salt decay experiments are frequently published as studies in desert geomorphology (Smith and McGreevy, 1988) and studies of fire damage to stone are examined in the context of bush fires (Allison and Goudie, 1994).

This seeming denial of the wider implications of such studies is matched by a suspicion amongst architects and conservators of "academics", who by definition are concerned with the "theoretical and speculative" rather than the "technical, applied and professional" (Collins Concise Dictionary, 2001). In doing this, however, valuable insights into decay processes and alternative perspectives are ignored or missed entirely and work is often duplicated. So that, even in excellent texts on stone decay (Amoroso and Fassina, 1983) there are few, if any, references to parallel studies in natural environments. Likewise, until very recently, standard texts on weathering (Ollier, 1984) made little or no reference to building materials.

At a more fundamental level, the lack of a clearly defined and generally recognised academic base, together with an emphasis upon problem solving, has left urban stone decay without a unifying conceptual framework. The absence of a framework is particularly telling when questions of spatial and temporal variability of decay arise. In comparison, such questions are central to geomorphological and geological research, and have traditionally provided core paradigms within which studies of weathering can be set and their implications projected. It is this ability to provide a structure to decay studies that may eventually be the most significant contribution to be made by natural weathering research. In addition, however, there are many direct lessons to be learnt from the interactions between natural weathering processes and the very special conditions created once stone is taken, shaped and placed in buildings within the built environment.

3. Process Interactions

In recent decades, geomorphological and geological research into weathering has been preoccupied with the detailed explanation of processes that operate, frequently to the detriment of understanding the broader issues of resultant weathering forms and materials. Nonetheless, it has resulted in a large corpus of literature on physical and chemical processes and the factors that control them. Central to this has been the recognition of complicated feedback relationships between processes, fresh and weathered rock, surface morphology and the weathering environment experienced at the rock surface. Change in one variable inevitably triggers a chain of responses in the others and weathering is invariably discontinuous in space and time and highly dependent upon the breaching of stability thresholds within weathering systems. Interactions are numerous, and include such classic salt weathering forms as honeycombs and cavernous hollows (Fig. 1), which once initiated create humid micro-environments suitable for the retention of any deposited salt (Smith and McAlister, 1986). In such interactions a distinction can be drawn between mechanisms responsible for initiating change and those responsible

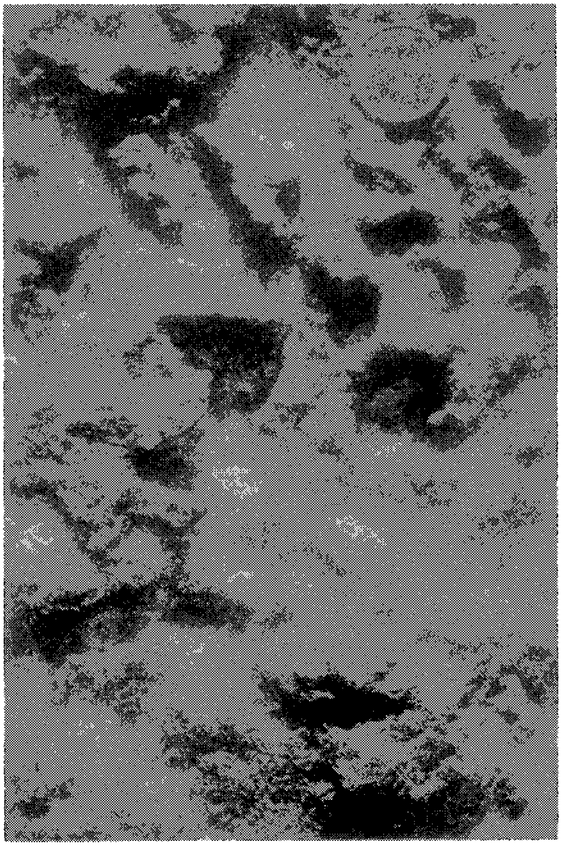

Fig. 1. The accumulation of a salt efflorescence within the interiors of honeycombs sheltered from rainwash (Salamanca, Spain).

for exploiting changed conditions. The most striking example within urban environments is that of granite. Of itself, "fresh" granite is a highly durable stone, relatively immune to attack from, for example, salts and chemical alteration. However, if microfractures are present or are initiated by other mechanisms (dilatation induced by pressure release during quarrying or directional loading within a building (Fookes *et al.*, 1988) then these can in turn be exploited by a range of other mechanisms (Neill and Smith, 1996). Interactive relationships extend beyond the roles of precursors to include catalytic effects such as enhanced silica solution in the presence of salts and the combined effects of mechanisms/processes acting in sequence related to fluctuating environmental conditions. So that, for example, porous stone containing suitable salts may be subject at different times to expansive forces associated with differential thermal expansion, hydration/dehydration and solution/crystallisation. In addition to which, the same stone may experience periodic freeze-thaw and thus be subject to a stress regime of highly variable magnitude and frequency.

The most widely accepted example within building stone decay literature of the role of natural processes is to be found in studies of limestone solution (see review by Inkpen *et al.*, 1994). Solution loss in polluted environments is a product of the effects of sulphur-rich "acid rain" and dry (gaseous) deposition and naturally carbonated rainfall — so-called karstic solution. There now exist a range of physico-chemical models which aim to identify the relative contribution of each solution process (Livingstone, 1992a and b; Webb *et al.*, 1992). Unfortunately, however, the emphasis appears to be on apportioning individual blame, rather than investigating interactions linked to variations in the chemical composition of precipitation over time, and possible synergisms associated with the chemically complex conditions of one rainfall event.

The processes and mechanisms highlighted above are in no way unique to the built environment. The range of salts present may be different from other salt-rich environments, such as coasts and deserts, but salt damage is not the preserve of any particular salt. Similarly, phenomena such as saline groundwater and groundwater rise are not restricted to buildings with defective damp courses. The effects of this overlap are most graphically illustrated where urbanisation occurs within naturally salt-rich environments. Thus, there now exists an extensive literature on damage to stone and concrete structures in areas such as the Middle East (Cooke *et al.*, 1982; Fookes, 1996) and Central Asia (Cooke, 1994) and coastal areas of the Mediterranean (Zezza, 1996). One of the most comprehensive overviews of process interactions was provided by Fookes *et al.* (1988). In this they identified the range of naturally occurring weathering processes associated with built environments and, more significantly, demonstrated that, although chemical weathering may be of significance in primarily hot, wet climates, many physical weathering processes are not restricted to what are perceived as aggressive climates. Moreover, they also demonstrated, through a survey of weathering rates from outcrops and structures in non-polluted environments, that significant natural alteration and surface loss can occur within the expected life spans of stone buildings or, over what they term as "engineering time".

4. Climatic Controls on Stone Decay

Most weathering studies (including that by Fookes *et al.*, 1988) rely upon macroclimatic distinctions when seeking to differentiate between environmental controls. These distinctions are normally drawn from meteorological observations collected in such a way as to rule out local variability and then averaged over varying periods to smooth out or remove fluctuations in time. It seems reasonable to assume, however, that these observations do not represent conditions experienced at the exposed stone surface of a building. Stone temperatures, for example, differ significantly from those of the overlying air and vary in response to many additional intrinsic and extrinsic variables. In turn, variations in temperature are the driving force behind most of the physical and many of the chemical processes responsible for stone decay. These include not only the obvious cases of freeze-thaw and thermal expansion/contraction, but also any processes influenced by wetting and drying. Because of this, geomorphologists with interests in desert landscapes have made significant contributions to understanding urban weathering environments. This is not simply a consequence of the presence of salts in both environments, but has much to do with a wider commonality, including large expanses of bare, unshaded stone/rock exposed to periodic wetting, high temperature ranges and absolute temperatures and rapid drying out assisted by strong winds (Table 1). Benefits have, however, accrued by the exchange of ideas in both directions and, in particular, processes of moisture absorption and loss from stone have been more systematically investigated on building stones than in relation to the far less

Table 1. A comparison of weathering in hot deserts and urban environments (modified after Winkler, 1973).

	Location/origins/timing	
Underlying causes	*Hot deserts*	*Urban environments*
Temperature contrasts	High	High (on walls)
Moisture from ground	High	High
Moisture from fog	Winter	Frequent
Moisture from condensation	Frequent	Frequent/winter
Salts	Desert floor/residual	Groundwater, stone weathering, polluted air, mortars
Damage	*Hot deserts*	*Urban environments*
Abrasion by wind	Strong	Some near street level
Frost action	Occasional/seasonal	High
Flaking by heat and moisture	Very strong	Moderate (stone-dependent)
Effloresence	Strong	Moderate but common
Sub-florescence	Strong	Moderate to strong
Case hardening/boxwork	Common, hollowed pebbles	Common between mortared joints
Rock coatings	Common, hard brown/black crusts	Light brown stains
Solution	Very slow	Very rapid in polluted atmospheres

predictable rains of desert regions. Thus, desert geomorphologists have much to learn from the work of building stone researchers in relation to water absorption and loss (see Camuffo, 1998 for a review).

4.1. Temperature Controls

Insolation, or temperature-induced weathering, was a preoccupation of desert geomorphology for much of the 20th century and no self-respecting review of desert weathering is complete without a table of rock surface temperatures (Cooke *et al.*, 1993; Goudie, 1997; Smith, 1994). There is debate as to the representativeness of these measurements and the extent to which they are biased by a pursuit of record high temperatures, but it does seem ironic that through them we probably know more about rock surface temperatures in the least populated parts of the world than in densely populated urban areas.

The process of insolation weathering was first generally invoked by returning desert explorers (Goudie, 1997), unsuccessfully simulated in early, somewhat crude experiments (Griggs, 1936) and finally reproduced as a series of minor modifications to stone surfaces (e.g. reflectance and microhardness) under carefully contrived laboratory conditions (Aires-Barros *et al.*, 1975; Aires Barros, 1977). However, the factor that is ignored or missed in these studies is that even under the supposedly sterile conditions found in deserts, temperature cycling of rock never operates in isolation from other processes or in the absence of other factors influencing the condition of the rock. Contrary to popular conception, water in small amounts is frequently available at rock surfaces via dew and fog, salts are often present in abundance and all rock outcrops and debris carry with them stress legacies reflecting, for example, their history of formation and exposure, past climatic regimes and, in the case of rock debris, possible transportation from areas of different climate as well as modification during transport (see Smith, 1994 for a review). The possibilities for these and other complicating factors are multiplied greatly for stone that is transposed to a built environment.

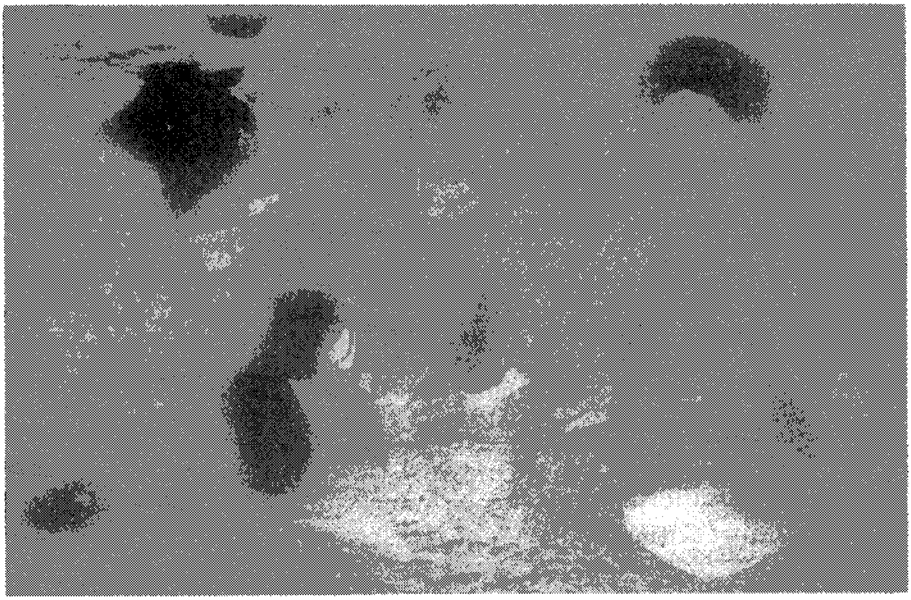

Fig. 2. Cavernous hollows in the Valley of Fire, Nevada, showing the concentration of active weathering in the shaded interiors of the hollows.

In addition to the hunt for proof of insolation weathering, the bulk of rock temperature data from deserts also reflects beliefs as to which temperature characteristics are most significant in controlling physical breakdown. Namely, the highest absolute temperature achieved, normally during summer, and the greatest diurnal temperature range. These values have in turn been those traditionally used in experiments designed to replicate not just insolation weathering, but also salt weathering and the relative durabilities of different rocks. More recently, however, alternative views on what constitute significant temperature controls have emerged.

(1) Firstly, it is readily apparent (Fig. 2) that most active weathering by salts within hot deserts (and on most buildings) takes place within cavernous forms (honeycombs and tafoni) and on shadow surfaces with greatly reduced maximum surface temperatures and diurnal regimes (Dragovich, 1967 and 1981; Rögner, 1987; Turkington, 1998). Within these caverns, moisture availability seems

to be the critical control on weathering rather than extreme temperatures. This view that was also expressed by Schattner (1961) working in the Sinai, who noted that granular disintegration of granites was more rapid and penetrated more deeply, where rocks were not subjected to the strongest insolation. Instead, disintegration was greatest on north- and west-facing slopes exposed to rain-bearing winds.

(2) Despite the perception of hot deserts as very homogeneous macroclimatic areas, in detail absolute temperatures and patterns of change over time are highly influenced by factors such as latitude, altitude, aspect (Smith, 1977) and time of year (Cooke *et al.*, 1993). With respect to the latter, environments that are perceived to be dominated by, for example, high temperatures and salt weathering may also be subject to processes such as frost weathering during winter months. It seems prudent to assume, therefore that resultant decay is the product of more than one process.

(3) The advent of thermistors and data loggers that allow a continuous record of temperature change, and infra-red thermometers that permit accurate measurement of surface temperatures, has focused attention on rapid fluctuation in surface and near-surface temperatures over minutes or tens of minutes. Jenkins and Smith (1990) showed, for example, that in the arid southwest of Tenerife, sandstone surface temperatures could fall up to 15°C within three to 15 minutes if insolation was blocked by cloud cover. The rates of cooling were in excess of 2°C per minute and were steeper than those experienced by the same test blocks during diurnal cooling at the end of the day. The significance of this is that, although such short-term fluctuations may only penetrate a few millimetres, they are concentrated in the zone where very important effects such as granular disintegration and multiple flaking occur. Moreover, there is the probability that fluctuations can occur many times during each day and that they would be particularly effective during winter months and/or at high altitudes where low air temperatures can lead to rapid cooling. These are times and places where, in the absence of high air temperatures, many thermally driven processes have been

presumed to "switch off". The identification of an additional level of thermal cycling also has possibly profound implications for the appropriateness and interpretation of weathering simulation experiments and building stone durability tests. In most cases, these use diurnal temperature cycles which penetrate several centimetres into a stone, but are designed to replicate damage and to measure material loss from grains within a millimetre or so of the surface.

(4) In the same way that it is dangerous to define any complex environment by a single thermal regime, it is misleading to impose it uniformly on the variety of rock types found there. Yet, this is precisely the strategy adopted in oven-based simulation and durability tests. There are good field observations to show that in the same natural environment, rock surface and sub-surface temperatures vary according to a range of thermal properties including thermal conductivity, heat capacity and, in particular, albedo (Kerr *et al.*, 1984). More recently, a combination of field exposure, heating under infra-red lamps and cycling in a conductive oven of four different rock types has confirmed this effect, and highlighted the fact that in nature, rocks such as basalt experience much more extreme temperatures than, for example, lighter coloured limestones and sandstones (Warke and Smith, 1998). The forcing of different rock types through the same heating/ cooling cycles in durability tests may also go some way towards explaining discrepancies between laboratory-based ratings of weathering effectiveness and stone durability on buildings exposed to natural climatic conditions.

4.2. Moisture Controls

As noted earlier, students of natural rock weathering have much to learn from the many detailed studies of moisture absorption, movement and loss that have been conducted in the course of research into urban stone decay. Understandably, such studies, at least of building exteriors, have tended to concentrate on damage associated with prolonged dampness or with moisture in excess. Hence, the emphasis on solution loss and damage caused by rising groundwater. However, studies of natural weathering in hot deserts have understandably tended to focus attention on constraints exerted by limited moisture availability, which may provide insights into the effects of limited quantities of water on stonework. Salt weathering, for example is principally concentrated on those parts of structures protected from direct rainwash and subject to direct precipitation from dew, fog and frost — in much the same way that many desert areas derive most of their moisture from these sources (Peel, 1975; Smith, 1994; Goudie, 1997).

One apparent consequence of frequent moistening with limited quantities of moisture in salt-rich environments is the development of a surface efflorescence that is unlikely to be dissolved except under exceptional circumstances of a severe storm or driven rain. It has been claimed, therefore, that under these circumstances salts crystallised near the surface might act as passive pore fillers (Smith and McAlister, 1986), preventing moisture penetration to any depth and effectively restricting any solution/crystallisation to an immediate surface zone of granular disintegration. Similar efflorescences appear on stone samples undergoing sodium sulphate durability tests and it seems evident that their development must affect the nature of these tests as they develop. Some preliminary experiments have shown, for example, that even after two or three cycles of wetting and drying with a weak salt solution (10%), the pattern of moisture loss from test blocks is altered. Solutions which initially penetrated both sandstone and Portland limestone blocks were seen to pond on the surface, leading to a rapid initial moisture loss by evaporation on heating, followed by a much slower loss of moisture sealed beneath a surface zone of salt-filled pores (Smith and Kennedy, 1999). The further significance of this observation is that tests which initially set out to quantify one aspect of stone durability may rapidly transform into a very different trial. So-called salt crystallisation tests might therefore become salt hydration tests or, in extreme instances of surface sealing, a differential thermal expansion test. Similarly, as successive cycles re-distribute salt within stone, the critical threshold for decay might not be the number and magnitude of the cyclic stresses to which it has been subjected, but the number of cycles required to concentrate salts in sufficient quantities within a critical zone needed to trigger effects such as scaling and flaking.

An additional effect noted in hot desert environments is that occasional, intense rainfall falling on bare rock surfaces is rapidly lost as overland flow. Similar effects have been described by Camuffo (1991) in Southern Europe, who noted the complete drying out of external and internal surfaces of monuments due to warming by strong solar radiation. As a consequence, rainfall from typical afternoon showers: "cannot initially penetrate into the pores and capillaries of the stone, because these are not lined by a monolayer of water molecules in the solid state that would allow for the liquid water to run over it" (p. 55). The combined effects of such drying out and possible passive pore filling, is to allow the development of a hydrophobicity in stonework that has not been investigated or appreciated in more temperate environments. Yet, its existence would require an important revision of the number and nature of the environmental cycles to which stone is deemed to be subject.

A final result of the regular deposition of moisture in small amounts on rock surfaces in deserts is the widespread development of iron- and manganese-rich rock coatings or varnishes (Oberlander, 1994). The wider range of surface coatings has been recently reviewed by Dorn (1998) who extends the classification to include lithobiontic coatings, carbonate crusts, case-hardening, heavy metal skins, silica glazes and oxalate crusts, whilst stressing that such crusts are not unique to hot desert environments. The study of such varnishes is relevant to stone decay at a number of levels. For example, data on the temperatures of varnished surfaces in deserts provide a range of insights into effects of a lowering of albedo and the impact this has on the thermal regimes to which soiled stones are subject (Warke *et al.*, 1996). Of equal importance, however, is the value of a large, parallel geological/geomorphological literature as a reference source for the growing number of observations of "urban" coatings, especially oxalate crusts (Del Monte *et al.*, 1987). The origins and implications of which remain largely unexplored. Literature on the effects of case-hardened layers might also help us to understand the consequences of the outward migration of iron in sandstones, both slowly under natural conditions and when accelerated by chemical cleaning. The breaching of these crusts and the hollowing out of weakened sub-surface layers is directly parallel to the formation of many cavernous hollows that are widespread across hot deserts and other salt-rich areas (Turkington, 1998).

5. The Direct Consequences of Placing Stone Within a Building

In urban environments, the act of placing a stone within a building exposes it to a range of additional stresses, most notably a range of potentially aggressive atmospheric chemicals. These can directly influence decay through reacting with the stone, or indirectly through either providing the ingredients (salts) for, or creating conditions amenable to, physical disruption. The latter can include the weakening of the stone through the selective dissolution of selected constituents or the creation of a secondary porosity that increases susceptibility to processes such as freeze/thaw. More significantly, and with less dependence upon local atmospheric pollution, placing a stone in any structure creates a wide range of physical and chemical conditions that make it more or less prone to damage from what would be considered as natural processes of weathering affecting an, albeit, somewhat unnatural rock outcrop. This includes modification of the climatic environment by the geometry of the structure and its relation to surrounding structures (see Ashton and Sereda, 1982), as well as modifications to the stone as a part of the construction process and the chemical and physical stresses exerted by surrounding materials. These factors can be grouped into three overlapping categories.

(1) *Temperature.* Building geometry can result in high temperatures on bare, exposed surfaces, but reduced temperatures and temperature ranges on shadow surfaces. Albedo can be lowered by soiling, leading to higher surface temperatures, increased diurnal ranges and higher internal temperature gradients. Urban heat island effects may reduce frost frequency and intensity.

(2) *Moisture.* Locally increased evaporation on surfaces exposed to insolation and where building geometry increases surface wind. Reduced evaporation in shadow areas with time of wetness also dependent on aspect. Selective wetting of surfaces determined by geometry, prevailing wind/rain direction and runoff pattern over

building surface. The possibility of rising damp if a damp course is absent or faulty and exposure to splash from road salts.

(3) *Construction effects.* Emplacement in a building can subject stone to compressive, shear and in some instances tensile stressing, but most importantly it typically constrains individual blocks during expansion caused by chemical alteration, expansion of interstitial salts and thermal and moisture cycling. Three dimensional geometry provides opportunities for "convergent" weathering as moisture, temperature and other environmental gradients interact across corners. The use of different stone types in combination can trigger decay where, for example, calcium sulphate salts produced by the reaction of atmospheric sulphur with carbonate stones can wash into adjacent, non-calcareous stonework (Cooper *et al.*, 1991). Similar contamination of non-calcareous stone can occur from surrounding mortars, whilst the use of "hard" mortars in combination with weaker stonework can lead to disruption of the stone during expansion, producing a honeycomb or "boxwork" effect as mortars are left proud of the retreating stone (Fig. 3). Finally, the surface dressing of the stone

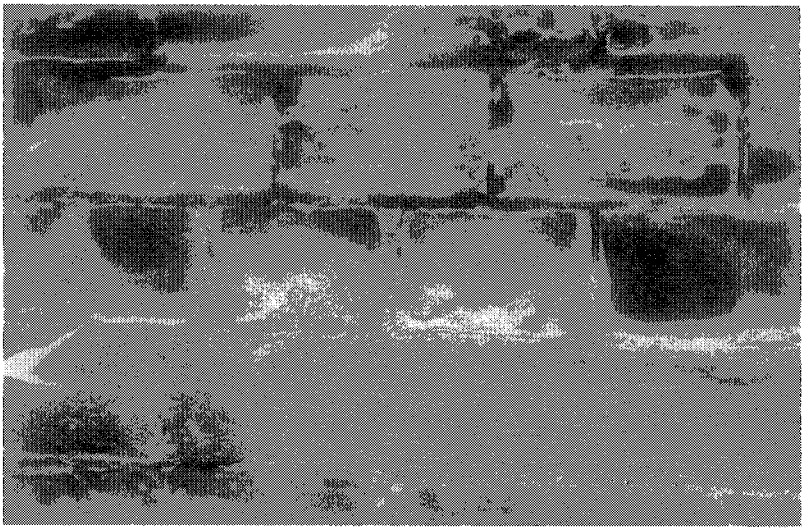

Fig. 3. A boxwork effect produced by the rapid weathering of sandstone blocks to leave a framework of harder and more resistant mortar (Durham Cathedral Close).

influences pollution deposition and patterns of decay. Roughened stonework provides a greater specific surface to react with the environment and sheltered hollows in which aerosols and salts can accumulate protected from rainwash. Smooth stone has reduced opportunities for particulate retention, but repeated environmental cycling normal to the exposed smooth surfaces increases the susceptibility of salt contaminated porous stone to effects such as contour scaling.

6. Rates and Patterns of Decay

Studies of natural weathering, whether by geologists or geomorphologists, take place within established conceptual frameworks. These may not necessarily be directly applicable to conditions experienced on buildings, but they do allow a systematic evaluation of long-term weathering variability in space and time that is beyond reactive studies of stone decay on often unique structures. Thus, because most studies of urban stone decay are dictated by the need to solve a specific problem, there is little underlying conformity in methods of study. Nowhere is the absence of theories and theorists more acutely felt than in consideration of rates of stone decay.

6.1. Temporal Variability

In the majority of cases where rates of decay have been interpolated between observations, or extrapolated from a short-term monitoring period, practitioners have assumed a steady and progressive change. This is loosely based upon geological principles of uniformitarianism, first developed in the 18th and 19th centuries, in which geological processes of erosion and deposition are perceived to occur at a steady, uniform rate and the processes responsible for present-day change are assumed to be the same as those that acted in the past to create similar effects. Such a rationale had the virtue, at the time, of moving geology away from the invocation of unspecified catastrophies to explain change, whilst drawing it closer to mainstream scientific ideas championing concepts of gradual evolution. Unfortunately, the strict application of uniformitarian principles to stone decay ignores many clearly observed characteristics of actual breakdown and loss. Invariably, damage is a response to discrete meteorological events such as a storm or a particularly severe frost and consequently much decay occurs episodically. Exposed stone is in fact generally characterised by long periods of quiescence or very gradual alteration interspersed with periods of rapid change, when internal resistance thresholds are exceeded and sometimes catastrophic damage occurs (Smith, 1996). These thresholds can be breached either by sudden exposure to severe conditions, as with frost, or they may represent the end-product of the gradual accumulation of stress within stonework. A common cause of this stress increase is the internal build up of pollution-derived salts such as gypsum. Indeed, it is generally accepted that it is pressure exerted by repeated crystallisation, hydration and/or differential thermal expansion of interstitial salts that is the main cause of urban stone decay in non-calcareous stones. An example of a hypothetical sequence of episodic decay is given in Fig. 4. This shows the high degree of unpredictability associated with decay and illustrates the difficulties of forecasting the lifetime behaviour of building stone from short-term observations of decay. Clearly, measurements taken during a period of quiescence will over-predict durability, whereas observations during a period of rapid change (disequilibrium) will produce an underestimate. Most importantly, however, Fig. 4 demonstrates the complexity of stone decay, its interactions with environmental factors and the way in which it invariably results from the synergistic interaction of more than one weathering mechanism. In this way, stone can reach a number of critical points during its lifetime when, once rapid decay is initiated, it either stabilises or accelerates until often complete blocks of stone are consumed by processes such as granular disintegration and multiple flaking (Fig. 5). At present, there is no clear understanding of what triggers the positive feedbacks within stone decay systems that lead to this progressive, catastrophic decay, nor the negative feedbacks required to stabilise stonework once rapid decay is initiated. Negative feedbacks may be related to factors such as a limited depth of weakened stone that is rapidly removed to expose a more resistant interior or the loss of salts concentrated near the stone surface. Whereas a

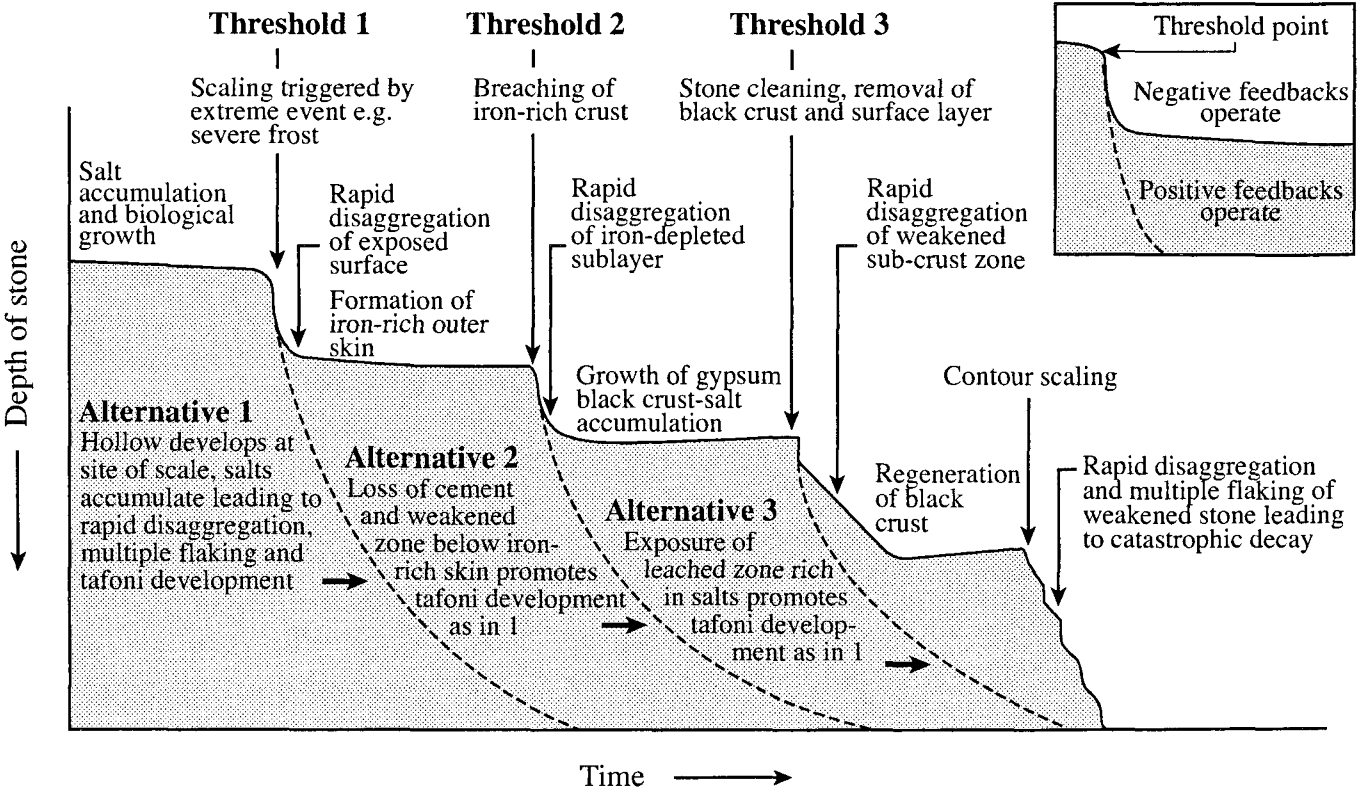

Fig. 4. Hypothetical schematic diagram illustrating the episodic decay of non-calcareous quartz sandstones in a polluted, salt-rich environment, with inset showing feedback options under threshold conditions (modified from Smith *et al.*, 1994).

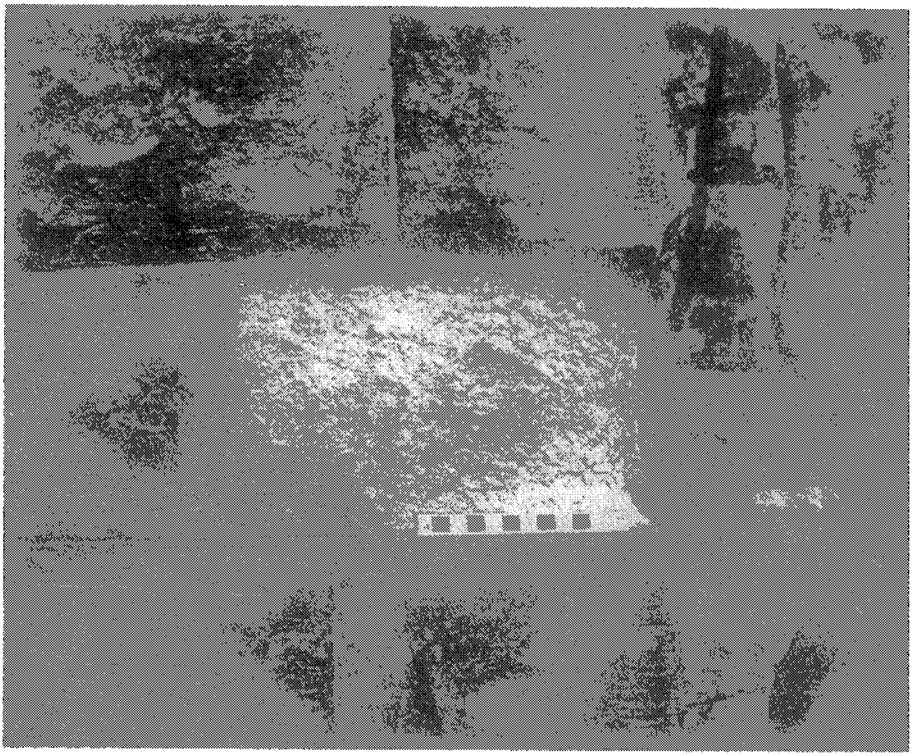

Fig. 5. Rapid, catastrophic decay of a sandstone block by a combination of granular disintegration and multiple flaking (Belfast).

positive feedback may be triggered by the creation of a humid microclimate in hollowed-out stonework that encourages a range of weathering processes. Whatever the mechanisms involved, it is likely that they are complex, interactive and most probably site and stone-type specific.

Whilst such episodic models of decay are most obviously applicable to stones such as sandstones, that are prone to effects such as sudden contour scaling (Fig. 6) and to processes such as salt weathering, they do have a wider applicability. Solution loss is, for example, by definition episodic — only occurring during and after precipitation.

Fig. 6. Contour scaling of a 19th century sandstone headstone to reveal a gypsum crypto-florescence (Belfast). For approximately 100 years, the stone would have exhibited little overt evidence of decay before the instantaneous loss of the contour scale.

Moreover, recognition of its episodic character allows a clearer appreciation of changes that occur between rain falls. This includes surface sulphation that would enhance subsequent solution loss and the possibility of physical weathering.

6.2. *Spatial Variability*

Assumptions of uniformity have also governed views on the spatial distribution of decay on buildings, yet it is self-evident that stone decay is spatially concentrated. This is often in relation to quite subtle environmental differences (exposure to rain, wind or sun), but also variations in materials properties such as porosity. This can be clearly seen on any complex building where, for example, black gypsum crusts accumulate only in areas protected from rainwash to produce an unappealing "patchwork" effect (Fig. 7). However, even on a flat surface of the same stone of the same age, individual blocks weather at different rates and exhibit different patterns of breakdown. This natural variability often confounds architects and owners of buildings

Fig. 7. The highly variable formation of gypsum black crusts on a church in the city of Bath, related to microclimatic conditions created by the geometry of the building.

who cling to the ideal of a building that "mellows" uniformly. It also means that prediction of decay over a whole building is very difficult, especially when durability predictions that dictate the initial choice of stone are often based on tests of a few small samples under unnaturally aggressive laboratory conditions (Smith, 1996).

7. Inheritance Effects

Natural weathering and erosion operate over such long time spans that it is normal to assume that rock outcrops and debris have long, complex and individual stress histories (Smith and Warke, 1997). This could be produced by climate change, spatial re-location (for example, from mountains characterised by frost weathering to lowlands dominated by chemical processes), or by changing conditions as rocks formed at depth are gradually exposed at the earth's surface. It should not be a surprise, therefore, that apparently identical building stones decay in different ways and at different rates because of different environmental and stress histories. Some of this legacy would have been put in place before the stone was quarried and/or prepared and used in construction (Table 2), but other effects reflect subsequent exposure to, for example, pollution. The most obvious instance of the latter is where pollution-derived salts accumulate within stone over a period of time, but it can include changes in stone properties such as porosity which exert a strong influence on salt weathering and solution loss. Some examples of pre- and post-emplacement effects are given in Table 2. Their greatest significance is that their influence can be unrelated to present-day conditions. Thus, removing atmospheric pollution may not halt decay that is driven by pollutants and weaknesses which accumulated in the past under "dirtier" conditions. This so-called "memory effect" must be an important consideration when projecting the likely success of any strategies for stone conservation or cleaning. In particular, it is the principal reason why replacement stone should not necessarily be sought as a match to the original, unweathered stone, but that it should be chosen to be visually, chemically and structurally compatible with the weathered stone.

Table 2. Possible inheritance effects found in urban stonework (from Warke, 1996).

Causative factors	Inheritance effects
Pre-emplacement factors	
Dilatation effects	Removal of overburden leads to compressional stress release in stone causing gradual opening of joint systems and microfracturing.
Microfracturing caused by quarrying	Quarry blasting can initiate microfracture development and/or propagate existing fracture lines.
Cutting and dressing of stone	May cause roughening of stone surfaces creating potential sites for subsequent accumulation of moisture, salts and organic matter.
Post-emplacement factors	
Thermally-induced microfracturing	Differential thermal expansion and contraction of surface mineral grains and interstitial salt deposits in response to long- and short-term temperature fluctuations may eventually lead to microfracture development.
Frost-induced microfracturing	Repeated freezing of moisture in pore spaces and microfractures may eventually lead to shattering of stone and loss of material.
Chemical dissolution	Dissolution of stone fabric alters surface pore dimensions and may facilitate the subsequent ingress of salt and moisture.
Soiling of stone surface	Soiling of stone surface by particulate deposition changes albedo, increasing absorption of solar radiation and hence surface/subsurface temperature conditions.
Surface crust development	Crusts act as salt reservoirs and can contribute to a decrease in substrate strength as material is leached out.
Salt accumulation and deposition	Interstitial deposition of salt contributes to stone decay through the mechanisms of intergranular crystallisation, hydration/dehydration and thermal expansion/contraction.

Table 2. (*Continued*)

Causative factors	Inheritance effects
Changes in surface morphology	Prolonged exposure to weathering processes leads to increased stone surface roughening allowing accumulation of moisture, salts and general particulate material which facilitate surface weathering processes.
Cleaning	Removal of crusts may expose a weakened substrate to attack by weathering mechanisms resulting in accelerated decay. Additionally, high pressure washing may drive salts deep into the stone fabric and application of biocides may damage individual grain structure and/or intergranular bonds.
Conservation treatments	Application of stone consolidants and other surface preparations alter surface characteristics, and may influence stone response to weathering processes.

8. Concluding Observations and Implications for Stone Conservation

Increased urban pollution undoubtedly accelerates building stone decay, especially on limestones where loss is primarily related to dissolution. Generally, however, it is salts derived from reactions between pollutants and stonework that are the most damaging agents of decay. The precise roles of pollution-derived salts in causing decay are however, very complicated. Firstly, salts can also originate from other sources ranging from groundwater and road salting to natural marine aerosols. It is therefore often difficult to dissociate pollution damage from underlying rates of weathering. Secondly, salt weathering rarely produces a gradual, widespread loss of material. It tends to attack certain blocks or surfaces and for many years there may be few overt signs of damage as salts accumulate and stone is weakened internally. This relative quiescence can be interrupted by a dramatic loss of material, which may eventually be halted as stone achieves a new equilibrium, but can also result in the complete destruction of stone blocks. This sudden breakdown can be triggered by an extreme event such as a severe frost or it can represent the culmination of a long buildup of stress within the stone which finally exceeds the stone's strength to resist. If the existence and nature of episodic decay is not understood, it is very tempting to ascribe accelerated decay simply to increases in pollution levels. This ignores decay that results from the long accumulation of pollution effects and is an overall function of the age of the structure. In crude terms, the older the building the more susceptible it becomes to damage and the more rapidly it weathers.

This willingness to explain accelerated decay solely in terms of increased atmospheric pollution, is also symptomatic of an attitude amongst many people that once stone is placed in a building it should last for ever. This forgets that all stone weathers naturally and that, even without the added complications of pollution, placing stones within a building exposes them to greater stresses than they would experience in natural outcrops. These can result from concentrated loading by other stones, contact with chemically aggressive mortars and renderings and placement next to other, chemically incompatible stone types.

The fact that building stones can carry a "memory" of past pollution and treatment is frequently ignored or discounted when stone is cleaned. This applies especially to structures that do not arouse public interest and thus do not generate specific research into their condition. Under these circumstances many of our "lesser buildings" are prone to "cleaning by formula". This may successfully remove superficial grime, but possibly at the expense of also removing a layer of underlying stone, the mobilisation of salts into areas where they can cause damage or the exposure of weakened sub-surface layers. Without careful consolidation of the newly exposed stonework, decay may therefore proceed more rapidly than on the original, grimy surface.

Much cleaning is also being carried out in the belief (or promise) that pollution legislation has successfully created urban environments in which it is once again safe to expose clean stonework. Local emission-based regulation cannot, however, legislate for continued

Fig. 8. The rapid re-soiling of the Portland Limestone of Belfast Technical College, some seven years after cleaning in the mid-1980s. Note the decrease in soiling away from road level.

transregional inputs of pollution. Similarly, most legislation is retrospective in that it is the reaction to a particular problem, filtered by the time that national and international legislatures need to agree on an important strategy. By the time that one pollution source is countered (for example, domestic burning of sulphur-rich coal), the problem is invariably superseded by a new pollution source. In the UK, we are seeing this effect on our buildings as soiling is increasingly concentrated near ground level in response to vehicle emissions. Thus it is now common to see buildings that were cleaned a few years ago — in the belief that urban smogs were a thing of the past — beginning to show the re-growth of black stains and crusts (Fig. 8).

Finally, much of society's attitude towards building stone decay, not the least those of owners, is that once constructed, buildings should remain pristine. It may be more realistic and ultimately much less expensive, if we come to accept that buildings naturally change and decay over time. Because of variations in microclimate and materials, different parts of buildings will weather in different ways and at different rates. Moreover, the gradual accumulation of natural and anthropogenic stresses within stonework is likely to mean that rates of decay will accelerate over time. Thus, whilst striving not to add unduly, through pollution, to the stress that structures are subject to, we have to accept that they have a finite service life.

Acknowledgements

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CHAPTER 3

MECHANISMS OF AIR POLLUTION DAMAGE TO STONE

C. Sabbioni

1. Introduction

Stones constitute one of the most widely used materials in historic monuments and buildings. Therefore, the study of the effects of air pollution on these materials was one of the first to be undertaken with the aim of understanding the physico/chemical, and more recently, biological mechanisms leading to the degradation of the cultural heritage. There is general consensus and wide evidence (Fig. 1), that the damage encountered on building stones in urban environments is predominantly due to air pollution (Winkler, 1973; Amoroso and Fassina, 1983).

While the main qualitative processes involved in pollution-related stone degradation are generally accepted to be gypsum formation and carbonate dissolution, knowledge on the quantitative relationship between pollutants and stone damage remains sparse and continues to generate debate.

The damaging effects of gypsum arise from its far greater solubility in water compared to calcium carbonate. During wet periods, gypsum can dissolve and be transported deep into the pore system of stone. When the stone dries, gypsum re-deposits on or inside the stone, where it produces further damage, due to its higher specific volume compared to calcite, through cycles of dissolution-crystallisation and

(a) (b)

Fig. 1. Stone decay in urban environments has rapidly increased over the last hundred years. The two photographs show a marble bas-relief dated 1377: **(a)** taken in the early years of the 20th century (Poppi collection, Historical Archives of the Cassa di Risparmio di Bologna), and **(b)** as it is today.

hydration-dehydration (Arnold, 1981; Lewin, 1982). On the basis of S isotope ratios, Pye and Schiavon (1989) demonstrated that the sulphur found in gypsum crusts on building stones always originates from an atmospheric source. Therefore the formation of calcium sulphate on calcareous stone occurs through a reaction with the sulphur species contained in the air (dry deposition) or dissolved in rainwater (wet deposition).

Stone decay is also attributed to the acidity of rainwater, caused by contaminants such as sulphur and nitrogen oxides, as well as carbon dioxide. "Acid rain" corrodes the stone by penetrating the pore structure and reacting with the materials. In particular, calcium salts, which often serve to bind the crystal grains, are highly susceptible to dissolution by acid solutions. Evidence of such processes has been reported in Europe and America (Martinez and Martinez, 1991).

Numerous studies have addressed this very serious problem; in general, they have proceeded in three major directions: (1) studies performed directly on monuments and historic buildings with the aim of identifying the different components due to atmospheric pollution responsible for stone damage, (2) chamber tests performed in the laboratory to examine the interaction between pollutants and stones, and (3) field exposure tests to study the damage produced on stones by different microclimatic and pollution conditions. The main results of these investigations are summarised below.

2. Damage on Stone Buildings and Monuments

Henley (1967) showed that the calcium carbonate (calcite) in stones may be almost completely replaced by gypsum or by a hard black carbonaceous deposit. This pioneering study showed how gypsum formation does not affect the stone homogeneously; the matrix material is almost completely transformed, while the fossil contained in the limestone has little or no deposit, a discrepancy that permits the estimation of the rate of erosion.

Since then a number of studies have been performed on monuments and historic buildings with the aim of identifying the different typologies of damage layers, their composition and origin. In spite of this, the availability of quantitative data remains relatively limited.

In studies on damage, the classification of stone types needs to be related more clearly to degradation mechanisms than geological criteria (genesis, grain size and mineralogical composition). The key properties of stone with reference to deterioration are: (a) chemical composition and (b) porosity (Viles *et al.*, 1997). For this reason, the papers reported in the literature are reviewed here according to the following categories: (1) marble and limestone, (2) stone with high porosity, such as sandstone, and (3) granite.

2.1. Marble and Limestone

The earliest and most extensively studied stones are marble and limestone, largely because they have been widely used internationally in statuary and buildings. At the same time, they represent a more simple system than other stones thanks to their chemical homogeneity, being almost entirely composed of calcium (or, more rarely Ca and Mg) carbonates, and low porosity which permits the identification of an interaction interface between the atmosphere and stone.

The damage typologies observed on monuments built in marble and limestone are related to the way rainwater wets the surface. *White areas* are found where rainwater runoff dominates, producing the dissolution of the carbonate rock so that the original colour of the stone is evidenced. *Black areas* are observed on stone surfaces wetted by rainwater but sheltered from intensive runoff, being the areas where atmospheric pollutants accumulate, along with the products of reactions between stones and atmospheric gas and aerosol. Protection from leaching by rain washout favours the formation of crusts, which are black in colour due to the atmospheric particles they embed during their growth. Water from fog or dew is in general insufficient to "activate" any dry deposit on stone surfaces or to dissolve the calcite (Camuffo *et al.*, 1982).

White areas

To determine the material loss of stone buildings and monuments incurred by wet deposition, typical of white areas, several methods have been employed.

Microerosion measurements have been made of the difference in depth of erodable material using fossil fragments that protrude above the present-day surface as reference level; the fossil fragments were considered to be weathering resistant and to represent the original surface of the stone. In a similar way, lead plugs filling holes have also been used as a reference plane for the original stone surface (Sharp *et al.*, 1982). Using these methods, the rate of surface recession of Portland limestone measured on St. Paul's Cathedral over the period 1980–1985 was on average 0.06 mm/y (Trudgill *et al.*, 1990).

A number of studies have been performed on tombstones. Baer and Berman (1983) measured the depth and thickness of inscriptions on tombstones in marbles from Vermont, Georgia, Massachusetts and Mississippi. They found recession rates ranging from 3.6 mm/100y (Philadelphia, PA) to 2.8 mm/100y (Cypress Hills Cemetery, NY) for urban areas and the value of 1.7 mm/100y for a suburban site (Long Island Cemetery, NY). They concluded that finer grained marbles are eroded more rapidly than coarse-medium grained stones or dolomitic marbles, and that local sources dominate the deposition of pollutants.

Another way of evaluating the wet material loss of a stone is to collect and analyse runoff water, i.e. rain water that has flowed over its surface. This method also provides insight into the leachable reaction products forming during the rainfall event (Leysen *et al.*, 1987; Roekens and van Grieken, 1989; La Iglesia *et al.*, 1994). Measurements performed on St. Paul's Cathedral, London, gave a rate of limestone erosion of 0.27 mm/y, much higher than the values obtained from microerosion meter measurements. The relative standard deviation, found to be 115%, reflects the complex nature of the erosion process (Butlin *et al.*, 1985).

At Gettysburg (Pennsylvania, USA), runoff from small, well-defined catchment areas washed almost entirely by direct precipitation, was collected from two Carrara marble statues, a Carrara obelisk and a Pennsylvania blue marble obelisk (Dolske, 1995). Current meteorological and air quality data were collected to compute the dry deposition of sulphur dioxide (SO_2), nitric acid and sulphate and nitrate aerosol between the rain intervals. Thus both wet and dry deposition of atmospheric pollutants was examined. The data indicate that marble loss from a complex carved surface is several times greater than that from flat vertical surfaces of comparable petrography and exposure history. The author points to the need for adjusting weathering rates based on simple geometry when applied to monuments and statues with more complex surface geometry. The sulphur flux calculations indicate that the bulk of the sulphur is deposited when the marble is dried.

Black areas

Black crusts, studied extensively by numerous authors on monuments all over the world, are found to be composed mainly of calcium sulphate (identified as gypsum) and carbonaceous particles (soot). Most of the literature gives evidence of these components on the basis on analyses performed by optical microscopy, scanning electron microscopy and X-ray diffractometry; examples are reported for monuments in Turkey (Caner *et al.*, 1988), Poland (Haber *et al.*, 1988), Spain (Carretero and Galan, 1996), Greece (Chabas and Lefevre, 1996) and Italy (Garcia-Valles *et al.*, 1997).

The gypsum crust presents a crystalline habit, generally laminar and only rarely globular or acicular, depending on the growth rate of the crystals (Lewin and Charola, 1978; Alessandrini, 1992) and can vary in thickness between 10 μm and 10 mm (Del Monte *et al.*, 1981; Margolis *et al.*, 1988).

The origin of sulphur in gypsum crust formation on monuments has recently been investigated by means of sulphur isotope measurements (Torfs *et al.*, 1997). Relatively large variations of sulphur have been found in gypsum crusts on monuments situated in the centre of Antwerp (Belgium), its suburbs and the surrounding area. More heavy sulphur is encountered in the centre of Antwerp. The variation in the sulphur (S) isotopic composition of the crusts coincides geographically with the variation of SO_2 in the atmosphere, although generally the crusts present a higher $^{34}S/^{32}S$ ratio than the surrounding atmosphere. The petrochemical industry in the harbour is thought to be the main SO_2 emitter in the north of Antwerp, while in the southern region, the local brickyard industry influences the isotopic composition of SO_2 and the damage layers on the stone. The authors conclude that SO_2 makes a greater contribution to gypsum crust formation on stone than the sulphate (SO_4^{2-}) from rainwater.

The atmospheric particles embedded within the gypsum crusts have been analysed and, on the basis of their morphology and elemental composition, different types of particles have been identified, which can be summarised under three general categories: porous carbonaceous particles (soot), smooth aluminosilicate particles, and metal particles mainly composed of iron (Del Monte *et al.*, 1981; Esbert *et. al.*, 1996; Derbez and Lefevre, 1996). The pollution sources emitting these particles have been identified as fuel oil combustion in domestic heating systems and electric power plants, coal combustion, gas oil emission (Sabbioni, 1995), vehicle exhaust (Rodriguez-Navarro and Sebastian, 1996) and biomass combustion (Ausset *et al.*, 1992).

Whether atmospheric particles simply incur aesthetic damage or play a role in the actual formation of the gypsum crust has been the subject of debate. Carbonaceous particles have been cited as damaging to stones since they are responsible for the blackening of the patina, seriously impairing the appearance of monuments, and are catalysts of the SO_2 oxidation process on stone surfaces (Amoroso and Fassina, 1983).

Few quantitative data are reported on the concentrations of the main components present in the black crusts (Table 1). The amount of sulphate is generally over 30% and among minor components, nitrate and chlorides are present in amounts around or above 1%.

When gaseous and aerosol pollutants were measured at different heights on the Column of Marcus Aurelius in Rome, the composition of the black crust was found to relate to the concentration in the air of SO_2 and total suspended particles mainly emitted by domestic oil heating and traffic, particularly diesel engines. Although the high NO_x concentration measured in air is not reflected in the presence of nitrates, the hypothesis is advanced that nitrogen dioxide (NO_2) can enhance the oxidation of SO_2, especially in the presence of metal and carbon particles, which act as catalysts (Brocco *et al.*, 1988). These data are in agreement with Livingston (1985), whose review of nitrate measurements on carbonate stones (marble and limestone) indicated that the nitrite (NO_3^-) concentration never exceeds 3% in weight, which is a factor of ten or more lower than that of SO_4^{2-}.

Table 1. Soluble salt concentrations (%) measured in the black crusts.

	Brocco *et al.* (1988)	Fassina (1988)	Sabbioni and Zappia (1992a and b)	Torfs and van Grieken (1997)	Moropoulou *et al.* (1998)
SO_4^{2-}	41.3	43.7–69.7	31.5–48.5(*)	31–40 (+)	39.4–60.8
NO_3^-	0.17	0.01–0.25	—	0–0.5 (+)	0–1.36
Cl^-	0.05	0.07–0.52	0.02–0.7	0.1–0.9 (+)	0.13–0.76

Note: (*) Calculated from $CaSO_4.2H_2O$ concentrations.
(+) Only data referring to black crusts are reported.

The sulphation process, that is the transformation of calcium carbonate into calcium sulphate dihydrate, can proceed via two principal reactions:

(1) SO_2 is adsorbed on the stone and reacts with calcium carbonate and water to form calcium sulphite as an intermediate product, which is then further oxidised to gypsum;
(2) SO_2 can also be transformed to sulphuric acid (H_2SO_4), either directly on the stone or in the air, and the subsequent attack on the carbonate leads to the formation of a gypsum crust.

To better understand the importance of the first reaction pathway, Roekens *et al.* (1989) measured the sulphite (SO_3^{2-}) and SO_4^{2-} content on the limestone of two historic buildings in Belgium using ion chromatography (IC) and spectrophotometry. A mean concentration of SO_3^{2-} of 0.05% was found, far lower than the SO_4^{2-} concentration, which ranged from 2 to 37%; the SO_3^{2-}/SO_4^{2-} is on average 0.73.

Quantitative data on sulphite in damage layers are also provided by Gobbi *et al.* (1998) in their presentation of a new methodology for the simultaneous identification and quantification of sulphite and main anions present in the black crusts. The data obtained, ranging from 210 to 2600 ppm, confirm the formation of sulphite as an intermediate stage in the mechanism of interaction between SO_2 and carbonate stones. Bacci *et al.* (1997) propose the principal component analysis of diffuse reflectance near-infrared spectroscopy (NIR) as a non-destructive methodology for discriminating $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ in calcareous samples.

The carbon compounds present in the damage layers on building materials may have four different origins: (1) calcium carbonate, deriving almost exclusively from the stone (Zappia *et al.*, 1993); (2) deposition of atmospheric particles containing elemental and organic carbon, as primary and secondary pollutants (Saiz-Jimenez, 1993; Turpin and Huntizcker, 1995); (3) biological weathering due to the action of micro organisms such as fungi and lichens, one of the major products of which is oxalic acid, which reacts with the underlying materials, leading to the formation of calcium oxalates (Sabbioni and Zappia, 1991; Saiz-Jimenez, 1995); and (4) surface treatments (oils, waxes, proteins, etc.) frequently used in the past to protect monuments and historic buildings (Rossi Manaresi, 1996).

The total carbon (C_t) present in the black crusts can be considered as being composed of two main fractions:

$$C_t = C_c + C_{nc} \tag{1}$$

with C_{nc}, composed by:

$$C_{nc} = C_e + C_o \tag{2}$$

where C_c is the carbonate carbon, basically due to the stone, and C_{nc} is the non-carbonate carbon, which includes the organic carbon C_o of biogenic and anthropic origin, while the elemental carbon C_e is predominantly a product of combustion processes. The measurements performed on black crusts from stone monuments and buildings in Bologna and Rome were found to contain mostly non-carbonate carbon (90% of Ct), showing concentrations ranging between 2.69 and 1.48%, of which 40% is formed by elemental carbon, a parameter which is linked to the soot embedded within the damage layers. The remaining organic fraction is mainly composed of oxalates, along with other organic compounds, such as formates, acetates n-alkanoic acids, polycyclic aromatic hydrocarbons (PAH) and ethyl esters (Sabbioni *et al.*, 1996a). These organic constituents are tracers of specific anthropogenic sources typical of urban areas, such as vehicle exhaust, road dust, industrial combustion and domestic heating systems (Rogge *et al.*, 1993a and b).

Among organic compounds, calcium oxalates have been widely encountered on stone building surfaces and have been identified as whewellite and weddellite, the mono- and dihydrate calcium oxalate, respectively (Cipriani and Franchi, 1958; Franzini *et al.*, 1984; Guidobaldi *et al.*, 1985; Alessandrini *et al.*, 1989). Whether their origin is linked to protective treatments, biological weathering or pollutant deposition is the subject of controversy, and at present the data are generally insufficient to exclude any of the origins suggested (Realini and Toniolo, 1996), except in the case of studies specifically performed on single monuments.

A number of metals have been measured within the black crusts and some average concentrations found in the damage layers sampled

Table 2. Average concentrations (ppm) of heavy metals measured in the black crusts on stone monuments in different urban sites.

	V	Mn	Fe	Ni	Cu	Zn	Pb
Marble and limestone							
Milan*	72	236	18796	13	50	258	883
Venice*	29	58	3779	38	11	59	123
Rome*	44	133	8061	22	195	118	532
Bologna*	58	113	14090	<10	49	177	427
Eleusis†	20	200	9000	40	40	300	300
Sandstone and calcarenite							
Brussels‡	186	120	16116	13	105	873	516
Bologna¶	34	152	653	12	20	48	160
Granada§	18		1655	13	12	40	40

(*) Sabbioni and Zappia (1992a)

(†) Torfs and van Grieken (1997)

(‡) Leysen *et al.* (1990)

(¶) Sabbioni and Zappia (1992b)

(§) Rogriguez Navarro and Sebastian (1994)

on marble and limestone monuments in towns of the Mediterranean Basin are reported in Table 2. It can be observed that iron is the most abundant metal at all the sites and the concentrations of remaining metals show a similar order of abundance, indicating that the components contributing to black crust formation have a common origin.

The enrichment factor (EF) of various elements with respect to the carbonate rock have been calculated to identify the component due to the deposition of atmospheric gas and aerosols on the stone surfaces. The average elemental composition of carbonate rock reported by Mason (1966) is used and Ti has been assumed as indicator element:

$$EF_{\mathrm{carb.}}(X) = \frac{(X/Ti)\,\mathrm{Black\ crust}}{(X/Ti)\,\mathrm{Carb.\ rock}} \tag{3}$$

where X is the concentration of the investigated element and Ti the concentration of the indicator element in the black crusts and carbonate rock, respectively. By convention, a "cut-off" EF value of 5, a purely arbitrary value, is used to distinguish the origin of the elements. An EF < 5 was taken as an indication that the elements have a significant stone origin and they are considered non-enriched. An EF > 5 is assumed to indicate that a significant proportion has a non-stone origin and is enriched due to atmospheric deposition. At various Italian urban sites, Mg, Al, Si, K, V, Fe, Ni, Mn and Sr were not enriched and the elements showing a non-stone origin were Na, S, Cl, Cu, Zn, Br and Pb (Sabbioni and Zappia, 1992a and b). It should be noted that although iron presents the highest concentration among the heavy metals, it is not due to atmospheric deposition. In maritime sites of the Mediterranean Basin, Torfs and van Grieken (1997) found enrichments for Cl and Na in all sites, while S and Pb were found in some cases; for the other elements the EF were very small, indicating almost no deposition.

2.2. Sandstone

Porous limestones have been widely used in buildings and monuments, thanks to the ease with which they are quarried and worked. Less attention has been focused on damage to stones of high porosity, such as sandstones and calcarenites (Stambolov and van Asperen de Boer, 1972; Rosvall, 1988). Sandstones are sedimentary rocks composed mostly of mineral and rock fragments within the sand-size range (2 to 0.06 mm) and a minimum of 60% free silica, cemented by various materials, including carbonates, while calcarenites are limestone composed predominantly of clastic sand-size grains of calcite (ASTM, 1989).

In the literature, the main degradation mechanisms proposed for these materials are:

(1) The formation of damage layers mainly composed of gypsum on the surface, weakly linked to the underlying rock and therefore subject to easy exfoliation (Rossi Manaresi, 1975; Andersson, 1985; Weber H, 1985; Twilley and Podany, 1986; Mirwald *et al.*, 1988; Fobe *et al.*, 1993). The process is due to the sulphation of the carbonate component of sandstone owing to atmospheric deposition, with the formation of a gypsum patina embedding carbonaceous particles and soil dust (Sramek and Eckert, 1986;

Leysen *et al.*, 1989, Pavia Santamaria *et al.*, 1996). The structure of the stone controls the rate of gypsum formation, which is claimed to alter the original porosity of the stone (Kozlowski *et al.*, 1990).

(2) The dissolution and transport of soluble salts by water circulating within the stone (Winkler, 1982; Subbaraman, 1985; Blaeuer, 1985); the subsequent recrystallisation of these salts produces mechanical stress which can disaggregate the material (Lewin and Charola, 1978).

(3) The formation of calcium oxalate layers (Jones and Wilson, 1985), identified as whewellite and weddellite by Alaimo *et al.* (1986). These alteration patinas have been linked to biological weathering due to the action of micro organisms, such as fungi and lichens, at the stone surface (Krumbein, 1988; Warscheid *et al.*, 1990).

(4) Mechanical erosion due to the action of sand and marine salts transported by the wind (Lal, 1978). This kind of damage produces the segregation of grains, the formation of step profiles and leaves a rough, honeycombed surface (Agrawal *et al.*, 1986).

Only the first two mechanisms are considered to be related to the effects of air pollution, while the third is the subject of discussion, as already mentioned for marble, and the fourth is a typical effect of natural weathering.

The damage patterns on sandstone or calcarenite present entirely different visual features from those described for marble and limestone, the surfaces being blackened homogeneously, regardless of their geometry (Sabbioni and Zappia, 1992b; Camuffo, 1998). The diverse damage feature is ascribed to the different mechanisms of deposition and resuspension of atmospheric particles (particularly carbonaceous particles, responsible for the colour of the crusts) occurring at the surface of the monument. Such stones present high surface roughness due to their intrinsic porosity and mineralogical dishomogeneity, which prevent smoothing and polishing. Furthermore, the wetness of a surface is highly favoured by the presence of pores and capillaries, since condensation occurs at relative humidity below 100%. Surface roughness and high porosity facilitate the deposition of gas and particles, at the same time reducing the removal of particles and damage products by resuspension and washout. Thus on porous stones, the mechanisms of particle deposition and capture are more efficient, while those mechanisms tending to remove particles from the surface after their deposition are less efficient. These synergistic effects produce the homogeneous blackening typical of historic buildings and monuments built in porous stones.

The distribution of damage patterns has been examined on churches built in sandstones in the West Midlands, England, where the total blackened stone was found to be less than 10% in rural environments, while reaching values greater than 40% in urban areas. The use of coal as the dominant domestic and industrial fuel appears to have been an important source for much of the blackening encountered (Halsey *et al.*, 1996).

On sandstone and calcarenite, two damage layers of surface damage have been distinguished: (1) a surface layer (A) of a few millimetres thickness with a composition similar to the black crusts analysed on marble and limestone and (2) a disaggregate layer (B) of the order of one centimetre, where the dissolution of the carbonate matrix occurs due to atmospheric acid deposition, which produces the decohesion of the sandy grains. The detachment of layer A also causes the complete loss of layer B, exposing the underlying undamaged stone to a new cycle of damage (Sabbioni and Zappia, 1992b). The multiplication of decay layers, progressing from the outer surface of the exposed stone toward the interior was first described by Lewin (1982).

Layers A found in Bologna presented average concentrations of 64.4% of gypsum and 1.1% of non-carbonate carbon (C_{nc}), which is assumed as a quantitative marker of the amount of embedded carbonaceous particles (essentially soot) deriving from fossil fuel combustion (Sabbioni and Zappia, 1992b). Concentrations of heavy metals measured on sandstone and calcarenite monuments in European towns are reported in Table 2.

The deposition of atmospheric particles on the sandstone surface is indicated to increase the rate of gypsum formation. Black soiling is also claimed to increase stone deterioration by physical stresses due to a lowering of the albedo of the stone, which increases the absorption of incident solar radiation. As a consequence, the blackened surface layer experiences increased heating/cooling cycles, wetting/drying cycles and thermal expansion: gypsum hydration/dehydration cycles exacerbate stress, producing the detachment of the surface layer A of the stone (Halsey *et al.*, 1996).

2.3. Granite

Granitoid rocks have received scant attention although they have been widely employed because of their good mechanical properties and durability (Lazzarini, 1993).

Two types of damage layers, of different composition and origin, have been found on granite:

(1) Gypsum crusts, where almost all constituents are allochthonous and are due to the deposition of air pollutants; and
(2) Clay-calcitic layers, whose constituents are due to the original rock and must be considered as weathering layers, being a natural evolution of granite (Jeannette, 1980 and 1981).

Pollutants and particularly pollution-derived salts, such as gypsum, are initially confined to the surface stone, but they represent potential agents of degradation as they produce a widespread microfracture network, which confers a much higher porosity than would normally be encountered on such rocks. The secondary microporosity allows the penetration of pollution-derived salts which produce mechanical and chemical change in the rock mass (Neill and Smith, 1996). Alongside gypsum, calcium chloride and calcium nitrate have also been found (Urquhart *et al.*, 1996). The presence of roadside dust and fly ash particles has been shown on granite buildings in urban environments and the fly ash is claimed to be a possible source of the gypsum, which forms a thin black crust (Smith *et al.*, 1993). In some cases, many successive layers of degradation have been recognised, all of them similar in character, with thicknesses ranging from a fraction of a millimetre to 1 or 2 mm (Lewin, 1982).

3. Chamber Tests

In dry deposition, sulphur may either adsorb and react directly with the stone surface, or may first react with the water present in the stone, and subsequently, with the calcareous material. The rate of SO_2

deposition depends on a number of factors. The concentration of SO_2 is obviously important, since the number of molecules colliding with the surface in a unit of time is linearly dependent on it. The presence of oxidants, such as NO_2 or ozone, may strongly enhance the process, since they catalyse the oxidation of the adsorbed species containing four-valent sulphur or calcium sulphite to sulphate. Humidity also plays a major role in the process. Finally, the nature of the stone itself affects the rate of SO_2 deposition to a considerable degree. Polished marbles have been found to adsorb less SO_2 than rough and porous limestone surfaces. The susceptibility of various stones to the corrosive action of SO_2 was found to depend strongly on their pore structure, which in turn can control moisture equilibrium in the stones (Kozlowski *et al.*, 1992). So far, very little is known on how stone-corroding pollutants are distributed in the materials (Mirwald, 1991).

One approach towards defining the key physical and chemical parameters is to conduct controlled laboratory studies set up to determine their impact. The literature reports laboratory tests on building stones performed primarily with the aim of studying the effects of exposure to SO_2.

Simulation tests on various stones, notably marbles, limestones and sandstones, have been performed in the laboratory utilising both static and flow climatic chambers for the control of temperature and relative humidity with different gas concentrations (mainly SO_2, NO_x and O_3) and particles.

SO_2 deposition was determined indirectly by measuring the decrease in the gas concentration in a chamber after exposing the test specimens (Gilardi, 1966; Braun and Wilson, 1970). This indirect method may be prone to significant experimental error owing to deposition on to the chamber walls. The alternative method of directly measuring the amount of material deposited on specimens requires long exposure periods or abnormally high SO_2 concentrations in the chamber to increase the amount of deposit and facilitate direct analysis (Johansson *et al.*, 1988; Gauri *et al.*, 1989). Radioactive sulphur ($^{35}SO_2$) has been used in chamber studies and the deposition on material surfaces measured directly by beta-counting techniques (Spedding, 1969a; Serra and Starace, 1973; Fuzzi and Vittori, 1975). The effects of wet deposition of SO_2, NO_x and ozone (O_3) were investigated in a flow chamber, which allowed the rinsing of the specimens with different kinds of water solution, in analogy to field exposure tests, where the runoff is collected and chemically analysed (Dickinson *et al.*, 1988).

Accelerated tests have generally been designed in order to: (a) investigate the degradation process; (b) study the durability of different building materials, and (c) evaluate the efficiency of a specific preservation treatment (Gauri *et al.*, 1973; Rossi Manaresi *et al.*, 1979). This section will briefly address only point (a).

The results achieved using accelerated weathering tests can be grouped according to three lines of research:

(1) The influence of various parameters with potential impact on the degradation process.
(2) The study of the synergistic action of such parameters.
(3) The consideration of the way in which the transformation takes place at the stone surface.

However, the current reality is that the quantity of detailed results on stone materials of relevance to monument conservation is both very limited and heterogeneous with respect to the above-mentioned research topics. In view of this, it is hardly surprising that modelling in the field is in a very unsatisfactory state. As yet, there is no state equation available for stones that is valid in ambient conditions, and only mostly descriptive damage functions have been proposed. Such difficulties explain why no reliable quantitative predictions exist for stone damage.

Radioactive labelling of SO_2 ($^{35}SO_2$) has shown that the rate of absorption and transformation of SO_2 to the oxidised state depends on relative humidity and surface characteristics.

Spedding (1969b) reported that the saturation of a stone surface with SO_2 is reached rapidly, with the rate of uptake depending on relative humidity (SO_2 was taken up only by the matrix material and not by the fossil). Measurements of SO_2 uptake in laboratory exposure apparatus showed that a humidity of around 90% is essential for the progress of the corrosion reaction (Serra and Starace, 1978). These early results indicated that it is the presence of water which is the key factor in the conversion of calcite to gypsum, and thus, in the corrosive action of an SO_2-containing atmosphere on the stone.

Spiker *et al.* (1992 and 1995) found that the surface reaction process is controlled below a critical relative humidity, which is 70% for a limestone (Indiana) and 95% for a marble (Vermont), confirming the crucial role of pore size distribution in determining the degree of damage.

According to the results achieved in simulation chamber experiments (Gauri and Holdren, 1981; Mangio and Johansson, 1989; Gauri and Gwinn, 1982; Johansson *et al.*, 1988; Sabbioni *et al.*, 1996b), the sulphation of stones takes place through two basic mechanisms: (1) the direct formation of gypsum and (2) the formation of calcium sulphite, as an intermediate stage, followed by oxidation into calcium sulphate dihydrate. The reactions occurring at the stone surface are:

$$SO_2 + H_2O \Rightarrow SO_2 \cdot H_2O \tag{4}$$

$$CaCO_3 + SO_2 \cdot H_2O \Rightarrow CaSO_3 \cdot 0.5H_2O + CO_2 + 0.5H_2O$$

$$2CaSO_3 \cdot 0.5H_2O + O_2 + 3H_2O \Rightarrow 2CaSO_4 \cdot 2H_2O$$

$$CaCO_3 + H_2SO_4 + H_2O \Rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

Analyses of the crystalline species forming on the samples agree in identifying sulphate in the form of calcium sulphate dihydrate (gypsum), while sulphite is generally found as calcium sulphite hemihydrate (Gauri *et al.*, 1982; Kozlowski *et al.*, 1992; Johansson *et al.*, 1988). In particular, Gauri and Gwinn (1982) revealed that moisture in the liquid phase was essential for oxidising calcium sulphite into gypsum, while at relative humidity (RH) $< 80\%$ no change in the sulphite took place. In the early literature, calcium sulphite dihydrate ($CaSO_3 \cdot 2H_2O$) was reported as an intermediate product of the interaction between SO_2 and calcium carbonate ($CaCO_3$), as mentioned by Amoroso and Fassina (1983), although this failed to be confirmed in later studies. The possible formation of a tetrahydrate, $CaSO_3 \cdot 4H_2O$, or a double salt, $Ca_3 (SO_4) (SO_3)_2 \cdot 12H_2O$ is advanced by Mangio *et al.* (1991), but no further data substantiate their hypothesis.

Whether the SO_2-carbonate interaction is enhanced or not by the presence of NO_2 is the subject of debate, as investigators have produced controversial results. Gauri and Gwinn (1982), for instance, did not detect any calcium nitrate in marble exposed in a flow chamber to levels of 6 and 12 ppm NO_2, but X-ray diffraction measurements are unable to detect low levels of crystalline phases. Livingston (1985) suggests that no intermediate product is formed in the NO_x-$CaCO_3$ interaction. Consequently, NO_x appears to be only slightly physically adsorbed into the carbonate structure, leading to much lower kinetics for the formation of calcium nitrate, while SO_2 is strongly chemisorbed.

Johanson *et al.* (1988) found that the SO_2-carbonate interaction is enhanced by the presence of NO_2 and stated that, when deposited on a stone surface, SO_2 is first reversibly adsorbed and then reacts to form the relatively stable $CaSO_3 \cdot 0.5H_2O$ phase, which is eventually oxidised to gypsum $CaSO_4 \cdot 2H_2O$. Due to the saturation of the surface with SO_2 (ads), the deposition and corrosion rates soon drop to low levels. In humid atmospheres (90% RH), NO_2 catalytically oxidises SO_2 (ads), thereby promoting the adsorption of more SO_2 molecules. Further, NO_2 promotes the formation of gypsum from $CaSO_3 \cdot 0.5H_2O$. However, at moderate values of RH (i.e. 50%), NO_2 does not influence the SO_2 deposition rate on calcareous stones.

The following reaction scheme for the interaction of SO_2 with marble is proposed:

$$SO_2(g) \overset{\text{rapid}}{\Leftrightarrow} SO_2(ads) \overset{\text{slow}}{\Leftrightarrow} CaSO_3 \cdot 0.5H_2O(s) \overset{\text{slow}(*)}{\Leftrightarrow} CaSO_4 \cdot 2H_2O(s) \tag{5}$$

The reaction marked with an asterisk (*) is rapid in the presence of NO_2 at high humidity. This scheme indicates that the oxidation process may become the rate-limiting step.

Johnson *et al.* (1990) and Hanef *et al.* (1992) confirm that a wet stone surface revealed greatest reactivity with SO_2, as compared to nitrogen monoxide (NO) and NO_2. Umierski (1995) found that when adding NO_2 as second pollutant, no sulphate was detected on the stone samples, and no real increase in total sulphur deposition was found, comparing single SO_2 exposure with a gas mix of SO_2 and NO_2.

The deposition of SO_2 on marble is strongly enhanced by the presence of ozone, especially at high RH: O_3 acts as an oxidiser on the loosely bound sulphurous species on the surface, increasing the rate of conversion of these species. Ozone also increases sulphate production by oxidising crystalline calcium sulphite (Mangio and Johansson, 1989).

The deposition of NO, NO_2, HONO, HNO_3 and PAN on Ihrlerstein sandstone was studied in the laboratory by Behlen *et al.* (1996). The reactivity of the gases differed considerably and the following order of succession was found $HNO_3 > HONO > NO_2 > PAN > NO$.

The effects of HF and/or SO_2 on calcareous stones and sandstones were investigated by Vales and Martin (1986a and b). In the case of calcite, the reaction with HF primarily leads to an increase in porosity and the reaction occurring is represented by the equation:

$$2HF + CaCO_3 \Rightarrow CaF_2 + CO_2 + H_2O \tag{6}$$

The formation of CO_2 in this reaction is indicated to be another important alteration factor, particularly in conditions of high humidity, as it causes the transformation of the original calcium carbonate into bicarbonate, a much more soluble compound. In sandstones, exposure to an atmosphere of HF in saturation humidity conditions causes a greater change in silicates, the dissolution of silica, and hinders the formation of crystalline phases; the reaction products are probably gaseous or volatile, such as silicon tetrafluoride or even fluosilicic acid, and are thus released from the surface of the samples. The synergistic action of HF and SO_2, leading to the formation of fluorite and gypsum, produces more marked effects than those observed when each pollutant acts alone, such as cracks.

The role of the gaseous pollutants HCl and SO_2 was investigated by Hutchinson *et al.* (1992a), who found that HCl reacts rapidly with calcium carbonate to produce a soluble product, $CaCl_2$. Unlike the relatively insoluble $CaSO_4 \cdot 2H_2O$, it is readily washed away, allowing a continuous reaction which gives rise to crust development.

A number of tests have recently been performed on the interaction between stones, SO_2 and aerosol. Cheng *et al.* (1987) show that fly ash covering marble in a simulation chamber with high SO_2 concentration (100 ppm) favours gypsum formation. Hutchinson *et al.* (1992b) performed experiments on carbonate stones using fly ash produced by fuel oil and coal combustion, and concluded that fly ash particles play no active role in the sulphation process and actually screen the surface, providing a certain degree of protection. This screening role is confirmed by Ausset *et al.* (1996) for soot particles produced by light fuel oil combustion in diesel motors, while fly ash produced by heavy fuel oil combustion is found to play a role in fixing sulphur compounds on stone.

In agreement with these results, carbonaceous particles, emitted by oil fuelled power plants and domestic heating systems, are found to be catalysts of the SO_2 oxidation process on stone surfaces, mainly due to their heavy metal content (Sabbioni *et al.*, 1996b). The role in sulphation of particles from vehicle exhaust confirms a close relationship between the composition of the particulate matter and sulphate on the stone surface: diesel engine exhaust, primarily comprising soot and metallic particles composed mainly of Fe and Cr, Ni, Cu and Mn as trace elements, plays the most important part in the catalytic oxidation of SO_2; emissions from gasoline engines, composed of small quantities of soot and high concentrations of Pb and Br result in less gypsum formation (Rodriguez Navarro and Sebastian, 1996).

Boke *et al.* (1996), during experiments using clay minerals, active carbon and metal oxide, found that the presence of particulate matter does not significantly change the extent of sulphation, but affects the ratio between calcium sulphite hemihydrate and gypsum, showing that particles produce a considerable acceleration of the oxidation process at the carbonate surface; these data underline the importance of quantifying both sulphite and sulphate formed by the interaction between SO_2 and material surfaces. The results are confirmed by Umierski (1995) with reference to stone samples treated with solutions of transition metals, i.e. Fe, Mn, Cu, Pt and V. The total sulphur uptake was only slightly increased by the catalysts, but the sulphites are lower than on untreated samples or completely absent, with Cu and Mn showing the highest catalytic effect.

Defining the role of carbonaceous particles in crust formation is particularly important as gypsum can be autonomously nucleated by soot (Del Monte *et al.*, 1984). In addition, gypsum has been found on materials containing no calcium, such as bronze (Riederer, 1973), a result that induced some researchers to ascribe all gypsum found on monuments to atmospheric deposition alone, without any contribution from the stone (Rossi Manaresi, 1975). Laboratory tests have shown that the gypsum nucleated by carbonaceous particles is negligible (no more than 0.04%), compared to the total gypsum forming by the interaction between SO_2 and stones during the experiment (Sabbioni *et al.*, 1996b).

The dry deposition of pollutants to surfaces is typically expressed as a flux; the relationship between mass flux per unit time per unit area to the surface F (g cm^2 s^{-1}) and the airborne pollutant concentration C (g cm^{-3}) in the vicinity of a structure yields a coefficient referred to as the dry deposition velocity in cm s^{-1}:

$$v_d = F/\,[C]. \qquad (7)$$

The inverse of the deposition velocity is the resistance to mass transfer described in terms of electrical analogy following Slinn *et al.* (1978) as:

$$v_d = (r_a + r_b + r_c)^{-1} \qquad (8)$$

where r_a is the aerodynamic resistance, which is a function of wind speed and air turbulence, r_b is the boundary layer resistance depending on molecular diffusivity and turbulence, and r_c is the surface uptake resistance, i.e. a function of surface chemistry (material composition), surface roughness, porosity and surface moisture. The dry deposition rate differs for different materials by the magnitude of r_c: materials with some acid-buffering capacity (carbonate minerals for example) tend to have low surface resistance and, consequently, a relatively high SO_2 deposition velocity.

A compilation from the literature of SO_2 dry deposition velocity data for various stones estimated in laboratory tests is reported in Tables 3 and 4. For nitrogen compounds, the deposition velocities measured by Behlen *et al.* (1996) for NO, NO_2, HONO and HNO_3 in the chamber at 80% RH were respectively 1.8, 0.12, 0.02, 0.006 and < 0.001 cm s^{-1}.

Few published estimates of r_c for building materials are available: Lipfert (1989a) estimated r_c in the range of 2.12–3.85 s cm^{-1} for limestone at about 85% RH, while for dry limestone and sandstone the value was 2–2.5 s cm^{-1}. Spiker *et al.* (1992) measured r_c values of 1.3 and 34 s cm^{-1} for fresh limestone and fresh marble, respectively, at 75% RH, 26°C and 50 ppb SO_2.

Table 3. Deposition velocity (v_d) of SO_2 measured in chamber tests.

Deposition surface	Conc. (mg m^{-3})	Flow (m s^{-1})	RH (%)	v_d (cm s^{-1})	Reference
Marble (dry)	1.1	low	50;60	0.03	Calc. from Gilardi (1966)
Marble (wet)		low	100	0.13	Calc. from Gilardi (1966)
Marble	10 ppm		100	0.08	Coburn *et al.* (1993)
Carrara marble	0.09 ppm		50	0.006	Mangio and Johansson (1989)
Carrara marble	0.09 ppm		70	0.015	Mangio and Johansson (1989)
Carrara marble	0.09 ppm		90	0.02	Mangio and Johansson (1989)
Carrara marble	1.44 ppm		50	0.001	Mangio and Johansson (1989)
Carrara marble	1.44 ppm		70	0.002	Mangio and Johansson (1989)
Carrara marble	1.44 ppm		90	0.02	Mangio and Johansson (1989)
Carrara marble	0.4	0.001	90	0.058	Henriksen (1995)
Carrara marble	3 ppm		90	0.02	Calc. from Sabbioni *et al.* (1996)
Pentelic marble	0.4	0.001	90	0.069	Henriksen (1995)
Pentelic marble	0.3 ppm		90	0.049	Calc. from Sabbioni *et al.* (1996)
Oolitic marble	0.36		11	0.16	Calc from Spedding (1969b)
Oolitic marble	0.28		13	0.09	Calc from Spedding (1969b)
Oolitic marble	0.1		79	0.83	Calc from Spedding (1969b)
Oolitic marble	0.37		81	1.26	Calc from Spedding (1969b)
Dolomite	10 ppm		100	0.05	Coburn *et al.* (1993)
Limestone	1–5	low	85	0.097	Calc. from Braun and Wilson (1970)
Limestone	1.1	six times than low	85	0.967	Calc. from Braun and Wilson (1970)
Limestone (wet)		low	100	0.21	Gilardi (1966)

Table 3. (*Continued*)

Deposition surface	Conc. (mg m^{-3})	Flow (m s^{-1})	RH (%)	v_d (cm s^{-1})	Reference
Travertine limestone	3 ppm		90	0.01	Calc. from Sabbioni *et al.* (1996)
Trani limestone	3 ppm		90	0.01	Calc. from Sabbioni *et al.* (1996)
Portland limestone	0.3 ppm		90	0.231	Calc. from Sabbioni *et al.* (1996)
Vicenza limestone	0.4	0.001	90	0.1	Henriksen (1995)
Sandstone (dry)	1.1	low	50;60	0.09	Calc. from Gilardi (1966)
Serena sandstone	0.4	0.001	90	0.093	Henriksen (1995)
Sandstone (wet)		low	100	0.2	Calc. from Gilardi (1966)
Baumberger sandstone	2.66		95	0.0336	Umierski (1995)
Granite (dry)	1.1	low	50;60	0.01	Calc. from Gilardi (1966)
Granite (wet)		low	100	0.002	Calc. from Gilardi (1966)
Granite red and grey	0.4	0.001	90	0.038	Henriksen (1995)
Monzonite blue	0.4	0.001	90	0.009–0.018	Henriksen (1995)
Monzonite green	0.4	0.001	90	0.027	Henriksen (1995)
Soapstone	0.4	0.001	90	0.007–0.04	Henriksen (1995)
Syenite red	0.4	0.001	90	0.027	Henriksen (1995)

Table 4. Deposition velocity (v_d) of SO_2 measured in the chamber in the presence of other gases.

Deposition surface	SO_2 (mg m^{-3})	NO_2 (mg m^{-3})	RH (%)	v_d (cm s^{-1})	Reference
Carrara marble	0.4	0.4	70	0.052	Henriksen (1995)
Carrara marble	0.4	0.4	80	0.084	Henriksen (1995)
Carrara marble	0.4	0.4	90	0.135	Henriksen (1995)
Pentelic marble	0.4	0.4	70	0.094	Henriksen (1995)
Pentelic marble	0.4	0.4	80	0.115	Henriksen (1995)
Pentelic marble	0.4	0.4	90	0.136	Henriksen (1995)
Vicenza limestone	0.4	0.4	70	0.115	Henriksen (1995)
Vicenza limestone	0.4	0.4	80	0.120	Henriksen (1995)
Vicenza limestone	0.4	0.4	90	0.125	Henriksen (1995)
Serena sandstone	0.4	0.4	70	0.090	Henriksen (1995)
Serena sandstone	0.4	0.4	80	0.100	Henriksen (1995)
Serena sandstone	0.4	0.4	90	0.109	Henriksen (1995)
	SO_2 (ppm)	O_3 (ppm)			
Carrara marble	1.44	0.25	50	0.002	Mangio and Johansson (1989)
Carrara marble	1.44	0.25	70	0.015	Mangio and Johansson (1989)
Carrara marble	1.44	0.25	90	0.070	Mangio and Johansson (1989)
Carrara marble	0.09	0.25	50	0.035	Mangio and Johansson (1989)
Carrara marble	0.09	0.25	70	0.080	Mangio and Johansson (1989)
Carrara marble	0.09	0.25	90	0.240	Mangio and Johansson (1989)

Simulation chamber tests have also been employed to predict the thickness of the gypsum crust forming on samples exposed for up to 4500 hours in the laboratory (100% RH and 10 ppm SO_2), and the following equations have been proposed:

$$t = C_{Bo}/\ k_s C_{As} \cdot \delta l \tag{9}$$

$$t = C_{Bo}/\ k_s C_{As} \cdot \delta l + C_{Bo}/\ C_{As} D_{eg} \cdot \delta l^2 \tag{10}$$

where t is the time of exposure in seconds, δl is the thickness of the crust, C_{as} and C_{Bo} are the SO_2 and calcite concentrations expressed as moles/cc, respectively, and k_s and D_{eg} are the surface rate constant and effective diffusion coefficient calculated as 4356 cm/h and 0.193 cm_2 h^{-1}, respectively (for Georgia marble). Equation (9) is proposed for the initial portion of the reaction, which is kinetically controlled, while equation (10) is proposed for the entire reaction, encompassing the initial reaction as well as the latter part, when diffusion becomes significant as the reaction progresses. These equations were also applied to the weathering of marble in Chicago for an exposure period from 1912 to 1978 (0.1 ppm SO_2 and 60–80% RH), where a gypsum crust of nearly 90 mm was found (Gauri *et al.*, 1989).

An expression for the crust thickness (δ) in terms of deposition velocity and SO_2 concentration is proposed in Coburn *et al.* (1993):

$$\frac{d}{dt}(\delta) = \frac{1}{\gamma}\frac{M}{\rho} v_d C_{so_2} \tag{11}$$

where γ represents the stoichiometric coefficient of SO_2 in the reaction ($\gamma = 1$ for marble and $\gamma = 2$ for dolomite), M is the mass of solid product formed, ρ is product density, v_d the deposition velocity, and C_{SO_2} the concentration of SO_2 in mol cm^{-3}. The authors employ the equation for calculating the average rate of crust growth for surfaces unexposed to rain washings, assuming 0.01 ppm SO_2 concentration and deposition velocities of 0.08 cm s^{-1} for marble and 0.05 cm s^{-1} for dolomite: crust growth rates of 1.10 µm y^{-1} for marble and 0.79 µm y^{-1} for dolomite are obtained.

4. Field Exposure Tests

Material loss from stone may occur through two main mechanisms. Physical mechanisms, leading to loss through abrasion, erosion, flaking, spalling or cracking, are important in areas of buildings sheltered from rain washout; such mechanisms are difficult to model and do not represent the main portion of material removed from stones with low porosity, such as marble and limestone. Chemical mechanisms, basically due to the interaction of calcium carbonate and rainwater, take place predominantly in the unsheltered, rain-washed areas.

The dissolution of carbonate stone occurs in a number of ways. The first is the karst effect, named after the geological phenomenon where limestone dissolves in rainwater in the absence of air pollution. This process, which is specifically dealt with in Chapter 2, is represented by the following equation:

$$CaCO_3 + H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (12)$$

The second mechanism is the acid rain effect. Thus, a chemical reaction of the following type is envisaged for limestone:

$$CaCO_3 \text{ (solid)} + 2H^+ \Rightarrow Ca^{2+} + H_2O + CO_2 \text{ (gas)} \qquad (13)$$

In other words, an acid-based reaction proceeds, with the acid rain solution being neutralised through reaction with the calcium carbonate minerals from the limestones.

Several studies have dealt with the major processes affecting the dissolution of rain-washed limestones in the environment by field exposure tests. The approach involves exposing samples of materials in the environment at a number of different sites and measuring the accumulation damage: the advantage is that the samples are exposed to real ambient conditions, but only a limited number of sites are tested and experiments do not generally last long enough, at least ten years being necessary to obtain meaningful results. Three alternative types of measurement are proposed in the literature: surface recession, mass loss and the measurement of solutes dissolved from the surface in rainfall runoff.

Honeyborne and Price (1977) performed exposure trials over a ten-year period to determine the relative effects of pollutants in urban and semi-rural atmospheres, indicating the absence of a direct correlation between environmental pollutant levels and rates of limestone decay. Weber (1985) studied the weathering resistance of different building stones for two years in a closely monitored urban atmosphere at several sites in the city of Vienna. He determined the flux rate of the sulphurous compounds in the atmosphere, taking into account the different bulk densities of the stone under investigation (quartz-sandstones, marble, compact and porous limestones). Theoretical surface erosion for a time period of 100 years was calculated from mass loss and values up to 6.2 mm/100y were obtained, which were considered reasonably fitting with *in situ* observations. Jaynes and Cooke (1987) exposed stone samples on carousels in rain-exposed and rain-sheltered positions under monitored environmental conditions at several sites in southeast England. The weight loss of exposed samples was attributed to both solution and sulphation, the latter being estimated to account for 39% and 44% of loss for Portland and Monk's Park stone, respectively.

In work carried out as part of the United States National Acid Precipitation Assessment Programme (NAPAP), Youngdahl and Doe (1986) and Reddy *et al.* (1986) attempted to quantify acid rain damage on carbonate rocks (Shelburne marble from Vermont and Salem limestone from Indiana), discussing the form of a preliminary equation to relate environmental damage factors. They also showed how much of the environmental damage on stone results in surface material loss, usually by reaction and dissolution processes, but also by the accumulation of surface and sub-surface reaction products which subsequently become detached together with parts of the unreacted stone. Their experiments included quantitative measurements to evaluate erosion of the stone material using gravimetric and interferometric laser profiling techniques, as well as chemical analyses of runoff solution from the stone surface. Marble recession was correlated with hydrogen ion deposition to the rock. They conclude that the contribution of acid rain to the chemical damage ranges between 5–20% for dry deposition of SO_2, between 7–26% for dry deposition of HNO_3 and around 10% for wet deposition.

Working in the same programme, McGee and Mossotti (1992) investigated gypsum accumulation on carbonate stones by examining crusts on limestone and marble samples from monitored sites and also from ancient buildings in the same materials. Gypsum layers on a limestone sample exposed for two years range from 100–250 μm, approximately ten times thicker than the 10–30 μm on the identically exposed marble samples, a discrepancy owing to the different water-accessible porosity, which is 17 and 0.3% for limestone and marble, respectively. Furthermore, gypsum crystal formation was mostly superficial: no crystals were observed below a depth of 0.2 mm, although elevated levels of sulphate (varying from about 10.000–40.000 ppm) were detected within the interior of stones. Particles were observed by SEM to be readily trapped by the bladed network of gypsum crystals that cover the exposed stone surface.

Again within the NAPAP, Baedecker *et al.* (1992) quantified the effect of the wet and dry deposition of H^+, SO_2 and HNO_3 on stone erosion. The physical measurements of the surface recession at five material exposure sites ranged from 15–30 μm y^{-1} for marble and from 25–45 μm y^{-1} for limestone; these values are double those based on the observed calcium content of runoff solution. The manifest differences between physical and chemical recession are basically attributed to the loss of mineral grains from the stone surface, not measured in the runoff experiments. They conclude from their chemical analyses of runoff solutions that as much as 30% of erosion by dissolution could be due to the wet deposition of H^+ and dry deposition of SO_2 and HNO_3 between rain events. The remaining 70% of erosion by dissolution is attributed to the solubility of calcium carbonate in rain, which is in equilibrium with atmospheric carbon dioxide (“clean rain”).

Girardet and Furlan (1991) used pyrolysis and infra-red analyses in an effort to distinguish between the respective contributions of gas and aerosol in the dry deposition of sulphur on field-exposed stone samples, finding that deposits from gaseous sulphur predominates over those from aerosol sulphur. In Milan, a typical example of a large industrialised city, the contribution of aerosol sulphur represents only 2–5% of the total sulphur taken up from sandstone samples, while, for the same stone exposed in a low polluted site, such as a rural area, its contribution rises to 5–20% of the total.

Butlin *et al.* (1992) reported the results obtained in the National Materials Exposure Programme (NMEP), covering 29 sites located throughout the United Kingdom, where samples of stones (Portland limestone, White Mansfield dolomitic sandstone and Monk's Park limestone) were exposed mounted on freely rotating carousels in rain-exposed and rain-sheltered positions. For the unsheltered samples, the weight loss ranged from 0.16% (Portland limestone) to 1.22% (Monks Park limestone) per year, and a significant correlation was found between weight changes and SO_2 concentration, rainfall volume and hydrogen ion loading (mg H^+ m^{-2}). The sheltered samples, as expected, gained weight as a result of dry deposition (negative correlation). Chemical analyses of soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) by ion chromatography were also performed at different depths in the specimens, and were expressed as variations in concentration (μg g^{-1}) with respect to blank samples. As expected, the data showed an increase in acid species in the sheltered samples evidencing two main effects: the marine effect, with a correlation of Cl^-, Na^+, K^+ Mg^{2+}, Ca^{2+} concentrations with each other and weight change, and a pollution effect, where SO_2 and NO_2 correlate with SO_4^{2-} and NO_3^-, respectively, and with weight change. The SO_2 deposition velocity was also calculated to range from 6 to 15 mm s^{-1}.

A linear equation containing the annual average SO_2 and NO_2, rainfall and rainfall acidity (accounting for at least > 60% of the measured variations in weight change) for unsheltered Portland and White Mansfield stone is proposed:

$$\begin{aligned}\text{Wt loss} = {} & 0.08 + 0.010\ [SO_2] - 0.00012\ [NO_2] \\ & + 0.00016\ R + 0.0026\ [H^+] \qquad (14)\end{aligned}$$

$$\begin{aligned}\text{Wt loss} = {} & 0.37 + 0.017\ [SO_2] - 0.0090\ [NO_2] \\ & + 0.00004\ R + 0.0039\ [H^+] \qquad (15)\end{aligned}$$

where weight change is in %, SO_2 and NO_2 in μg m^{-3}, rain (R) in mm and H^+ in mgH^+ m^{-2}.

Field trials in the United Kingdom (Webb *et al.*, 1992) on Portland limestone exposed at nine sites for periods of up to three years show that the average weight loss over all samples is 0.14 g $m^{-2}d^{-1}$, equivalent to a 24 μm y^{-1} surface retreat, a value within the range reported by Honeyborne and Price (1977) and Jaynes and Cooke

(1987). No residual effect on stone loss due to nitrogen oxide concentrations was found. A model for the chemical dissolution of rain-washed limestone was derived considering the ion and mass balance between the incident rainwater and runoff rainwater and fitting the measured loss rates. The authors attempted to express the most important processes affecting the dissolution of rain-washed limestone, as (1) conversion of the limestone to calcium sulphate by dry deposition of SO_2 and its subsequent dissolution, (2) dissolution of $CaCO_3$ due to normal interaction with H_2O and atmospheric CO_2, and (3) dissolution due to the neutralisation of the excess acidity in rain as a result of air pollution:

$$\begin{aligned}\text{stone loss} \cong\ & SO_4^{2-} \text{ due to dry deposition}\\ & + \text{“natural” bicarbonate solubility}\\ & + \text{rain acid neutralisation}\end{aligned}$$

As a generic case, they propose the following chemical model:

$$\begin{aligned}\text{stone loss(moles)} \cong\ & ADv_dC_{SO_2}\\ & + (K_HK_1P_{CO_2} / 2[H^+]_r)\ \Sigma\ (A_iR - E_{vap})\\ & + ([H^+]_i / 2)\ \Sigma A_iR \qquad (16)\end{aligned}$$

where C_{SO_2} is the mean SO_2 concentration during the exposure of duration (D), v_d is the deposition velocity, A is the surface area of the stone exposed, A_i is the rainfall interception area, $[H^+]_r$ and $[H^+]_i$ are the volume-weighted mean hydrogen ion concentrations of the runoff and rainfall, respectively, E_{vap} is the volume of rainfall evaporated from the stone sample, K_H and K_1 are the equilibrium constant of carbonate and bicarbonate in equilibrium with atmospheric concentration of 350 ppm CO_2 (Stumm and Morgan, 1970) and R is the amount of rainfall (in mm). They concluded that in determining stone loss, the natural solubility of limestone in water turns out to be the dominant term in the model, accounting for 50–90% of the stone loss. The dry deposition of SO_2 accounts for less than 5–50%, and the neutralisation of rainfall acidity always represents the least significant contribution, being between 0.3 and 3.2%.

In addition, Vleugels *et al.* (1994) investigated the alteration of the surface composition in naked and treated limestones of different origin (French Massangis limestone, Belgian Balegem and Gobertange limestone) after environmental exposure, also comparing the effects of wet versus dry deposition. After a six-month exposure period, the totally exposed surfaces were chemically indistinguishable from the reference interior material, while after one year of exposure, gypsum formed from dry sulphur compound deposition was observed (with a thickness of about 500 μm), together with NH_4^+ on the sheltered surface. However, in this area, the contribution of NO_3^- and Cl^- weathering salts was very small compared to the SO_4^{2-} salts. In particular, the SO_4^{2-}, Cl^- and NO_3^- ranged respectively from 0.01–1.45% in weight, 0.03–1.20% and 0.01–0.56%.

Wittenburg and Dannecker (1994) and Steiger and Danneker (1994) measured the enrichment of soluble salts (particularly nitrate and sulphate) in the surface of typical sandstones (Obernkirchen, Ihrlerstein and Sander sandstone), calculating the deposition velocities of SO_2 and NH_3, and the flux of sulphate, nitrate and ammonium. Furthermore, to identify the contribution of HNO_3, NO_2 and particulate nitrate ($p\text{-}NO_3^-$) to the total input, multiple regression analysis was used, as reported in the following equation:

$$F\text{-}NO_3 = v_{dHNO_3} \cdot c[HNO_3] + v_{dNO_2} \cdot c[NO_2] + v_{dNO_3^-} \cdot [NO_3^-] \tag{17}$$

where the deposition velocities for the single species (respectively 0.64 ± 0.06 cm s^{-1} for HNO_3, 0.002 ± 0.004 cm s^{-1} for NO_2 and 0.006 ± 0.03 cm s^{-1} for $p\text{-}NO_3$) appear as coefficients. The product of deposition velocity and average concentration of each component gives the contribution of each species, which turns out to be 88, 8 and 3% for HNO_3, NO_2 and $p\text{-}NO_3$, respectively. It was finally shown that there may well be a significant contribution due to the deposition of calcium-rich particles from the atmosphere to large gypsum accumulations in sandstone.

Henriksen (1994 and 1995) studied dry deposition on stone surfaces by means of field studies conducted in Norway, also calculating the deposition velocities. The penetration depth of SO_2 into the stone was found to be in the range of 1.2 to 5.0 mm, with as much as 90% of the SO_4^{2-} in the upper 0.3 mm.

The deposition velocity of SO_2 and HNO_3 obtained by field exposure tests are summarised in Tables 5 and 6. As can be observed

Table 5. Deposition velocity (v_d) of SO_2 measured in field exposure tests.

Deposition surface	Site	v_d (cm s^{-1})	Reference
Carrara marble vertical	Gettysburg (Pennsylvania)	0.06	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.33	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.23	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.75	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.07	Dolske (1995)
Carrara marble	Borregaard (Norway)	0.80	Henriksen (1995)
Carrara marble	Oslo (Norway)	0.31	Henriksen (1995)
Carrara marble	Milan (Italy)	0.38	Pantani *et al.* (1998)
Carrara marble	Ancona (Italy)	0.12	Pantani *et al.* (1998)
Pentelic marble	Borregaard (Norway)	0.44	Henriksen (1995)
Pentelic marble	Oslo (Norway)	0.37	Henriksen (1995)
Blue marble	Gettysburg (Pennsylvania)	0.07	Dolske (1995)
Blue marble	Gettysburg (Pennsylvania)	2.20	Dolske (1995)
Blue marble	Gettysburg (Pennsylvania)	0.22	Dolske (1995)
Travertine limestone	Milan (Italy)	0.41	Pantani *et al.* (1998)
Travertine limestone	Ancona (Italy)	0.18	Pantani *et al.* (1998)
Vicenza limestone	Borregaard (Norway)	0.80	Henriksen (1995)
Vicenza limestone	Oslo (Norway)	0.60	Henriksen (1995)
Portland limestone	Milan (Italy)	0.89	Pantani *et al.* (1998)
Portland limestone	Ancona (Italy)	0.45	Pantani *et al.* (1998)

Table 5. (*Continued*)

Deposition surface	Site	v_d (cm s^{-1})	Reference
Trani limestone	Milan (Italy)	0.40	Pantani *et al.* (1998)
Trani limestone	Ancona (Italy)	0.19	Pantani *et al.* (1998)
Obernkirchen sandstone	Germany	0.41^{*}	Wittenburg and Dannecker (1994)
Obernkirchen sandstone	Germany	$0.06^{\dagger}$	Wittenburg and Dannecker (1994)
Ihrlestein sandstone	Germany	0.67^{*}	Wittenburg and Dannecker (1994)
Ihrlestein sandstone	Germany	$0.42^{\dagger}$	Wittenburg and Dannecker (1994)
Sander sandstone	Germany	0.57^{*}	Wittenburg and Dannecker (1994)
Sander sandstone	Germany	$0.15^{\dagger}$	Wittenburg and Dannecker (1994)

(*) SO_2 concentration lower than 50 $\mu g \cdot m^{-3}$.

(†) SO_2 concentration higher than 50 $\mu g \cdot m^{-3}$.

Table 6. Deposition velocity (v_d) of HNO_3 measured in field exposure tests.

Deposition surface	Site	v_d (cm s^{-1})	Reference
Carrara marble vertical	Gettysburg (Pennsylvania)	0.06	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.17	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.18	Dolske (1995)
Carrara marble	Gettysburg (Pennsylvania)	0.16	Dolske (1995)
Carrara marble	Milan (Italy)	0.32	Pantani *et al.* (1998)
Carrara marble	Ancona (Italy)	0.09	Pantani *et al.* (1998)
Blue marble	Gettysburg (Pennsylvania)	0.16	Dolske (1995)
Blue marble	Gettysburg (Pennsylvania)	0.17	Dolske (1995)
Travertine limestone	Milan (Italy)	0.32	Pantani *et al.* (1998)
Travertine limestone	Ancona (Italy)	0.16	Pantani *et al.* (1998)
Portland limestone	Milan (Italy)	0.54	Pantani *et al.* (1998)
Portland limestone	Ancona (Italy)	0.62	Pantani *et al.* (1998)
Trani limestone	Milan (Italy)	0.33	Pantani *et al.* (1998)
Trani limestone	Ancona (Italy)	0.40	Pantani *et al.* (1998)
Sandstone	Germany	0.64	Wittenburg and Dannecker (1994)

comparing Tables 3 and 6, the velocities calculated from field studies are much higher than in climate chamber tests, showing the importance of synergistic effects. Surface recession rates on building materials were extensively summarised by Lipfert (1989b), and Table 7 is therefore limited to more recent results.

The United Nation Economic Commission for Europe (UN ECE) Material Exposure Programme measured several parameters of deterioration for two types of stones (Portland limestone and White Mansfield dolomitic sandstone) at 39 test sites in 12 European countries, the United States and Canada under conditions of wet and dry deposition (Kucera and Fitz, 1995). After the eight-year exposure period (Butlin *et al.*, 1998), they concluded that SO_2 is the main contributor to the degradation of calcareous stones in areas of high pollution; wet deposition and natural dissolution are less important and can be considered relevant only in places where pollution concentrations are low. Linear functions for unsheltered Portland and White Mansfield stones have been formulated:

$$WL = -0.0071\ [SO_2] - 2.4\ 10^{-4}\ R \tag{18}$$

$$WL = -0.0085\ [SO_2] - 1.9\ 10^{-4}\ R \tag{19}$$

where WL is the percentage weight change $((W1-W_0)/W_0 \times 100$, W_1 being the mass after each year of exposure and W_0 the initial mass), $[SO_2]$ the concentration of SO_2 ($\mu g\ m^{-3}$) and R the yearly total rain (mm).

For the sheltered samples, SO_4^{2-} is correlated with weight gain and SO_2 concentration, confirming the predominance of SO_2 as the most reactive pollutant. The high concentrations of Cl^- found in many samples are linked to marine influences and also to industrial pollution (possibly HCl).

Few studies report the modification of the surface structure of exposed samples. From optical and scanning electron microscopy (SEM) observations, the blackening of stones exposed in the NAPAP experiment is reported and attributed to the presence of carbonaceous particles (Ross *et al.*, 1989). Studies on surface modifications using SEM-EDAX were conducted by Smith *et al.* (1994) and Smith and Whalley (1996), revealing the presence of etching at the rain-washed

Table 7. Surface recession rate of marble and limestone from field tests.

Deposition material	Site	Exposure time (y)	Recession rate (mm y^{-1})	Reference
Portland limestone	13 sites (U.K.)	1–3	24	Webb *et al.* (1992)
Shelburne marble (*Vermont*)	5 sites (USA)	10	15–30	Baedecker *et al.* (1992)
Salem limestone (*Indiana*)	5 sites (USA)	10	25–45	Baedecker *et al.* (1992)
Laspra dolomite (*Spain*)	Garston-Westminster	1	41.1–47.6	Grossi *et al.* (1995)
Hontoria limestone (*Spain*)	Garston-Westminster	1	11.8–11.4	Grossi *et al.* (1995)
Portland limestone (*UK*)	Garston-Westminster	1	12–13.9	Grossi *et al.* (1995)
Combe Down limestone (*UK*)	Garston-Westminster	1	40.8–42.7	Grossi *et al.* (1995)

surface, along with crystal gypsum formation and cenospheres deriving from oil and coal combustion containing sulphur and detectable levels of V, Ti and Mn. Colourimetric analyses, performed on stone specimens exposed in a polluted urban area (Milan) for three years showed a relationship between the blackening and exposure time; the deposition of particulate matter rich in carbon particles turns out to incur a significant change in the surface reflectance (Realini *et al.*, 1997).

Brüggerhoff *et al.* (1996) and Simon and Snethlage (1996) have developed exposure programmes which provide a basis for using natural stone samples (sandstone and marbles) as a sensitive material for environmental control under different climatic conditions.

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CHAPTER 4

MECHANISMS OF AIR POLLUTION DAMAGE TO BRICK, CONCRETE AND MORTAR

T. Yates

1. Introduction

The degradation of building materials due to the natural environment is generally relatively slow, and as a result, the service life normally exceeds the time taken for serious damage to occur. Air pollution, however, especially in the form of acidic deposition has accelerated the degradation rate in some materials to such an extent that the costly maintenance is necessary (Building Effects Review Group, 1989; Coote *et al.*, 1989; Cooke and Gibbs, 1993). The focus, in recent years, has been on the increased deterioration rates of architectural structures and monuments, and has in the main been attributed to the effects of sulphur dioxide (SO_2) pollution (House of Commons, 1984; Amorose and Fassina, 1983; Baboian, 1986). The bulk of research work has therefore been concentrated on metals and non-metals such as stone, as a result other building materials such as concrete, brick and mortar have been largely ignored (Yates *et al.*, 1989).

It is known that concrete, brick and mortar are all susceptible to attack by air pollution although the rate and magnitude is usually much lower than for calcareous stones and ferrous metals (Butlin, 1991). However, given that most modern buildings are constructed from concrete, brick and mortar, any degradation can have serious economic consequences.

This chapter aims to review research on the effects of SO_2, oxides of nitrogen (NO_x) and carbon dioxide (CO_2) on concrete and brickwork.

2. Air Pollutants

The air has never been clean in the sense of containing only nitrogen (N_2), oxygen (O_2), CO_2, water (H_2O) and the inert gases because of natural pollutant sources. Man has increased the frequency and intensity of pollutants especially since the industrial revolution. With respect to material degradation, especially brick masonry, the important pollutants to consider are CO_2, SO_2 and NO_x, and "secondary pollutants" formed from these such as sulphuric acid (H_2SO_4), (HNO_3) nitric acid and carbonic acid (H_2CO_3) (Hughes and Bargh, 1982; Wayne, 1985).

In considering air pollutant attack, we must first consider transport processes, concentrations and chemical type of pollutants. The length of time pollutants remain in the atmosphere, the distance they travel, and the atmospheric concentrations they attain will depend on meteorological conditions and deposition processes (Garland, 1978). The processes for transportation from the atmosphere to a surface are usually considered under two main headings — dry and wet deposition.

Dry deposition is defined as the direct collection of gaseous and particulate species on a surface. The processes involved are complex and can be considered in terms of the "deposition velocity" which is a combination of the atmospheric concentration and the resistance of the surface to deposition.

Wet deposition arises from the incorporation of pollutants in cloud droplets ("rainout") their removal by falling precipitation ("washout"), or a combination of the two. Again, this is a complex process, involving the intensity of the rain, its origin and the previous exposure history of the surface (Garland, 1978; Jaynes and Cooke, 1987).

Pollutants which are considered to have an important role in the degradation of building materials are CO_2, SO_2, NO_x, hydrogen chloride (HCl), hydrogen fluoride (HF) and (O_3) along with "secondary pollutants" formed from the above in the atmosphere, such as H_2SO_4 and HNO_3 for example (Wayne, 1985; Franey and Gradel, 1985).

The most abundant minor gas in the atmosphere is CO_2 at an average level of 320 ppm or 0.032% by volume. CO_2 atmospheric concentration is increasing due to industrial smoke and automotive exhausts which can result in localised urban concentrations of up to 2500 ppm (Amorose and Fassina, 1983). The rate of increase of CO_2 concentration has been estimated at 0.1–0.3%/year (Callender, 1958; IPCC, 1990) and has been directly correlated with increasing fossil fuel combustion (Amorose and Fassina, 1983; IPCC, 1990).

The dissolution of CO_2 in the atmosphere will make rain acidic due to the formation of H_2CO_3 (aq). If you assume the background concentration to be 320 ppm, the pH of "natural rain" will be approximately 5.6 by equilibrium calculation (Charola, 1987), which is in agreement with measured values (Lipfert, 1987). The result of increased urban peak concentrations could be rainfall events with a pH as low as 5.2 (Lewry, 1988).

Combustible fossil fuels contain a certain amount of sulphur which results in the formation of SO_2 and sulphur trioxide (SO_3) during burning. The amount of SO_2 produced is approximately between 1 and 10% of the total sulphur oxides (SO_x) and its lifetime in the atmosphere is normally very short due to combination with water vapour to form H_2SO_4 (Amorose and Fassina, 1983; Wayne, 1985). The atmospheric oxidation of SO_2 to H_2SO_4 adds to H_2SO_4 concentrations and it is estimated that 20% of SO_2 emissions are deposited by wet deposition (Lipfert, 1987). Average rural levels of SO_2 have been measured at around 17 ppb rising to a maximum of 105 ppb (Guidabaldi, 1974) in urban areas. Assuming 20% of the total SO_2 is converted to H_2SO_4, a dibasic acid, and a range of 40 to 200 ppb in a highly polluted area, the rainfall could have events with a pH in the range between 2.6 to 2.8 (Lewry, 1988).

Fossil fuel combustion also results in the formation of NO_x, which represents nitric oxide (NO) and NO_2. NO is unstable and is oxidised photochemically to NO_2 in a reaction chain involving O_3 (Amorose and Fassina, 1983). O_3 is also involved in the atmospheric reactions which convert NO_2 to HNO_3, and HNO_3 has been detected in the atmosphere, and nitrates (= acid + aerosol particulates) have been found in the range 0.5 to 1.0 mg cm^{-3} (Guidabaldi, 1974). This would mean an acid equivalent of 0.2 to 0.4 ppm and rainfall events with a pH values between 3.2 to 3.3.

3. Concrete and Cement

3.1. Introduction

Concrete and steel-reinforced concrete are used extensively in the modern building industry (Yates *et al.*, 1989). The weathering and decay of other non-metallic materials have been extensively investigated, for example building stone (Schaffer, 1985). In recent years, the focus has been on the increased deterioration rates of architectural structures and monuments, and this has in the main been attributed to the effects of SO_2 pollution (for example House of Commons, 1984; Amorose and Fassina, 1983; Baboian, 1986). It is known that concrete or reinforced concrete is susceptible to acidic attack (Woods, 1968), but it has not been established that it is significantly affected by acidic deposition from air pollutant sources other than CO_2. In the next section, we will consider the material and its simplified chemistry and properties.

3.2. Cement And Concrete Chemistry

Concrete is made from cement, aggregate and water resulting in a chemically basic material due to the presence of calcium hydroxide ($pH \approx 13$).

Three main cement types are commercially available (Shireley, 1975).

(1) Portland cement (PC).
(2) Blended Portland cement (PC blended with other materials such as pulverised fuel ash or ground blast furnace slag).
(3) High alumina cements (also known as calcium aluminate cements).

PCs are the most common cements used in the United Kingdom (Neville, 1981) and this section is focussed on PCs and PC-blended cement. In their unhydrated form, PCs mainly consists of four minerals (Lea, 1970).

(1) Tricalcium silicate, $3CaOSiO_2$ (abbreviated to C_3S).
(2) Dicalcium silicate, $2CaOSiO_2$ (abbreviated to C_2S).
(3) Tricalcium aluminate, $3CaOAl_2O_3$ (abbreviated to C_3A).
(4) Tetracalcium alumino-ferrite, $4CaOAl_2O_3Fe_2O$ (abbreviated to C_4AF).

When mixed with water, PCs undergoes a sequence of hydration reactions which slowly transform the cement paste to a hardened matrix of hydrated products. The most important hydration are those involving C_3S and C_2S which lead to the formation of calcium silicate hydrate (C-S-H) gel (of variable composition and structure) and calcium hydroxide, mainly in the form of Portlandite crystals (Page and Treadaway, 1982). The formation of calcium hydroxide results in a highly alkaline material ($pH \approx 12.5-13.0$) which is sufficient to induce "passivation" of embedded steel in reinforced concrete. The metal is protected from corrosion by a thin surface layer of oxide — γFe_2O_3 (Hausmann, 1967).

The capacity of concrete to act as a physical barrier against the penetration of aggressive environmental components is critical in the degradation processes, especially when reinforcement is being protected. Unfortunately, concrete is not a perfect barrier because of its continuous pore system and tendency to form surface cracks. Water/gas permeability is associated with the water/cement (W/C) ratio (Tonni and Gaudis, 1980), a higher W/C ratio leading to increased porosity and as a result greater permeability.

Due to its high alkalinity, concrete is subject to acidic attack (Woods, 1968) which generally occurs in four ways:

(1) Dissolution of the hydrated and unhydrated cement compounds.
(2) Dissolution of calcareous aggregate.
(3) Physical stresses induced by deposition of soluble salts from the acid/alkali reaction and the subsequent formation of new solid phases within the pore structure.
(4) Salt-induced corrosion of the reinforcing steel.

3.3. The Effect of Carbon Dioxide

Carbonation reactions

The carbonation of concrete normally involves a chemical reaction between atmospheric CO_2 and the products of cement hydration. It is argued that all the hydrates in the cement paste matrix can react with CO_2 at its atmospheric concentration of 0.03% by volume but the important reaction appears to be with calcium silicate hydrate (C-S-H) and calcium hydroxide (Parrott, 1987). This results in the formation of calcium carbonate and silica gel (Brown and Clifton, 1988):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$10((CaO)_{1.7}SiO_2.4H_2O) + 17CO_2 \rightarrow 17CaCO_3 + 10SiO_2(aq) + 40H_2O$$

Note: $(CaO)_{1.7}SiO_2.4H_2O$ is the approximate composition of C-S-H.

There has been very little work until recently on the mechanisms of C-S-H carbonation and opinions differ as to whether this reaction occurs after or simultaneously with the carbonation of Portlandite. Earlier research has indicated simultaneous carbonation of $Ca(OH)_2$ and C-S-H in a blended cement. Dunster's work (1989) proposed that C-S-H reaction with CO_2 removes calcium-releasing silicate radicals which condense with further silicate anions in C-S-H. Silicate chains of higher molecular weight are initially produced and continued calcium removal causes further cross-linking, eventually producing silica — a 3-D silicate network.

Unhydrated cement compounds can also react with CO_2 at very elevated levels (>10%) but at atmospheric concentrations are regarded as unreactive (Parrott, 1987).

The carbonation reactions are restricted by the amount of moisture present and require the presence of some condensed moisture to become significant. The most favourable conditions are reported as a relative humidity between 50 and 70% in an exposed alternatively wet and dry atmosphere (Beckett, 1984). This maxima can be explained by consideration of the pore water/CO_2 interactions. At low humidities there is insufficient pore water to dissolve the CO_2 resulting in no significant degree of reaction (Hilsdord *et al.*, 1984). Carbonation can occur readily under saturated conditions but

CO_2 has to diffuse through the carbonated surface layer to reach the reaction zone. Gaseous diffusion will be a slow process if the pores are saturated with water resulting in a maximum carbonation rate at intermediate moisture contents (Verbeck, 1958).

Rates of carbonation

The rate of carbonation is thought to be controlled by CO_2 diffusion or by water diffusion and increases with temperature, CO_2, concentration and porosity (Verbeck, 1958; Daimon *et al.*, 1971).

By considering the law of permeability and using Fick's law, several workers have derived expressions of the following form:

$$d = k.\sqrt{t}$$

where d = depth of carbonation
k = coefficient
t = time.

Two such expressions (Ying-Yu and Qui-Dong, 1987) include a term for the partial pressure of CO_2 in their coefficient, k, leading to the expression:

$$D = k_1.\sqrt{Pco_2.t}$$

where Pco_2 = partial pressure of CO_2.

Expressions of this type appear to hold true for long-term exposure (>10 years) in atmospheric conditions (Fukushima, 1987) but the prediction of carbonation based solely on diffusion relationship is not accurate (Baweja *et al.*, 1987). This is to be expected because these relationships do not account for any properties of the material, such as water/cement ratio which will significantly effect the porosity of the concrete.

The relationship between carbonation depth and CO_2 concentrations of:

$$d = \alpha\sqrt{Pco_2}$$

does not appear to hold for the degree of carbonation observed for all CO_2 concentrations. The carbonation weight gain versus CO_2

concentration would be expected to be a parabolic relationship, but if this data is plotted, the curve obtained does not resemble a parabola. The weight gain observed for up to 1% of CO_2 is very steep and approximately linear, between 1–5% there is a sharp curve, almost a discontinuity, and finally at concentrations >5% CO_2 the weight gain levels out; slowly increasing with CO_2 concentration. This sharp change in gradient between 1–5% of CO_2 could indicate limiting factors in the processes involved or two mechanisms occurring; one below 1% CO_2 and one above 5% CO_2, the area in between being the "change-over" region. Accelerated testing occurs at CO_2 levels of approximately 4% V/V and in light of the above data, the value of using such tests in predicting the carbonation effects on outside structures is brought into question.

The carbonation reaction is known to occur at sites on the pore wall (Lin and Fa, 1987) and the carbonation reaction has been shown to decrease concrete's gas permeability (Zhang, 1985). This indicates that the growth of calcite crystals in the pores is "clogging" them up, probably resulting in a slowing down of transportation processes to the reaction front.

When considering exposure in the natural environment, reaction conditions vary considerably. The conversion of $Ca(OH)_2$ to $CaCO_3$ and any removal of reaction products, in the form of the soluble $(Ca(HCO_3)_2$, are dependent on the excess of dissolved CO_2 (Amorose and Fassina, 1983; Wayne, 1985). This suggests that condensing conditions may dominate the carbonation depth whilst the action of rain may be involved with the leaching of compounds and as a result surface erosion effects.

The effect on material properties

When concrete contains Portland cement, carbonation results in an increase in strength and reduced permeability, neither of which are a problem in practice (Matousek, 1980; British Standard, 1997).

On carbonation, concrete is observed to shrink which appears somewhat paradoxically. This is because the conversion of Portlandite to calcite will result in a molar volume expansion of 11% (Brown and Clifton, 1988). The shrinkage due to drying of the concrete has also been shown not to be a contributory factor (Verbeck, 1958). This leaves the possible shrinkage of C-S-H on carbonation, which appears to be a point of controversy. Sauman (1972) has studied the carbonation of C-S-H on a microstructural level and reports no structural or volume change. Conversely, Brown and Clifton (1988) report a molar volume shrinkage of 80% on carbonation of C-S-H which would certainly explain the phenomena of "carbonation shrinkage" but such a dramatic change would almost certainly lead to shrinkage cracks and a subsequent loss of the improvement in properties. The degree of C-S-H shrinkage also seems very high when the typical values observed in hydrated Portland cement are of the order of 0.1% (Verbeck, 1958) by volume.

The effect of carbonation on Portland cement appears to be one of a slight improvement in material properties. However, when the concrete is steel reinforced, carbonation reduces the pH of the affected material from approximately 12.5 to values as low as 8 which removes the "passivating" effect of the concrete on the embedded steel. Therefore, it is necessary to ensure that the concrete cover is thick enough to prevent corrosion during the lifetime of the structure.

3.4. The Effects of Other Pollutants

Apart from CO_2, the other common pollutants in the atmosphere are SO_2 and NO_x, and their acidic derivatives, H_2SO_4 and HNO_3.

Nitrogen oxides and nitric acid

Very little information is available on the effect of NO_x on concrete. However, it is known that HNO_3 will attack concrete in the following manner (Webster and Kukacka, 1986):

$$Ca(OH)_2 + 2HNO_3 + 2H_2O \rightarrow Ca(NO_3)_2.4H_2O$$

The acid will also cause decomposition of C-S-H into amorphous silica but this reaction is independent of the anion and is dependent on proton attack (Brown and Clifton, 1988). Complete nitric acid attack will potentially cause a large molar weight change (approximately 200% for the above reaction). However, damage does not occur due to salt crystallisation but appears to be due to the high solubility of the calcium nitrate hydrates and their subsequent leaching after formation. If this form of decomposition were to occur throughout the concrete, then the remaining solid volume would be approximately 18% of the original solid volume with a greatly increased porosity. The development of a more porous, weaker cement matrix will expose the sub-surface to further attack and leave it susceptible to other forms of deterioration.

Sulphur dioxide and sulphuric acid

As with the NO_x, very little information is available on the effect of the gaseous pollutant, SO_2, on concrete. It is known, however, that SO_2 and concrete react to yield calcium sulphite.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$$

Under dry conditions, the reaction is limited to the surface but in the presence of moisture and oxygen the reaction becomes more significant. The reaction can now occur in the concrete's sub-surface with oxidation producing some gypsum (Webster and Kukacka, 1986).

Accelerated testing has been used to study the effects of acid precipitation on concrete (Orantie and Ruohomaka, 1988; Kong and Orbison, 1987; Attiogbe and Rizkalla, 1988; Fattuhi and Hughes, 1988) but this had normally taken the form of immersion in H_2SO_4 solutions of pH between 1 and 5 for several months. This type of testing has general drawbacks in its simulation of acidic precipitation. Firstly, in the majority of cases the solution is static, rather than continuously flowing (Fattuhi and Hughes, 1988), which means equilibrium conditions are probably reached, a state which is unlikely in real conditions. The acid solutions used are normally of pHs between 1 and 5, although the most commonly used are between 1 and 2 which is a hydrogen ion concentration of 100 to 10,000 times that observed in rainfall. This high level of acidity appears unrealistic and could lead to different mechanistic processes occurring, especially with respect to the dissolution processes. The use of accelerated testing with H_2SO_4 (aq) solutions are unlikely to model the attack of acidic precipitation but despite this, they are the only indicators available.

The rate of deterioration of concrete has been shown to increase with an increase in cement content, water/cement ratio or acid concentration (Kong and Orbison, 1987; Fattuhi and Hughes, 1988; Sersale, 1998). An accelerated test study (Attiogbe and Rizkalla, 1988) has also shown that acid attack is a surface phenomenon with deterioration starting at the surface of the concrete and progressing inward. A later study conducted at the Abiko Research Laboratory (Abiko, 1995) reached a similar conclusion from a series of tests that exposed samples of concrete to "artificial acid rain". They found that the erosion depth was related to the pH, and which after 4000 mm of rainfall, ranged from 0.2 mm at pH 5.6 to 1.4 mm at pH 2.0. This is in agreement with Lewry and Pettifer (1988) which indicates that acidic precipitation causes surface erosion by leaching calcium ions from the cement matrix of concrete.

Webster and Kukacka (1986) have reported "crust formation" in their review, although no references to validate their statements concerning air pollution as a cause has been quoted. The same case study as above has examined a gypsum crust in a concrete specimen and attributed it to SO_2 deposition but its effects appear insignificant when compared to carbonation.

Other authors (Brown and Clifton, 1988; Figg, 1983) appear to regard the possible reaction of gypsum with other cement phases a problem. Apart from possible salt damage on crystallisation of the gypsum, the expansive reaction with hydrated tricalcium aluminate to produce ettringite ($3CaO.Al_2O_3.3CaSO_4.31H_2O$) is quoted as being a problem. However, the evidence linking such deleterious expansive reactions to acidic deposition is tenuous to say the least.

Experimental investigations have shown that steel reinforcement in an alkaline solution can be considerably damaged by sulphates and nitrates (Hensel, 1985). However, the views of Hensel (1985) and Skoulikidis (1982) that the action of NO and/or SO_2 in small amounts will cause steel reinforcement corrosion in concrete appear unfounded and are not substantiated by experimental evidence.

The view that acidic deposition is not responsible for significant concrete degradation or reinforcement corrosion was supported by the members of an EPA workshop (EPA, 1986), and by a number of other reports since then, for example Harter, 1988, Watts Committee, 1988, and Livingston, 1998. In some cases, they do however suggest further research to substantiate their views. This suggested research should, as a high priority, include any possible synergistic effects between SO_2, NO_x and CO_2. This is a possibility, as SO_2 and NO_x acidic deposition appears to weaken and leach out the cement matrix of concrete. This would result in an easier transportation route to the unreacted Portlandite resulting in an increased carbonation rate.

3.5. Conclusions

The mechanistic paths by which SO_2, NO_x and CO_2 attack cement or concrete appear to depend on the relative atmospheric concentrations. The atmospheric concentration of CO_2 (approximately 320 ppm, Brimblecombe, 1986) is approximately 10,000 times the concentration of SO_2 and NO_x (approximately 20 ppb, Brimblecombe, 1986), resulting in carbonation being a much more significant effect. However, carbonation is a not in practice a problem regarding concrete unless steel reinforcement is being protected. The use of a sufficiently thick layer of good quality concrete should rectify this problem.

Acidic deposition of SO_2 and NO_x is responsible for surface erosion and cracking of the cement matrix. This is only a "cosmetic" problem unless there is a synergistic effect with CO_2 resulting in increased carbonation rates.

4. Brickwork and Mortar

4.1. Introduction

The deterioration of brick masonry is a complex problem because of the two variable components — brick and mortar. Each component can have a large variation in composition and structure resulting in a large number of combinations when they are used together.

Brick and mortar are both susceptible to acidic attack to an extent (Charola and Laezarini, 1986), but little is known about the effects of acid deposition on the bricks of brickwork (Watt Committee, 1988). Brick components can rehydrate, carbonate and adsorb sulphate resulting in possible moisture expansion, cracking and exfoliation.

Mortars will also react with sulphate and other ions, resulting in expansion, erosion and structural deterioration. Transportation of any salts formed by chemical attack can also compound the problem by recrystallising (Hughes and Bargh, 1982).

The composition and firing history of the brick along with the composition and production history of the mortar will complicate the problem still further.

4.2. Brick Manufacture and Composition

Brick manufacture

Bricks are formed by three distinct methods (BIA, 1986):

(1) Soft mud method: soft muds are poured into moulds and dried before firing. This is not a commonly used practice in modern brickmaking.
(2) Stiff mud method: plastic clay is extruded through a die and then the bricks are cut to size.
(3) Semi-dry or dry press method: clay is pressed into a mould.

The second method often causes laminations and these are referred to as weakness planes. Lamination and the associated cracks are often blamed for failures, but Robinson (1984) suggests that this is improper and further investigations are necessary.

During the above "forming" processes, additives are commonly used to colour the brick or inhibit efflorescences.

Apart from the starting materials' composition, the firing temperature, the kiln type and the time kept at the temperature are probably the most important factors in determining the nature and quality of the brick produced (Robinson, 1984).

Three principal types of kiln are used:

(1) Scone kiln: constructed of unfired bricks which are plastered on the exterior. The bricks are stacked so that a channel allows heat to travel by convection. This kiln type is not commonly used.
(2) Periodic kiln: the shape may be beehive, rectangular or square. These kilns are dome-roofed with fire bases around the outside of the wall base.

(3) Tunnel kiln: commonly used because they are efficient and fire uniformly resulting in a cheaper, reproducible product.

The firing process generally controls the physical properties of bricks, differences of 50–100°C can radically alter properties. Firing is carried out by slowly raising the temperature and allowing volatiles to escape and oxidation to occur before raising the temperature further. Generally, water is removed by heating from 100–400°C which results in a material with a porosity of 30–40 vol% (Carlsson, 1988). This is followed by the removal of clay hydroxyl water and oxidation in the range 400–800°C. Above 800°C, the heating results in high temperature phases and fusion products. In the range 800–1400°C, sintering or densification occurs via chemical reactions, grain growth and development of a liquid phase. The porosity decreases as a result of sintering and lead to an increase in strength of the final product.

Generally, the ideal point to stop firing results in a brick which is "steel hard" with a low-water absorption. Overfiring wastes energy and underfiring generally results in poor quality bricks.

Brick composition

Bricks are normally produced from raw materials consisting of at least 50% kaolins and clays which together with water give the necessary plasticity to the materials when forming it into components.

The liquid phase, produced during firing, transforms to glass without crystallisation on cooling. The result is a brick usually composed of a crystalleric silicate phase, mullite ($3Al_20_3 \cdot 2SiO_2$), the remaining quartz from the raw materials and some minor phases, which are all bonded together by a glassy matrix. The porosity of the brick could still be as high as 20% and the glassy phase could constitute as much as 60% of the brick. This means that the brick is really a composite with the crystalline phases embedded in the glassy matrix whose typical composition is given in Table 1.

Brick durability

When considering the durability, porosity and permeability are probably the most important physical properties because these

Table 1. The approximate composition of the glass in a ceramic such as brick (after Hermansson and Carlsson, 1978).

Component	Wt.%
SiO_2	71–77
TiO_2	1–4
Al_2O_3	7–16
Fe_2O_3	1–5
MgO	0–2
CaO	0–1
Na_2O	0–3
K_2O	4–8

characterise the accessibility of water to the brick's interior. Thermal and mechanical properties should also be considered in analysing decay. The physical nature of brick should first be considered. Therefore intergranular bonding, cementing matrix, pore shape and size are more important than the properties of individual grains. The durability of brick to weathering is determined by a number of variables, but the critical factors appear to be the porosity and pore system. Large pores and low porosity are widely held to give good durability but there is disagreement over possible critical pore-sizes. The work of Watson, May and Butterworth (Watson *et al.*, 1957; Watson *et al.*, 1962; May and Butterworth, 1962) indicates that pores smaller than 1 μm caused damage whilst those larger than 2 μm, or preferably 10 μm improved the brick durability. Davison (1980) has agreed a critical pore size of 1 μm; <1 μm implies low durability and >1 μm improves durability. Maage (1980 and 1984) investigated the relationship between pore size/volume and frost resistance of brick. He derived an empirical relationship relating to the two which quoted 3 μm as the critical pore size. Robinson (1984) determined the pore size distributions of good and poor durability brick. The critical pores sizes were in agreements with the work of Butterworth *et al.* with pores <1 μm predominant in low quality bricks whilst pores >2 μm were the majority in good bricks. Robinson (1984) also found that certain bricks exhibited a differential pore structure. The surface of brick having a much lower porosity than the centre. This surface "skin" prevents rapid migration of any pressurised water and as a result spalls due to crystallisation processes. Torraca (1985) also indicated that the presence of small pores (<1 μm) increased the susceptibility of brick to freeze-thaw and crystallisation damage.

The pore size distributions were determined in all of this work by mercury intrusion porosity. This method has a number of errors including assuming the mercury contact angle is between 124 and 130^0 and that the pores are cylindrical in shape (Ross, 1984). Despite this, the technique provides a first approximation of pore size and the pore structure for comparative work.

Robinson (1984) also investigated the effect of firing temperature composition of the raw materials and forming methods on the pore structure and durability. He found that firing did not significantly alter the pore size distribution but did lower the total porosity, thus increasing the final strength. Also insufficient time at the "maturing temperature" at the end of the firing process resulted in the differential pore structure earlier and subsequent failure in use at a later date.

The raw materials appeared to control the pore size distribution of the final brick. Pure clays have small pores and the addition of shale shifts the distribution only slightly. The addition of sand and crushed brick can be used to shift the distribution to larger pore sizes, improving the durability.

Hand moulded and pressed bricks exhibited the best pore size distributions whilst extrusion processes lead to a brick with the majority of pores >1 μm. Although pore size distributions appear to be a good indicator of durability, other factors such as water permeability and mechanical strength must be taken into account.

4.3. Pollutant Attack on Brick

The brick's glassy matrix is similar to acidic silicate glasses, and as a result is probably the most susceptible component to dissolution by neutral, acid or alkaline solutions.

Water attacks glass by leaching alkali ions from the surface and initially is a diffusion controlled reaction (Das and Douglas, 1967). After this period, a second surface controlled reaction becomes dominant which involves dissolution of the alkali ion-depleted layer (Paul, 1987). Dilute acid solutions ($pH > 2$) attack glass by preferentially dissolving the alkalis and basic oxides (Paul, 1987). Silica loss is less than that observed with water attack because the acid neutralises the leached alkalis, thus keeping the pH below a level where silica dissolution is important. The result of preferential leaching is to produce a layer twice as thick as those observed with water attack (Clark *et al.*, 1979), 1200A° as compared to 600A° after one hour. The alkali ions are replaced with smaller hydrogen ions inducing stress in the layer which will cause it to crack. The surface layer by this time is several microns thick and further shrinkage occurs if the hydrated silica layer loses water.

The deterioration mechanism above was observed in the glassy matrix of a brick exposed to concentrated H_2SO_4 (Lewin and Charola, 1979). On continued exposure, the leached layer crumbled away exposing the mineral with greater acidic resistance. The only problem is that the environment above is far too aggressive to simulate atmospheric pollutant attack and the rate of attack probably results in surface strain due to shrinkage and as a result loss of material. Robinson (1982) estimated that H_2SO_4 solution formed from pollutants increased the dissolution of the brick ten-fold. However, given that the maximum dissolution of the brick is usually 1%, then the resulting salts, because of their small quantity, only usually damage the appearance, particularly as staining and efflorescence.

Baronio *et al.* (1980) found that a water-saturated, SO_2-containing atmosphere deteriorated bricks by increasing their porosity and pore size. This does not seem like much of a problem as enlarging the pore size leads to greater durability.

El-Shamy's (1975) work on the chemical durability of glasses in acid solution found that HNO_3 attacked more aggressively than H_2SO_4. Although pollutant atmospheres will have some effect on brick, the rate of attack will be very much slower than a modern glass. This is because the glassy matrices' composition is reasonably high in Al^{3+} ions whilst having low levels of Na^+ and K^+ ions. This would lead to a glass of high durability and probably explains why attack on brickwork due to acidic deposition does not appear to be a problem.

A more serious problem can be efflorescence, i.e. the deposition of soluble salts on the brick surface (DOE, 1972) The salts can derive from rehydration of the soluble phase of the brick or from the mortar (Harding and Smith, 1983). This phenomena is normally temporary and only occurs when a new brick first dries out and persistent reccurrence is normally a sign of persistent water penetration (BIA, 1985). However, if salt recrystallisation occurs just below the surface, the result will be surface decay and spalling of the brickwork.

4.4. Mortar and Pollutant Attack

Good quality bricks will have great strength but mortar is just as important a component in brick masonry. Although the nature of mortar has changed considerably over time, modern masonry is usually a mixture of Portland cement (OPC), sand and lime (Charola and Laezarini, 1986).

The effect of acid deposition will depend on the particular mortar used.

Non-hydraulic lime mortars depend on exposure to air to harden, the slaked lime, i.e. $Ca(OH)_2$ reacts with CO_2 in the air (Ashurst and Ashurst, 1988).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On hardening, carbonation and drying will occur simultaneously, resulting in a volume contraction. The setting reaction above results in calcite formation, implying that a fully carbonated lime/sand mortar will behave in a similar manner to a loosely bound sandstone (Hoffman *et al.*, 1976) when considering air pollutant attack. SO_2 deposition can result in gypsum formation, which on recrystallisation could induce mechanical stresses into the mortar matrix (Charola and Laezarini, 1986). Setting plaster, however, is a mixture of Portlandite and calcite which can be further complicated in the case of dolomitic mortars when magnesium phases are also present. Carbonation and attack by SO_2 will occur simultaneously and there is the possibility of interaction. Carbonation, dissolution, re-precipitation and sulphation of the various phases will occur in the pore spaces on absorbed water films (Hoffman *et al.*, 1976).

Hoffman *et al.* (1976) have observed degradation as "flaking off" in the case of lime mortars and as disintegration with dolomitic lime mortars. On the basis of their experimental work, they attributed these phenomena to the sulphate concentrations in the surface area (up to 3 mm deep). This implies salt crystallisation damage but no damage mechanisms have been discussed or investigated.

Hydraulic mortars containing Portland cement are attacked by acidic precipitation which causes softening and disintegration of the surface (Ashurst, 1983). Air pollutant attack on concrete has been described above and will be only briefly summarised here. The main constituents of Portland cement which are susceptible are Portlandite, i.e. $Ca(OH)_2$ and calcium silicate hydrate (C-S-H). SO_2 reacts with $Ca(OH)_2$ to produce calcium sulphite ($CaSO_3$), which in the presence of moisture and oxygen will oxidise to gypsum (Figg, 1983). The resulting sulphate can further degrade the mortar by reacting with calcium aluminate (C_2A) to produce ettringite, i.e. $2CaO.Al_2O_3.3CaSO_4.31H_20$ (Brown and Clifton, 1988). Gypsum and ettringite formation are expansive reactions and can result in cracking in the mortar or brick depending on water movement.

Martinez-Ramirez *et al.* (1996) used an exposure chamber to examine the effect of different combinations of gases on lime mortar (1:3 lime:aggregate). The results showed that if both water and an oxidant were present, then the formation of salts was greatly increased. Their results also showed that under chamber conditions, SO_2 in combination with water and O_3 was far more reactive than NO or NO_2 under similar conditions.

Longer site exposure studies for mortar are described in Lewry (1992) and Lewry and Butlin (1993). The mortars used included 1:1:6 (cement:lime:sand) and 1:3 (cement:sand) with an air entraining agent. After three years of exposure at a range of urban and rural sites in the UK, the following observations were made:

(1) No visual signs of degradation were observed.

(2) The extent to which soluble slats were deposited was dependent on the pollutant concentrations at the exposure site.

(3) There was an upper limit to the concentration of soluble sulphate. Half the samples reached this limit after one year of exposure, the others took up to three years.
(4) The main product of air pollution was calcium sulphate and no signs of ettringite were found.

This final observation is also reported by Scholl and Knöfel (1991) from their work on cement paste.

A different form of deterioration of mortars is described by Ichitsubo *et al.* (1997). They describe colour changes in mortars that they attribute to the oxidation of iron in the cement. They link this to the dissolution of calcium hydroxide at the surface of the mortar which results in a concentration of iron.

The carbonation of Portlandite was discussed earlier, however rainwater, acidified with CO_2, leaches $CaCO_3$ from the surface, weakening the cement structure slightly (Charola and Lewin, 1979). In general, it has been observed that the effect of total carbonation doubles the strength of Portland cement mortars (Penkala and Zasum, 1988).

Although sand grading of mortars does not appear to be related to resistance to sulphate attack, the strength and frost resistance has been shown by Harrison (1986) to be reduced with the use of finely graded sands. This appears to be the result of increased porosity and shrinkage. In this context, it is interesting to note that Lewry and Butlin (1993) found that sulphate accumulated more slowly in the mortars made using finer sands.

4.5. Interactions Between Brick and Mortar

Mortar appears to be the only component of brickwork attacked by acidic deposition but the degree of susceptibility to chemical dissolution is fairly low. However, it is possible that salts produced by the reactants of air pollutant attack could cause damage to masonry.

Another source of salts is the bricks themselves which can contain Na_2SO_4. These occur if the fuels used during firing are sulphur-rich or the firing temperature is insufficient to decompose the salt. Na_2SO_4 is very soluble and on evaporation can recrystallise as the anhydrous salt, theriardite, or as the decahydrate, mirabilite, depending on temperature and humidity (Read, 1984). The stresses produced within a material by crystallisation pressure can be great (Winkler, 1973 and 1997) and will be in the case of brick work sufficient to inflict severe damage.

The deterioration of masonry due to salt crystallisation has been proposed by Lewin (1982) to be dependent on the position of where the salt solution evaporates. Salt crystallisation will depend on the capillary migration of the solution and the rate of evaporation.

De La Torre Lopez and Sebastian Pardo (1996) describe some of the longer term weathering effects that they observed on late 19th century church in Granada, Spain. They observed that the original mortar in the joints and the rendering was based on gypsum and is now around 70% gypsum with a very high porosity which was accentuated by dissolution. There was clear evidence that the gypsum had migrated into the bricks and was crystallising there. There was also some calcite in the bricks and this was being attacked by atmospheric SO_2.

Binda and Baronio (1985) have shown that the relative porosities of the brick and mortar are important, with the most porous material being the site of salt-induced deterioration. They proposed that if brick and mortar have similar properties, decay will occur over the masonry unit as a whole and will take a longer time. This appears to be a wide generalisation but warrants further investigations if the durability of masonry could be improved in this way.

The porosity of the brick is also important when considering the setting of the mortar. If the brick contains large pore sizes (> 20 μm), the suction effect is fairly low. Goodwin and West's (1982) work indicates that this produces a stronger mortar/brick bond due to better adherence of the Portland/ettringite layer as it can crystallise in the pores of the brick. However, when you consider the durability of brickwork as a whole, this is in conflict with the work of Harrison (1986) which showed that the mortar has a poorer strength and lower durability when subject to little or no suction from the brick.

4.6. *Conclusions*

The main mechanism of deterioration in brick masonry appears to be the crystallisation of soluble salts and frost damage. Soluble salts are either inherent to the original materials, introduced during production or possible from air pollutant sources. The resistance of masonry to deterioration is generally related to water penetration as this is a major factor in frost and wetting/drying damage and as the transport medium for salts.

The design and manufacture of the components is also very important, especially composition of the raw materials, production processes and firing conditions. Control of these could lead to low levels of sulphate and control of the pore size distribution, thus improving the durability in the long term.

In conclusion, there appears to be little or no problem concerning the effect of acidic deposition on brick. However acidic deposition on mortar could lead to increased amounts of salts and therefore an increased degree of salt damage on brick masonry as a whole.

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CHAPTER 5

SALTS AND CRUSTS

M. Steiger

1. Introduction

The mechanisms of degradation of inorganic porous building materials such as stone, brick, terracotta, concrete and mortar are commonly classified into chemical and physical mechanisms, including biochemical and biophysical processes. Chemical weathering refers to the dissolution or alteration of the mineral constituents of a material by chemical reactions. Physical weathering includes all processes generating mechanical stress either on a microscopic scale or to whole structures. There is quite a large number of different chemical and physical processes that can cause severe damage, such as granular disaggregation, delamination, spalling and complete structural decay. Unfortunately, the different types of damage can almost never be attributed to a specific damage mechanism. For example, granular disaggregation can be the result of chemical attack, frost damage or many other processes, as well. Moreover, one single process may manifest itself as different types of damage in different materials. Hence in practice, it is generally impossible to deduce the major causes of damage from visual observations. In order to assess the relative importance of different degradation processes and their rates, a detailed understanding of the underlying mechanisms is indispensable.

This chapter is concerned with salt damage which, from its very nature, is a physical damage process. However, salt damage cannot be clearly separated from chemical weathering because salts are also the products of chemical weathering reactions. Hence, the presence of salts in building materials is not only a potential cause of severe damage, but can also be an indicator of the degree of chemical weathering. First, I will briefly review the major sources of salt enrichment in building materials and then discuss the mechanisms of salt damage. Finally, an attempt is made to provide a short review of the most common effects of salts with special emphasis to air pollution.

2. Sources of Salts in Building Materials

2.1. Chemical Weathering

The chemical weathering of building materials involves the attack of water and associated acidity. The H^+ ion attack on the mineral components causes their dissolution and the formation of weathering products. Some examples of chemical weathering reactions relevant to stone deterioration are:

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + CO_2 + H_2O \tag{1}$$

$$\begin{aligned} &2KAlSi_3O_8 + 2H^+ + 9H_2O \\ &\quad \rightleftharpoons 2K^+ + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4^0 \end{aligned} \tag{2}$$

$$\begin{aligned} &Mg_5Al_2Si_3O_{10}(OH)_8 + 10H^+ \\ &\quad \rightleftharpoons 5Mg^{2+} + Al_2Si_2O_5(OH)_4 + H_4SiO_4^0 + 5H_2O \end{aligned} \tag{3}$$

Acid attack generally causes the mobilisation of metal cations from the parent minerals. The weathering of silicates also leads to the formation of new mineral compounds, e.g. iron oxyhydroxides and clays such as kaolinite, $Al_2Si_2O_5(OH)_4$. Table 1 lists the cations released from the weathering of some common mineral constituents of building materials. It can be seen that chemical weathering reactions mainly lead to the formation of sodium, potassium, magnesium, and calcium salts.

Table 1. Ions released from weathering of some common minerals in building materials.

Mineral name	Idealised formula	Ions released
Carbonate minerals		
Calcite	$CaCO_3$	Ca^{2+}
Dolomite	$CaMg(CO_3)_2$	Ca^{2+}, Mg^{2+}
Feldspars		
Plagioklase feldspar	$Na_xCa_{1-x}\ Al_{2-x}Si_{2+x}O_8$	Na^+, Ca^{2+}
Microcline (K-feldspar)	$KAlSi_3O_8$	K^+
Clay minerals		
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	K^+, Mg^{2+}
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	Mg^{2+}

Carbon dioxide (CO_2) is a major source of acidity in natural waters and it is the acid most responsible for rock weathering on a geological time scale. The solubility of carbonate materials in water is enhanced in the presence of CO_2 according to the reaction:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (4)$$

The equilibrium solubility of calcite in rain water in equilibrium with atmospheric CO_2 (5.5×10^{-4} moles/L) is about four times higher than in pure water. Thus, even in the absence of other sources of acidity, there is a natural dissolution reaction of carbonate minerals which is commonly referred to as the Karst effect. Although the dissolution rates of silicates are much slower than those of carbonate minerals, silicate minerals are also subject to chemical weathering (Drever, 1994; Lasaga *et al.*, 1994).

2.2. Acid Deposition

Acid deposition is the major source of H^+ in building materials. Here, acid deposition refers to, both, wet deposition, i.e. acid precipitation, and the dry deposition of gaseous and particulate pollutants. Atmospheric acidity is closely related to the atmospheric chemistry of sulphur dioxide (SO_2) and the nitrogen oxides (NO and NO_2) which become oxidised to sulphate and nitrate through gas and aqueous phase processes. The atmospheric chemistry of sulphur and nitrogen compounds is quite complex and can only be briefly summarised, here. More comprehensive reviews on acid deposition (Schwartz, 1989) including its effects on building materials (Fassina, 1988; Butlin, 1991) and the history of air pollution (Brimblecombe and Rodhe, 1988) are available.

The major pathways of acid deposition associated with SO_2 are depicted in Fig. 1. The gas phase oxidation of SO_2, mainly by reaction with OH radicals, ultimately leads to the formation of sulphuric acid (H_2SO_4) which will rapidly nucleate to form aqueous H_2SO_4 droplets, acting themselves as condensation nuclei for cloud droplets. The aqueous phase formation of H_2SO_4 proceeds via absorption of SO_2 in cloud droplets or moist particles and subsequent oxidation reactions. Finally, aerosol sulphate and gaseous SO_2 are subject to below cloud scavenging by rainfall. In effect, a large fraction of the atmospheric SO_2 is removed by acid precipitation. The dry removal of acidic sulphur compounds involves the deposition of gaseous SO_2 and acidic particulate sulphate.

The dry deposition of acidic species on material surfaces involves two different processes (Lipfert, 1989a). First, the transport of pollutants to a surface is controlled by aerodynamic factors, a detailed discussion of which is provided by Hicks (1983). Next, acidic trace

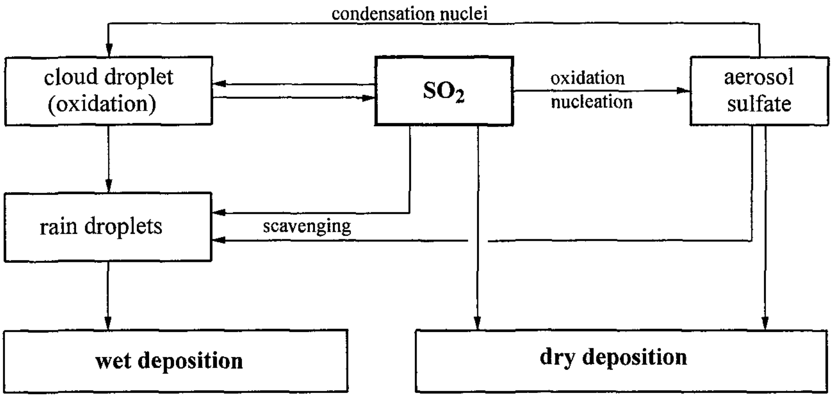

Fig. 1. Major pathways of SO_2 deposition.

species need to be irreversibly deposited to the surface, either by chemical reaction, or by physical processes, e.g. adsorption or dissolution. Thus, the overall rate of dry deposition is closely related to the material properties such as chemical composition and surface wetness, and the reactivity of the atmospheric trace gas of interest. The damage potential of acidic gases is therefore depending on both, their ambient concentrations, and the sensitivity of a particular material to that gas. Graedel and McGill (1986) provide a qualitative review of the sensitivity of various materials to a number of gaseous pollutants. A useful measure for quantitative comparisons of the sensitivity of different materials to dry deposition is the deposition velocity, V_D, defined as the ratio of the surface flux, F, i.e. the deposition per unit area and time, to the ambient concentration of the gas, C:

$$V_D = \frac{F}{C} \tag{5}$$

Sulphation was early recognised as a cause of decay of carbonate stone (Schaffer, 1932; Kieslinger, 1932) and due to its relatively high concentrations in urban areas, the dry deposition of SO_2 was the subject of many experimental studies. Lipfert (1989a) has presented a literature compilation of SO_2 deposition velocities to various materials. Typical values of V_D reported are largely dependent on the reactivity of the materials indicating that SO_2 dry deposition to many building materials is limited by surface processes rather than aerodynamic factors. The most likely deposition mechanism involves the dissolution of SO_2 in moisture films present on surfaces and the subsequent aqueous phase oxidation of S(IV) resulting in a decrease of the solution pH. The solubility of SO_2 strongly decreases with decreasing pH, thus, further deposition would ultimately stop. However, if the surface film is in contact with sufficiently reactive minerals such as calcite, the solution pH can be effectively buffered by the dissolution reaction (1).

Deposition velocities of SO_2 reported in the literature generally agree with the deposition mechanism described (Lipfert, 1989a). The highest deposition velocities are reported for reactive materials such as cement and limestone. Though much less data are available for sandstones and other less reactive materials, the reported deposition velocities are considerably lower indicating that the reactivity of the materials is the limiting factor. Also, higher deposition velocities are consistently found at high relative humidities (e.g. Spiker *et al.* 1995), such that aerodynamic factors (wind speed and turbulence) might become the limiting factors for the deposition of SO_2 to the most reactive materials at high relative humidities.

The dry deposition of particles to material surfaces is controlled by physical processes, including diffusion, inertial impaction, and gravitational settling (Hicks, 1983). The deposition velocities are strongly dependent on particle size. Inertial impaction and gravitational settling increase with particle size, whilst diffusion controlled deposition decreases with particle size. This results in a minimum of the deposition velocity for particles in the size range 0.1–1 μm. Most of the aerosol acidity is associated with particles of exactly this size range. Due to the low deposition velocities of acidic particles, their contribution to the total dry deposition of acidity is of minor importance only, which was confirmed in field exposure experiments (Girardet and Furlan, 1991; Wittenburg and Dannecker, 1992).

The total amount of acidity deposited to building materials by wet deposition is given as the product of the H^+ concentration and the total volume of rain deposited on the surface. A number of studies were carried out to determine the effect of acid rain. A useful experimental technique is the collection and analysis of stone run-off solutions (Rönicke and Rönicke, 1972; Reddy *et al.*, 1985; Livingstone, 1986; Cooper, 1986). Any differences in the concentrations between run-off and incident rainfall must be due to interactions with the stone. For carbonate stones, the "excess" calcium concentrations in run-off solutions provides a direct measure of stone dissolution. Here, excess calcium concentration refers to a corrected concentration taking into account contributions from the dry deposition of particles and the calcium concentrations in the incident rainfall itself (Reddy, 1988). Data obtained from run-off water experiments were used to determine the relative contributions of the Karst effect, the neutralisation of acid rain, and the dry deposition of SO_2 (Livingstone, 1992; Baedecker *et al.*, 1992). It was found that in urban areas with significant SO_2 pollution, the dry deposition of local SO_2 was dominant (Roekens and van Grieken, 1989; Livingstone, 1992).

The atmospheric chemistry of the nitrogen oxides is considerably more complex than that of SO_2. The deposition pathways of nitrogen compounds are summarised in Fig. 2. Nitric oxide (NO) is the major oxide formed during the high temperature combustion of fuels. Nitrogen dioxide (NO_2) is formed in the atmosphere by oxidation of NO. The final oxidation product of the nitrogen oxides (NO_x) is nitric acid (HNO_3) which is mainly formed by the reaction of NO_2 with the OH radical. HNO_3 is more volatile than H_2SO_4 and can exist in significant concentrations in the gas phase. However, it is also highly soluble and is readily absorbed by cloud droplets and moist aerosol particles. Another important reaction of HNO_3 is the neutralisation with ammonia (NH_3), which is the most prominent atmospheric alkaline species present in substantial concentrations. This reaction leads to the formation of ammonium nitrate aerosols (NH_4NO_3). Actually, there is a dynamic equilibrium between NH_3, HNO_3 and NH_4NO_3, and both, NH_3 and HNO_3 can revolatilise. Other reactions of NO_X with free radicals, including OH, RO, RO_2 and RCO_3, lead to a number of gaseous nitrogen compounds among which nitrous acid (HONO) and peroxyacetyl nitrate (PAN), $CH_3C(O)OONO_2$, are the

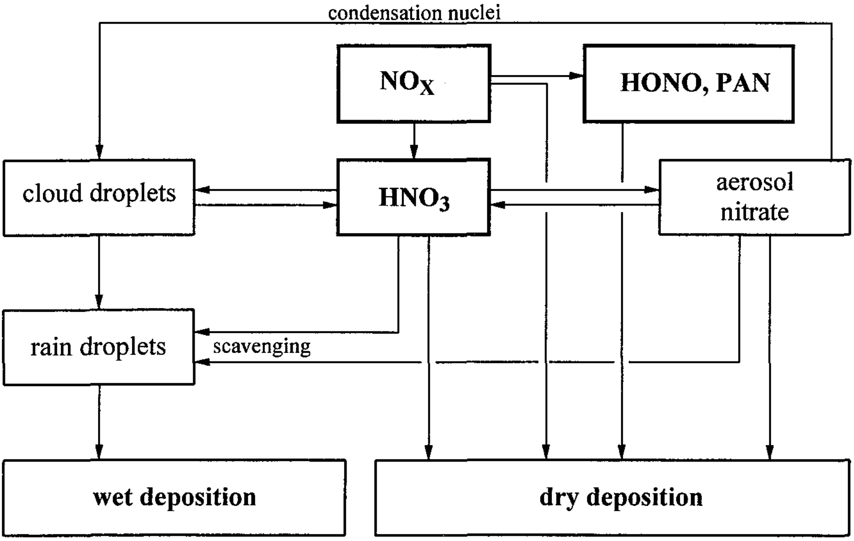

Fig. 2. Major pathways of NO_X deposition.

Table 2. Typical concentrations of some gaseous nitrogen species in rural and moderately polluted atmospheres, units are ppb (data from Finlayson-Pitts and Pitts, 1986).

Pollutant	Rural	Moderately polluted
NO	0.05–20	20–1000
NO_2	1–20	20–200
HNO_3	0.1–4	1–10
HONO	0.03–0.8	0.8–2
PAN	2	2–20
NH_3	1–10	1–10

most prominent species. Thus, the dry deposition of nitrate to surfaces includes several gaseous precursors and particulate nitrate. Table 2 lists typical concentration ranges of several gaseous nitrogen compounds for rural and moderately polluted atmospheres compiled by Finlayson-Pitts and Pitts (1986).

The incorporation of nitrate into precipitation follows similar paths than that of sulphate, including nucleation scavenging of nitrate-containing aerosols in cloud formation, absorption of HNO_3 by cloud droplets and precipitation scavenging of HNO_3 and nitrate-containing aerosols (washout). A major difference to the chemistry of SO_2 is the fact that aqueous phase oxidation of NO_X is of very limited importance in the atmosphere. This is largely due to solubility limitations, NO is practically insoluble in water, and NO_2 is only slightly soluble and not very reactive in solution at typical ambient concentrations (Lee and Schwartz, 1981).

Due to their low solubilities, much lower deposition velocities to wet surfaces are expected for the nitrogen oxides compared to sulphur dioxide. Indeed, early attempts to correlate the enrichment of nitrate in stone surfaces with ambient NO_X concentrations were unsuccessful (Luckat and Zallmanzig, 1985). In contrast, HNO_3 is known to deposit readily on virtually all material surfaces and was suggested as a major source of nitrate enrichment in calcareous materials (Livingstone, 1985; Sikiotis *et al.*, 1992; Fenter *et al.*, 1995). Due to its reactivity, it is assumed that the deposition velocity of HNO_3

is virtually not depending on surface chemical processes. Thus, turbulent transport to the material surface and the ambient HNO_3 concentration are the limiting factors controlling the delivery rate of HNO_3 to material surfaces. It can be seen from Table 2 that HNO_3 concentrations are considerably lower than those of the precursor gases. Behlen *et al.* (1996) have recently determined deposition velocities of NO, NO_2, HNO_3, HONO and PAN to a calcite cemented sandstone. Considering the ambient concentrations of these gases, they could show that the total deposition of nitrate is mainly due to HNO_3 and NO_2, with only minor contributions of HONO. The contributions of PAN and NO were found to be negligible.

Despite the sensitivity of virtually all materials to HNO_3, the degradation potential as compared to SO_2 might be limited due to the rather low atmospheric concentrations. In fact, there is experimental evidence from exposure experiments that sulphate accumulates more rapidly in calcareous stones than nitrate does (e.g. Jaynes and Cooke, 1987; Baedeker *et al.*, 1992; Sweevers and van Grieken, 1992). However, in view of strongly decreasing SO_2 concentration levels, increasing NO_X emissions, deposition of oxidised nitrogen species may play a more important role in the deterioration of building materials in the future.

The principal role played by NH_3 in the atmosphere is the neutralisation of acidic species such as H_2SO_4 and HNO_3, the main reaction products of which are ammonium sulphate, $(NH_4)_2SO_4$ and NH_4NO_3. Thus, the ammonium ion is an important constituent of both, cloud droplets and the submicron aerosol. It has been already mentioned that NH_3 can revolatilise from aerosols such that NH_3 and HNO_3 can co-exist in the gas phase according to

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \qquad (6)$$

Interest in the deposition of ammonium (NH_4^+) and NH_3 on building materials and soil mainly arises from the fact that NH_4^+ is biologically oxidised by the process of nitrification (van Breemen *et al.*, 1982; Mansch and Bock, 1998). This two-step process is given by the overall reaction:

$$NH_4^+ + 2O_2 \rightleftharpoons 2H^+ + NO_3^- + H_2O \qquad (7)$$

Thus, the deposition of NH_3 and NH_4^+ to building materials may be regarded as an indirect pathway of acid deposition. Wolters *et al.* (1988) determined rates of nitrification in various sandstones and concrete under idealised laboratory conditions, i.e. optimum temperature and unlimited supply with the substrate. They report very high rates of nitrification, clearly indicating that the limiting factor under ambient conditions will be the delivery of NH_3 or NH_4^+.

Due to its high solubility, NH_3 can deposit to materials through dissolution in moisture films present on surfaces. The ammonia solubility is strongly increasing with decreasing pH, thus in contrast to SO_2, the deposition velocities are considerably higher at low pH (Adema and Heeres, 1995). The dry deposition of NH_3 to material surfaces will therefore depend on the reactivity of the material and its ability to buffer the increase in pH caused by the formation of hydroxyl ions. Carbonate materials are particularly unfavourable in this respect, and it was shown that dry NH_3 deposition to calcareous stone is significantly lower than to silicate stones (Wittenburg and Dannecker, 1994).

Considering that atmospheric concentrations of NH_3 (cf. Table 2) are considerably lower than those of SO_2, it can be concluded that the contribution of NH_3 to the total input of acidity via dry deposition and nitrification is of minor importance, only. Typically, atmospheric concentrations of NH_3 are comparable to those of nitric acid, to which, however, most building materials are much more sensitive. Thus, the degradation potential of gaseous NH_3 appears to be of minor importance except perhaps for buildings directly affected by strong primary NH_3 sources, e.g. stock-farms.

Behlen *et al.* (1997) have determined the wet deposition of NH_4^+ to a brick masonry which was by far exceeding the dry deposition of both, NH_3 and particulate NH_4^+. The wet deposition of NH_4^+ can produce acidity through either of two mechanisms. Firstly, NH_4^+ can be oxidised by nitrification according to reaction (7). Next, NH_4^+ containing solutions can also react acidic if in contact with carbonate minerals, e.g. calcite, according to the following reaction:

$$\begin{aligned} &NH_4^+(aq) + CaCO_3(s) \\ &\quad \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq) + NH_3(g) \end{aligned} \tag{8}$$

However, it appears that this reaction has not yet been systematically studied as a potential source of calcite dissolution. Reaction (8) implies that it might be misleading to characterise wet acid deposition only by the free acidity, expressed as pH or the molar concentration of H^+. Similar arguments apply to bound acidity in the form of undissociated organic acids which might also be present in rainwater (Chebbi and Carlier, 1996).

2.3. *Other Sources of Salts*

Besides acid deposition, there are a number of other sources of salts in building materials. Sea salt is an important natural source of salts derived from the atmosphere. On a global scale, emissions of sea salt droplets ejected from the oceans are considered as one of the most important primary sources of the atmospheric aerosol (Blanchard and Woodcock, 1980). Sea salt particles are removed from the atmosphere by wet and dry deposition which are the major processes leading to their enrichment in building materials. In contrast to anthropogenic air pollutants, the concentrations of which have dramatically changed during the last centuries (Brimblecombe and Rohde, 1988), the enrichment of sea salt in historic buildings has been continuously progressing over much longer periods of time. Salt accumulations found today are representing an integral effect of sea salt deposition beginning with the time of construction of a building. Experience from many monuments located at coastal sites suggests that deposition and enrichment of sea salt can be a major cause of decay (e.g. Theoulakis and Moropoulou, 1988; Zezza and Macrì, 1995).

Sea salt particles in the atmosphere have a chemical composition very similar to that of bulk sea water. The contribution of the six ions sodium, magnesium, potassium, calcium, chloride and sulphate amounts to $>99\%$ by mass of the total solids dissolved. The major ions, sodium and chloride, account for 85.6% of the bulk sea salt. Oceans have a remarkably uniform composition and it can be assumed, that the relative abundances of the major ions did not significantly change over the milennia. Therefore, the relative abundances of the major constituents can be used as tracers for sea salt deposition (Zappia *et al.*, 1989). It has been shown that the enrichment of sea salt in buildings in coastal environments is considerably variable depending on a number of different influences including environmental parameters, and the geometry and constructional details of a building (Steiger *et al.*, 1997).

Sources of salts in building materials other than atmospheric have been reviewed by Arnold and Zehnder (1991) and are only briefly summarised here. A major source of salts is ground moisture carried into masonry by rising damp in the absence of damp coursing in a building. A more detailed discussion of salts associated with rising damp is provided in a later section. The use of alkaline building and cleaning materials, e.g. portland cement and water glass, can be an important source of salts (Arnold and Zehnder, 1991). Generally, these materials release sodium and potassium hydroxide and carbonate, which can react with salt mixtures already present in a masonry forming new, often more damaging salt mixtures. A simple example is the reaction of sodium carbonate with calcium sulphate according to

$$Na_2CO_3 + CaSO_4 \rightleftharpoons Na_2SO_4 + CaCO_3 \tag{9}$$

As will be shown below, the damage potential of sodium sulphate is greater than that of calcium sulphate. Other examples can be found in Arnold and Zehnder (1991). Alkaline materials are also excellent substrates for the deposition of SO_2 and CO_2 leading to complex mixtures of carbonates, bicarbonates and sulphates.

Chemicals used for cleaning treatments are sometimes acidic, e.g. containing hydrofluoric acid or formic acid. The chemical reaction of these acids with the mineral constituents of the building materials leads to the formation and enrichment of fluorides or formates (Zehnder and Arnold, 1984). Other sources of salts include de-icing salt, and particularly in historic buildings, the storage of salts in former times.

3. Mobility and Hygroscopicity of Salts

Salts in building materials are typically complex multi-component mixtures. In most practical situations, these salt systems are sufficiently characterised as a mixture of the cations Na^+, K^+, Mg^{2+} and Ca^{2+}, and

Table 3. Salt solubilities relative to gypsum ($CaSO_4{\cdot}2H_2O$) on a molal basis. Values refer to the thermodynamic stable hydrate at 25°C; the solubility of gypsum at 25°C is 0.0158 moles/kg.

	Cl^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-
Na^+	389	685	125	178	77
K^+	304	240	44	519	228
Mg^{2+}	367	310	191	0.0795	
Ca^{2+}	461	531	1	0.0097	

the anions Cl^-, NO_3^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}. These salts are commonly referred to as soluble salts. In fact, however, their solubilities differ by orders of magnitude. Table 3 lists the solubilities of the thermodynamic stable forms of these salts at 25°C relative to the solubility of gypsum ($CaSO_4{\cdot}2H_2O$). It is obvious that gypsum compared to all other salts except the alkaline earth carbonates is a sparingly soluble salt only.

The solubility is an important quantity determining the mobility of salts in porous materials. We might conveniently define mobility as the maximum amount of a salt present in a porous material that can just be dissolved if the pore space is completely filled with water. Salt mobilities can be calculated from the concentration and density of the saturated salt solution, and the porosity and density of the porous material. As an example, Fig. 3 depicts smoothed values of the mobilities of sodium chloride and gypsum as a function of the water accessible pore space for a number of natural stones. Porosities and densities of the stones (48 limestones and 88 sandstones) were taken from Grimm (1990). It is obvious that the mobility of a salt in a particular material is strongly depending on both, the solubility of the salt and the material properties. Comparing the mobilities depicted in Fig. 3 to the typical ranges of sodium and chloride concentrations found in building materials, it can be concluded that sodium chloride in the pore space will be completely dissolved and mobilised in all but the most extreme situations if water penetrates the material. In contrast, gypsum concentrations in building materials typically exceed the mobilities shown in Fig. 3 by several orders of magnitude. Thus,

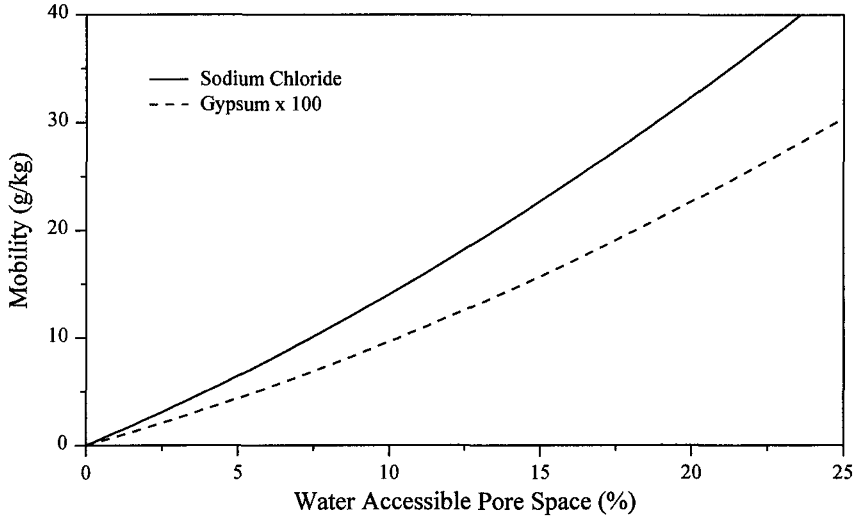

Fig. 3. Mobilities of sodium chloride and gypsum in building stones.

even if the pore space is completely filled with water, only a very small fraction of gypsum can be mobilised.

Apart from gypsum, most other salts are readily dissolved and mobilised in porous materials. It follows that the transport of salts in building materials is largely controlled by the movement of water due to capillary transport. Precipitation, ground moisture and condensation are the major sources of liquid water in building materials. The absorbed water is transported and released later by evaporation. As water evaporates, pore solutions become more concentrated and salts are typically accumulated in evaporation zones.

Arnold and Zehnder (1991) provide a detailed discussion of salt transport and accumulation in walls affected by rising damp based on extensive observations from a number of buildings. Initially, ground moisture penetrating a masonry is a dilute solution which is vertically transported due to capillary rise (cf. Fig. 4). Above ground level moisture evaporates from the wall and the solution becomes more and more concentrated while still being subject to capillary rise. As the solution becomes saturated during transport any further evaporation will cause crystallisation and immobilisation of the salt. In effect,

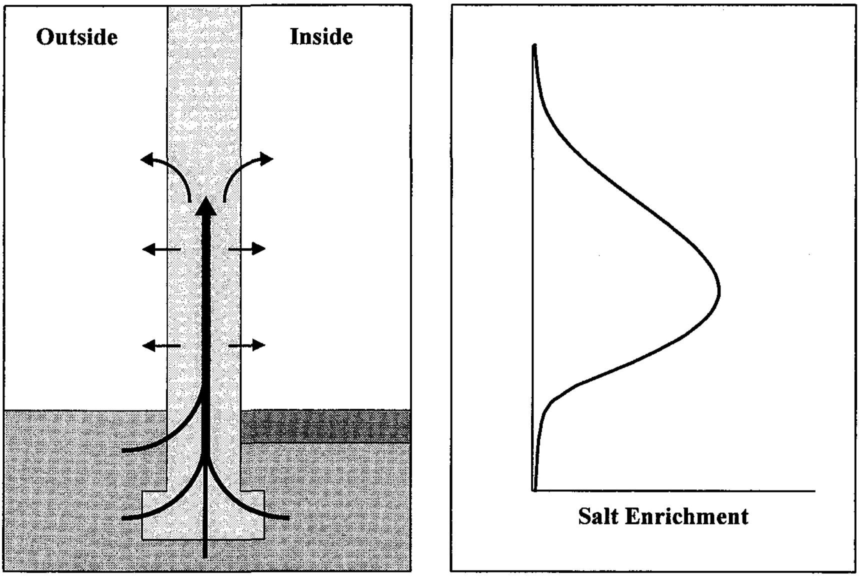

Fig. 4. Moisture transport and vertical profile of salt enrichment in masonry affected by rising damp.

a zone of salt enrichment evolves some distance above ground level. The height of the accumulation zone is dependent on the rate of evaporation and the solubility of the salt. The maximum height is given as the upper limit of capillary rise of moisture, i.e. the height at which the evaporation rate equals the supply of moisture from below.

Pore solutions originating from ground moisture typically contain several ions. During capillary rise and evaporation, less soluble salts will therefore reach saturation earlier than salts of greater solubility, resulting in a fractionation of the salts according to their solubilities. The composition of the pore solution continuously changes during transport and only the very soluble salts are transported as concentrated brine solutions to the upper evaporation zone. Arnold and Zehnder (1991) provide vertical profiles of ion concentrations in the zone affected by rising damp from a number of buildings. Maxima of salt enrichment were observed at heights from 0.5 m to about 3 m above ground level, and the profiles provide evidence for salt fractionation.

It is very difficult, however, to predict the precipitation sequences of minerals from an initially dilute multi-component ionic mixture. In addition to the salt minerals precipitated from a solution of a single salt, a large number of double salts can be formed in mixed solutions. Also, several salts can exist in anhydrous and different hydrated forms, e.g. sodium sulphate can exist as the anhydrous thenardite ($NaSO_4$) and as the decahydrate mirabilite ($Na_2SO_4 \cdot 10H_2O$). Furthermore the solubilities of several salts show considerable variation with temperature. Considering solutions of the major ions found in building materials, about 50 to 60 different evaporite minerals can be precipitated in the temperature range –30 to 40°C. According to Arnold and Zehnder (1991), more than 30 of these minerals have already been detected in building materials.

Though it is difficult to predict the precipitation sequences, due to solubility limitations there are certain restrictions for the composition of brine solutions evolving during transport and evaporation. As Hardie and Eugster (1970) have pointed out, the solubilities of the calcium and magnesium carbonates and of gypsum are so low compared to all other salt minerals of interest, that they provide a chemical divide. Figure 5 depicts the major pathways of fractionation and brine evolution from solutions initially containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-} and HCO_3^-. The evaporation of water from such solutions always leads to the crystallisation of the alkaline earth carbonates, i.e. calcite, dolomite or nesquehonite ($MgCO_3 \cdot 3H_2O$). Thus, concentrated pore solutions cannot contain calcium or magnesium and carbonate at the same time.

If the sum of the calcium and magnesium concentrations exceeds the total carbonate concentration, a carbonate poor solution will evolve due to the precipitation of carbonate minerals. Then, due to its low solubility, gypsum is precipitated next and acts as a second divide. If the initial calcium concentration exceeds that of sulphate a sulphate-poor, type I, solution evolves. Typically, the solubilities are very high in such mixtures, particularly if there are significant relative abundances of calcium or magnesium. Type I solutions are very often found in the upper evaporation zone of masonry affected by rising damp. Several examples can be found in Arnold and Zehnder (1991). If the initial solution contains more sulphate than calcium, a type II,

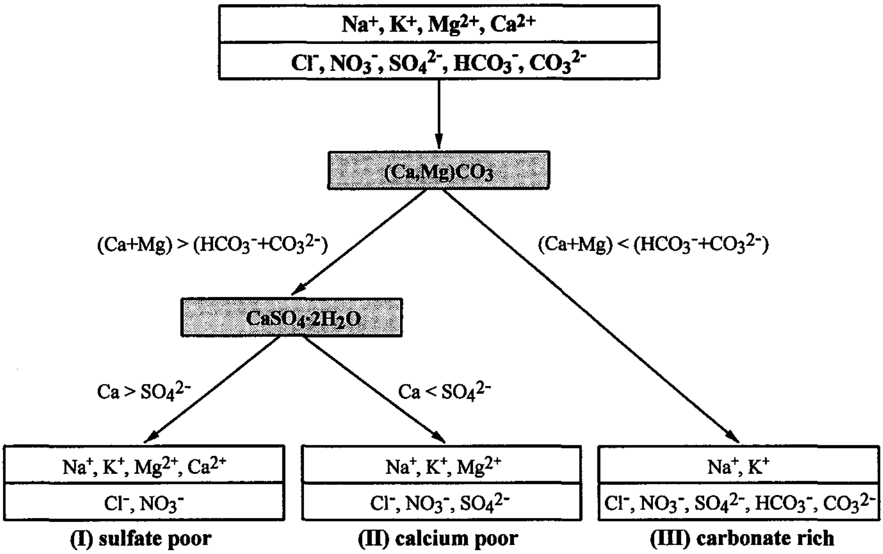

Fig. 5. Evolution of concentrated solutions of major types of hygroscopic salt mixtures.

calcium-poor solution evolves upon evaporation. For example, the evaporation of seawater leads to solutions of the latter type. Only if the carbonate concentration in an evaporating solution exceeds the sum of the calcium and the magnesium concentrations, a carbonate-rich, type III, pore solution can evolve. As was mentioned before, carbonate-rich salt systems are typically found in building materials that have been subjected to inappropriate materials and treatments.

In effect, the alkaline earth carbonates and gypsum are precipitated very early during transport and are thus accumulated at low heights, whilst the further fractionation of the remaining salt systems proves to be quite complicated. Though it is possible to deduce the fractionated crystallisation of complex salt mixtures from experimentally derived solubility diagrams (cf. Mullin, 1993), this approach requires solubility measurements on a huge number of mixture compositions covering the temperature range of interest. For some systems of geochemical importance, e.g. the composition of brines related to the evaporation of seawater, such data exist and were used to describe the formation of evaporite minerals (Braitsch, 1971). However, available data for the more complex salt systems typically found in building materials are not sufficient to adequately describe the required phase diagrams. Another approach to understand evaporite formation is based on chemical modelling of aqueous electrolyte thermodynamic properties. The most frequently used model is the ion interaction approach (Pitzer, 1991 and references therein) which was successfully applied to the prediction of mineral solubilities in natural waters (Weare, 1987). This same model approach has been recently utilised to study the behaviour of salt mixtures relevant to building materials (Price and Brimblecombe, 1994; Steiger and Dannecker, 1995).

Another important property of salts, closely related to the solubility, is their hygroscopicity, i.e. their ability to absorb moisture from the air. If a dry salt crystal is exposed to a gradually increasing relative humidity (RH), the crystal will pick up moisture from the air forming a saturated solution. The phase transition from the solid crystal to the liquid solution only occurs when the RH reaches a certain value, the deliquescence or saturation humidity of the salt. The deliquescence humidity is the RH of air in equilibrium with the saturated salt solution. Deliquescence humidities of several common salts as a function of temperature are shown in Fig. 6. The sodium and potassium salts and all sulphates show deliquescence humidities greater than 70% RH. The deliquescence of the alkaline earth chlorides and nitrates occurs at considerably lower relative humidities (< 60%). In contrast, the deliquescence humidity of gypsum is > 99.9% RH, hence, gypsum is essentially non-hygroscopic.

If a saturated salt solution is subjected to a further increase in the relative humidity, it continues to pick up moisture to achieve equilibrium and the solution becomes progressively more dilute. This is illustrated in Fig. 7 for several salts as the amount of water picked up by 1 g of salt as a function of the relative humidity. It is evident that there is a strong influence of salts on the hygroscopic moisture content of porous materials. Water vapour adsorption and capillary condensation are the major factors controlling the hygroscopic moisture of porous materials in the absence of salts (Camuffo, 1984). Garrecht (1992) studied the hygroscopic moisture uptake of sandstone contaminated with salts. Only considering moisture uptake

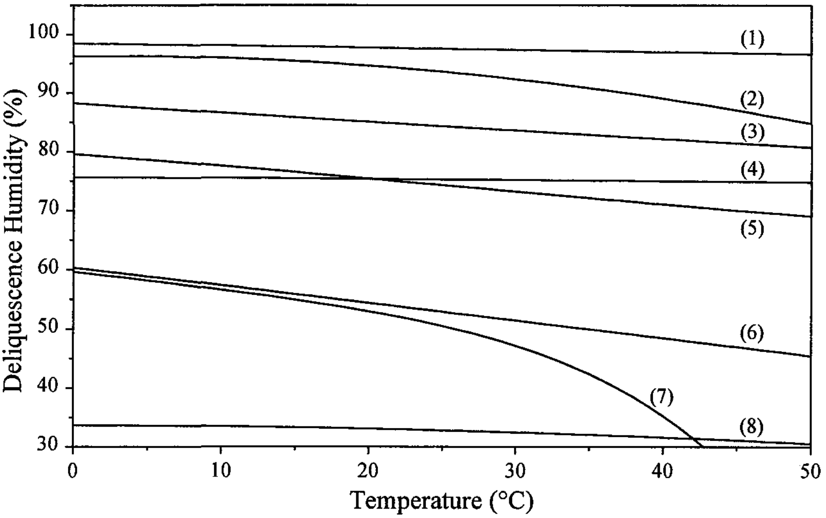

Fig. 6. Deliquescence humidities of several common salts: (1) K_2SO_4; (2) KNO_3; (3) KCl; (4) NaCl; (5) $NaNO_3$; (6) $Mg(NO_3)_2{\cdot}6H_2O$; (7) $Ca(NO_3)_2{\cdot}4H_2O$; and (8) $MgCl_2{\cdot}6H_2O$.

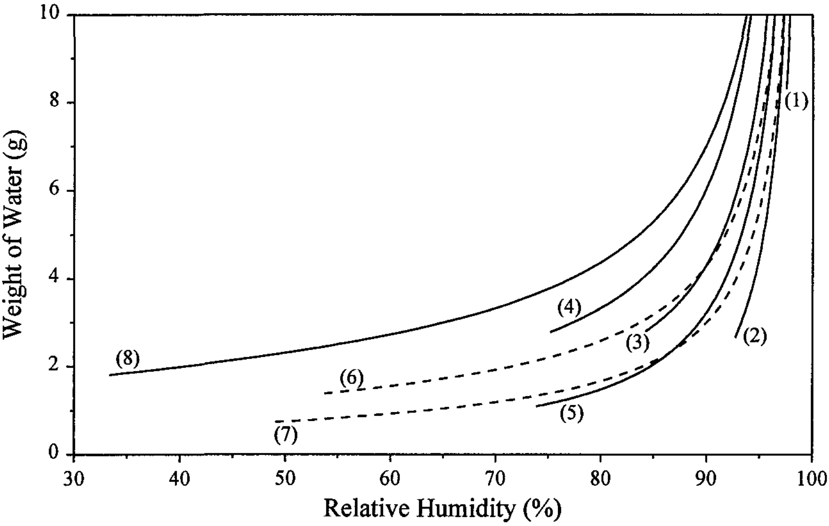

Fig. 7. Water uptake by 1 g of salt as a function of RH at 25°C: (1) K_2SO_4; (2) KNO_3; (3) KCl; (4) NaCl; (5) $NaNO_3$; (6) $Mg(NO_3)_2{\cdot}6H_2O$; (7) $Ca(NO_3)_2{\cdot}4H_2O$; and (8) $MgCl_2{\cdot}6H_2O$.

curves such as those shown in Fig. 7, he could predict to within experimental error the moisture content in the sandstone above the deliquescence humidities of the salts. At humidies below the deliquescence humidities, the hygroscopic moisture content of the stone was not affected by the presence of salts.

The fractionation of salts during capillary rise and evaporation of ground moisture leads to an accumulation of a very hygroscopic salt mixture. In effect, the moisture content in the upper evaporation zone of a masonry affected by rising damp is controlled by the hygroscopicity of the salt mixture. Moreover, as can be seen from Fig. 7, there will be a dynamic equilibrium between the moisture content and the ambient RH. Moisture is picked up as the RH increases and water evaporates from the masonry as the RH decreases. Upon evaporation, the pore solution becomes increasingly concentrated, and eventually, supersaturated with respect to one or several salt minerals which then crystallise out. The situation would be quite simple if the masonry was contaminated with a single salt. Then the salt would crystallise out if the ambient RH drops below its deliquescence humidity. However, the behaviour of salt mixtures is more complex. In their application of the thermodynamic model of Pitzer (1991), both Price and Brimblecombe (1994) and Steiger and Dannecker (1995) have shown that crystallisation in mixed salt systems occurs across a range of RH rather than at specific values.

In effect, the salts in the accumulation zone may either be present in dissolved form or as crystalline solids, only depending, for a given mixture composition, on the ambient temperature and RH. Steiger (1996) has analysed the behaviour of a salt mixture found in the ground moisture zone of a sandstone building. In this particular application, Na^+, K^+, Mg^{2+}, Cl^- and NO_3^- were the most abundant ions in the accumulation zone. Thermodynamic analysis of the phase behaviour of the mixture revealed the occurrence of salt crystallisation within a range of RH from 30–80%. Considering the range of temperature and RH variation in typical outdoor environments, it is evident that common salt mixtures in porous materials are subject to continuous phase changes. In contrast, gypsum, due to its low solubility, behaves different than most other salts. Gypsum is non-hygroscopic and most of the gypsum once deposited in the pore space remains in solid form at all times. Because of its low mobility, gypsum cannot be efficiently transported in porous materials and tends to be accumulated close to where it has been formed. The same arguments apply to other salts of low solubility, e.g. calcium fluoride and the calcium oxalates.

4. Mechanism of Salt Damage

It is generally recognised that crystal growth of salts in porous materials is a major cause of damage. Due to the complex behaviour of salt mixtures, there are a number of phase changes causing crystal growth in building materials including the crystallisation from supersaturated solutions, the change of the state of hydration, and chemical reactions causing the growth of new minerals at the expense of previously deposited phases. Also, the freezing of water and the growth of ice crystals is strongly affected by dissolved salts. Certain very soluble salts can depress the freezing temperature to –50°C and below (Spencer *et al.*, 1990).

The relevant phase changes are reversible processes. For example, a salt crystallises out as water evaporates due to a decrease in the ambient RH, and the salt will re-dissolve as the RH is increasing again. Thus, changes in the environmental parameters, namely temperature and RH, are the driving forces triggering salt damage. Damage does not necessarily occur where the maximum salt concentration in a material is found, but rather, where, for a given climatic situation, the composition of a salt mixture is such that fluctuations of temperature and RH cause damaging cycles of repeated phase changes.

Evans (1970), and more recently, Duttlinger and Knöfel (1993) and Goudie and Viles (1997) provide comprehensive reviews on the available literature on salt weathering, dating back to the early 19th century. Lewin (1989) has pointed out that many studies are qualitative in nature, i.e. they provide detailed descriptions of the manifestation of salt damage for a variety of materials such as delamination, spalling or granular disaggregation. Only few studies, however, propose detailed mechanisms of the processes which can generate the high internal pressures and disruptive stresses necessary to understand the observable weathering phenomena. Moreover, the discussion of the very nature of the processes has often been controversal, and hitherto, agreement among investigators has not been achieved. The question is not *if* crystal growth causes damage, but rather *how* crystal growth can generate disruptive stress.

4.1. Crystallisation Pressure

It is axiomatic that crystallisation can only exert stress if crystals are growing within confined spaces of a porous material. Thus, one necessary condition for salt damage is crystal growth within the pores of a material rather than on top of its surface. The site of crystallisation is determined by both, the rate of evaporation from the exposed surface of the material and the rate of supply of salt solution to the surface (Lewin, 1982). Figure 8 schematically illustrates the evaporation of water from a porous material initially saturated with a dilute salt solution [cf. Fig. 8(a)]. As water evaporates from the material surface, the solution eventually becomes supersaturated resulting in the precipitation of a salt mineral. As long as the rate of capillary transport of fresh solution to the surface equals the rate of escape of water from the surface, the deposition of the salt mineral occurs on top of the surface resulting in the formation of an efflorescence [Fig. 8(b)]. If salt crystals grow exclusively on top of the surface, there will be no damage. However, as more water evaporates the capillary transport of solution to the exposed surface becomes too slow and does not compensate for the escape of water at the surface. As a result, a dry zone evolves beneath the surface and crystal growth now occurs within the pores [Fig. 8(c)]. If the evaporating solution contains a mixture of ions, a second solid might crystallise out in addition to the first one. Salt crystals are then growing within confined spaces of the material and may generate disruptive stress causing damage [Fig. 8(d)].

A second necessary condition for damage to occur is, that a confined crystal continues to grow against a constraint, thus exerting stress. Becker and Day (1916) and Taber (1916) have experimentally shown that crystals can grow against substantial external loads. They called this phenomenon the force of crystallisation, which was later quantitatively measured by Correns and Steinborn (1939) using

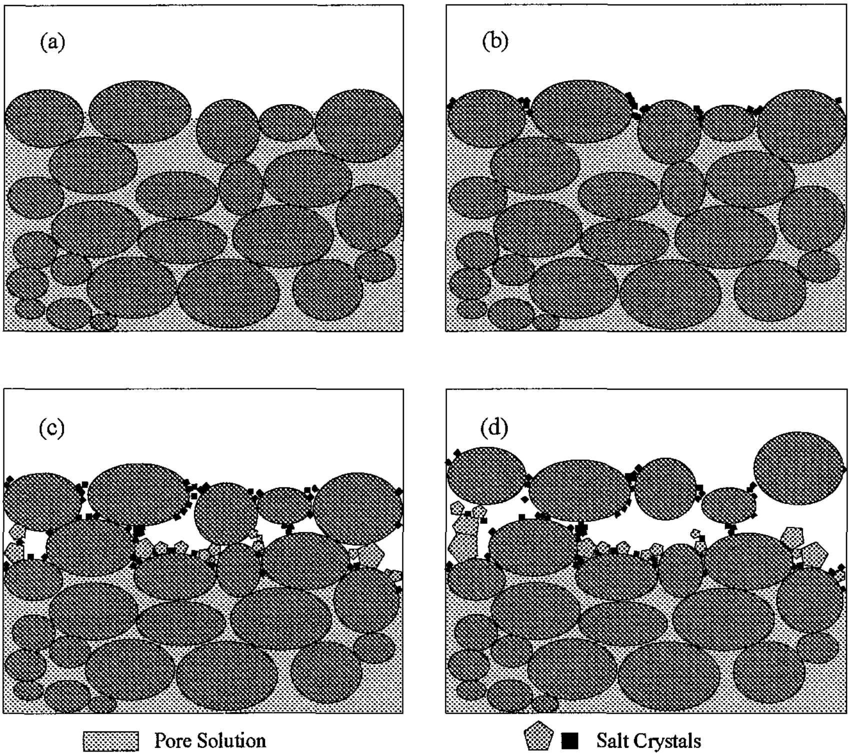

Fig. 8. Evaporation of water and crystallisation of salts in porous materials.

growing crystals of alum ($KAl(SO_4)_2 \cdot 12H_2O$). The experimental setup of these early experiments is illustrated in Fig. 9. It is important to note that the crystals in these experiments continued to grow upon their loaded surfaces despite the fact that the free surfaces were in contact with the salt solution as well. The pioneering experiments of Becker and Day (1916) and Taber (1916) provide evidence that growing crystals can exert stress despite the fact that there is a decrease in the total volume if a salt crystallises from its solution.

In order that a crystal continues to grow upon the loaded surfaces, a solution film must exist seperating at least one of the loaded faces from its constraint, otherwise deposition of mineral matter in the region of contact is impossible. The early observers have been well aware of the importance of such a solution film. Later, Weyl (1959)

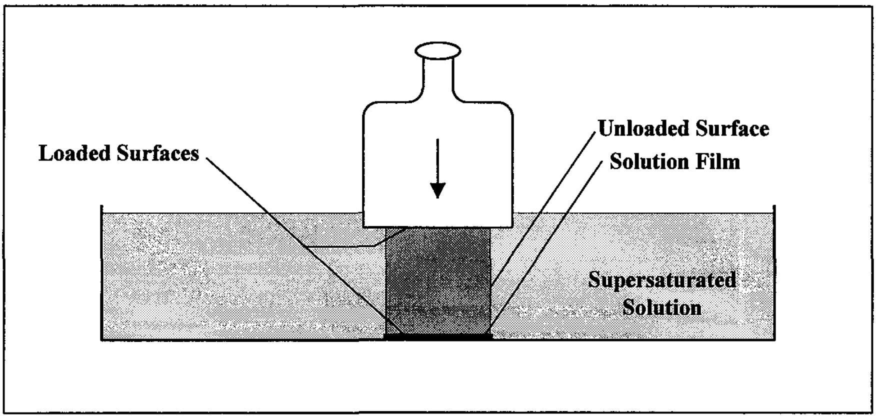

Fig. 9. Growth of a loaded salt crystal.

discussed the properties of the solution film in more detail, which must be of sufficient mechanical strength such that it is not squeezed out of the contact zone of the growing crystal and its support. In addition, the solution film must act as a diffusion path allowing for the exchange of matter between the unstressed solution and the stressed solid. Weyl (1959) gave a derivation of the rather complicated diffusion and mass transport equations and estimated the pressure distribution along the loaded surface of the growing crystal. In accordance with the observations of Becker and Day (1916) and Taber (1916), his model predicts the growth of loaded crystals with a hollow centre.

Another important requirement for the growth of loaded crystals arises from thermodynamic considerations. As a result of the increase of its chemical potential, a solid under stress exhibits a greater solubility than the stress-free solid. It follows that a growing crystal can only generate stress if the external solution is supersaturated. In other words, for a given supersaturation of the solution there is a maximum stress that can be built up. Considering an equilibrium between a solid under stress, σ, and a solution under hydrostatic pressure, p, Correns and Steinborn (1939) derived an expression for the maximum stress as a function of the supersaturation of the solution.

$$\Delta\sigma = \frac{RT}{V} \cdot \ln \frac{C}{C_0} \qquad (10)$$

where $\Delta\sigma = \sigma - p$ is the crystallisation pressure, R is the gas constant, T is the absolute temperature, V is the molar volume of the solid, C_0 is the concentration of the saturated solution of the solute under hydrostatic pressure, and C is the actual concentration of the solute. Winkler and Singer (1972) applied equation (10) to calculate crystallisation pressures for a number of common salts. However, to obtain crystallisation pressures exceeding typical tensile strengths of porous materials, they assumed extremely high supersaturation ratios. Lewin (1974) has pointed out that such supersaturations are very unlikely to be achieved in practice.

Apart from the fact that Winkler and Singer (1972) assumed unrealistically large supersaturation ratios, there is yet another reason why crystallisation pressures according to equation (10) are erroneous. A more rigorous analysis of the thermodynamics of solids under anisotropic stress (Paterson, 1973; de Boer, 1979) yields in fact an equation of the same form as equation (10), if the effect of the elastic strain energy is neglected, which was shown to be a reasonable assumption for stresses below about 100 MPa (de Boer, 1979). However, for dissociating solids (i.e. salt minerals), the supersaturation ratio C/C_0 in equation (10) has to be replaced by the respective ratio of the activity products. Thus, to calculate crystallisation pressures the stoichiometry of the dissociation reaction has to be considered. Since activities have to be used instead of concentrations, such calculations are considerably more complicated than implied by equation (10). It appears that Buil (1983) used the correct equation, though he did not provide details of the procedure used to calculate the activities.

Another interesting aspect arises from the fact that there is only a negligible effect of anisotropic stress on the unloaded surfaces of the growing crystal. The supersaturation of the solution with respect to the unloaded surfaces is therefore higher than with respect to the loaded faces. Clearly, the free surfaces are the most favourable faces for growth. The question arises if a sufficient level of supersaturation can be maintained that is required for the growth upon the loaded faces to continue. In principle, this has been confirmed by the experiments of Becker and Day (1916) and Taber (1916). Particularly favourable conditions for growth upon a loaded surface may exist in porous materials. As water evaporates from a porous material, migration of a pore solution towards the surface becomes increasingly slow. A situation might evolve where only the bottom of the growing crystal remains in contact with the supersaturated solution [Fig. 8(c)]. Then the crystal grows upon the loaded bottom surface and the diminishing effect of growth upon the free surfaces is greatly reduced or even absent. Zehnder and Arnold (1989) studied the habits of growing crystals during the drying of a porous material. As the moisture content of the material decreased, they observed columnar and fibrous habits of the growing crystals indicating growth from the bottom.

There is considerable evidence for the existence of the force of crystallisation which can only be explained by the solution film model of Weyl (1959). It is important to note that the condition of crystallisation from a supersaturated solution also applies to other models of the crystallisation pressure. For example, Fitzner and Snethlage (1982) derived an equation for the crystallisation pressure based on the frost damage model, proposed by Everett (1961). According to this model, crystal growth occurs preferentially in large pores due to the differences in the chemical potentials of small crystals compared to large ones. Stress can be generated if large pores are filled and crystal growth continues. However, as was discussed before, a growing crystal can only exert pressure if it is in contact with a solution of sufficient supersaturation. Hence, the maximum stress determined by the supersaturation of the solution also applies to the model of Fitzner and Snethlage (1982). However, the maximum crystallisation pressure of growing salt crystals has not yet been accurately calculated. Therefore, at present, theory is only qualitative and does not permit a complete understanding of field observations and results of laboratory simulation studies.

4.2. *Hydration Pressure*

Several common salts can exist in different hydrated forms. The phase change from the lower hydrated (or anhydrous) form to the higher

Table 4. Examples for hydration equilibria and associated volume expansion.

Lower hydrate	Hydrated form	Expansion
Na_2SO_4 (thenardite)	$Na_2SO_4{\cdot}10H_2O$ (mirabilite)	314%
$Na_2CO_3{\cdot}H_2O$ (thermonatrite)	$Na_2CO_3{\cdot}10H_2O$ (natron)	257%
$MgSO_4{\cdot}H_2O$ (kieserite)	$MgSO_4{\cdot}6H_2O$ (hexahydrite)	146%
$MgSO_4{\cdot}6H_2O$ (hexahydrite)	$MgSO_4{\cdot}7H_2O$ (epsomite)	10%

state of hydration causes an increase in volume. Due to this expansion, hydration is considered as an important cause of damage. Table 4 lists examples of hydration–dehydration equilibria relevant to building materials.

The phase diagram of the system $Na_2SO_4{\cdot}H_2O$ is depicted in Fig. 10. At high RH, sodium sulphate can only exist as an aqueous solution. At temperatures above the transition temperature (32.4°C), thenardite (Na_2SO_4) crystallises out as the relative humidity drops below the deliquescence humidity (curve 1). At temperatures below 32.4°C, mirabilite ($Na_2SO_4{\cdot}10H_2O$) is the stable solid in equilibrium with a saturated sodium sulphate solution (curve 2). Finally, curve 3 represents the hydration-dehydration equilibrium according to

$$Na_2SO_4 + 10H_2O(g) \rightleftharpoons Na_2SO_4{\cdot}10H_2O \qquad (11)$$

Thenardite is the stable solid at low RH, whilst mirabilite can only exist within a limited range of RH at temperatures below 32.4°C. Hydration damage can occur if thenardite is hydrated due to changes in either temperature, or RH, or both (cf. Arnold, 1976). Hence, at constant temperature, hydration damage occurs as the result of an increase in RH. A hydrating crystal can only exert stress if the crystal continues to grow against the confining pore walls. It follows from thermodynamic considerations that, due to the increase of the chemical potential of the stressed crystal, there is a maximum stress that can be exerted. Given the general form of a hydration reaction

$$A{\cdot}\nu_1H_2O + (\nu_2-\nu_1)\ H_2O(g) \rightleftharpoons B{\cdot}\nu_2H_2O \qquad (12)$$

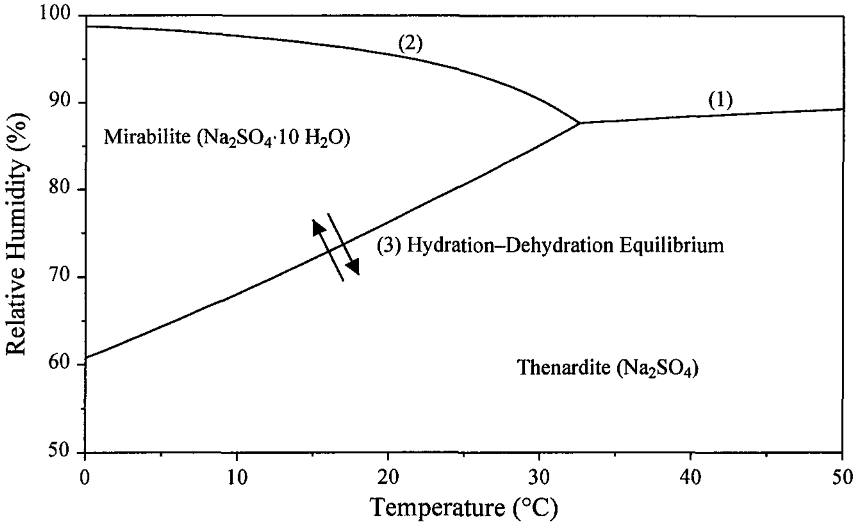

Fig. 10. The Na_2SO_4-H_2O system from 0–50°C.

the maximum hydration pressure is given by the following equation, which was first derived by Mortensen (1933):

$$\Delta\sigma = \frac{(v_2 - v_1)RT}{V_B - V_A} \cdot \ln\frac{P}{P_0} \tag{13}$$

Here, $\Delta\sigma$ is the hydration pressure, V_A and V_B are the molar volumes of the two solids, P is the actual partial pressure of water vapour, and P_0 is the water vapour pressure in equilibrium with the unstressed hydrated solid as shown in Fig. 10 (curve 3) for the thenardite–mirabilite equilibrium. It follows from equation (13) that the maximum hydration pressure is a function of the RH. Winkler and Wilhelm (1970) have calculated the hydration pressures of some common salts using equation (13). At very high RH, they obtained appreciable stresses exceeding the tensile strengths of many materials. However, they did not consider that there is an upper RH limit above which the calculation of hydration pressures is not meaningful. This is illustrated in Fig. 11 for the hydration of thenardite at 25°C. The solid line represents the hydration pressure calculated using equation (13) as a function of RH. The deliquescence of mirabilite occurs at 93.6%

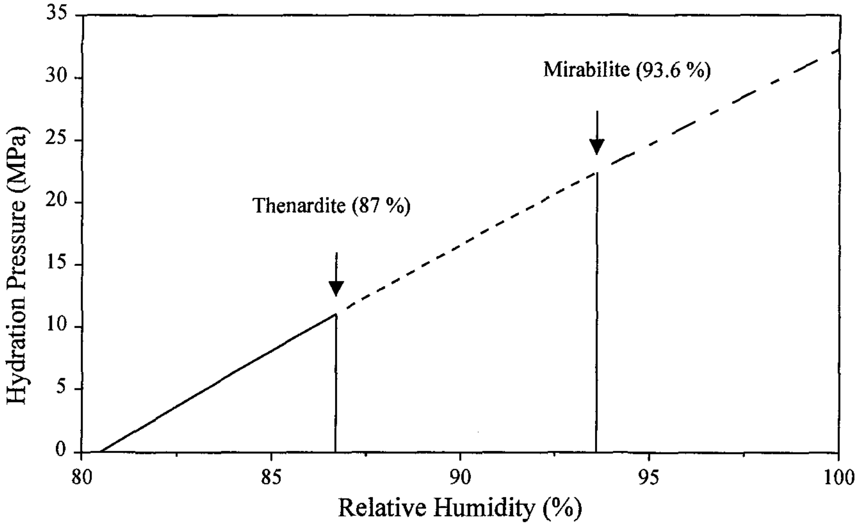

Fig. 11. Hydration pressure associated with the thenardite-mirabilite transition at 25°C.

RH. Thus, at humidities above 93.6% sodium sulphate exists as a solution and no hydration or crystallisation pressure can be exerted. Another important limitation arises from the deliquescence of thenardite occurring at 87% RH. As a thenardite crystal is subjected to a humidity increase, hydration will start as humidity exceeds 80.5% (cf. Fig. 10). Further increasing RH would increase the hydration pressure. As the deliquescence humidity is reached, however, thenardite will pick up water forming a sodium sulphate solution. Hence, the solid state hydration mechanism cannot proceed.

The deliquescence of thenardite represents a metastable equilibrium. The solution formed is saturated with respect to thenardite, but is considerably supersaturated with respect to mirabilite which will be precipitated from that solution. Thus, at RH above the deliquescence humidity of thenardite, the hydration reaction should follow a different reaction mechanism, namely a dissolution-recrystallisation mechanism. Equation (13), however, does not apply to that situation and the stress that might be generated is more realistically described as crystallisation pressure resulting from the growth of mirabilite from a supersaturated solution. The degree of supersaturation will depend on both, the dissolution kinetics of thenardite and the growth kinetics of mirabilite. It is obvious that the maximum hydration pressures calculated according to equation (13) are not meaningful. Similar arguments, of course, apply to the hydration reaction of other salts. Hydration will also follow the dissolution-recrystallisation mechanism as the reaction is initiated by the penetration of water, e.g. rainfall or condensation water, into a porous material containing crystals of the lower hydrated form. Sperling and Cooke (1985) and McMahon *et al.* (1992) carried out experiments to differentiate between the crystallisation and hydration pressures in salt weathering. Using sodium sulphate, they have shown that hydration is significantly less destructive than crystallisation from supersaturated solutions.

Finally, it is interesting to see how the hydration reaction is influenced by the presence of other salts. Using a $NaCl-Na_2SO_4$ mixture as an example, Steiger and Zeunert (1996) have shown that two effects may occur: (1) Depending on the mixing ratio of the salts, the hydration reaction can be entirely suppressed. (2) The solid state hydration is only possible if the respective salt mixture is not deliquescent at the respective RH. In a $NaCl-Na_2SO_4$ mixture, for example, the hydration of thenardite (or dehydration of mirabilite) always occurs in the presence of a solution.

Recent investigations further indicate that the solid state hydration is also kinetically hindered. Charola and Weber (1992) failed to hydrate thenardite even at high RH, which they have attributed to the formation of a mirabilite surface layer which prevents the complete hydration of the thenardite crystal. Using an environmental scanning electron microscope, Doehne (1994) has confirmed the formation of the mirabilite skin on large thenardite crystals. He could also show that the dehydration of mirabilite results in the formation of highly porous aggregates of submicron thenardite crystals which subsequently could be easily rehydrated. However, Doehne (1994) observed that the volume increase of the individual crystals is largely accommodated by the dead space available in the porous aggregates. In both studies, rapid hydration and growth of very large mirabilite crystals in the presence of liquid water were observed.

In conclusion, it appears that the idea of simple volume expansion during the direct hydration of thenardite or other salts in the presence of humid air is not sufficient to understand the deleterious effects of hydration. In particular, the calculation of hydration pressures according to equation (13) is of limited use only. Hydration damage might be more realistically understood as the result of crystal growth from supersaturated solutions if the hydration reaction proceeds via the dissolution-crystallisation mechanism.

5. Atmospheric Pollution and Salt Enrichment

The weathering of building materials causes dramatic changes in the appearance of a building façade, which often follow distinct spatial patterns, clearly dependent on the geometric configuration of the façade and the exposure to the local weather conditions. For example, black and white areas can usually be clearly distinguished on limestone and marble façades (Camuffo *et al.*, 1982; Amoroso and Fassina, 1983) corresponding to rain-sheltered and rain-exposed surfaces (cf. Fig. 12). However, different patterns of macroscopic appearance of sandstone façades are usually observed (Sabbioni and Zappia, 1992; Whalley *et al.*, 1992). Crusts, discolouration, organic growth, soiling, patina etc. are other commonly used terms to describe visual changes of the macroscopic appearance of building materials. However, it often appears that different authors use a different terminology describing the same weathering phenomena and *vice versa.*

Following Zehnder (1982), a crust is generally defined as a compact surface layer, the composition of which is different from the underlying material. The term "black crust" which is often used to describe any form of black deposit on a material surface, however, appears to be ambiguous. There are several different mechanisms that can cause the formation of crusts or deposits. For example, black deposits on sandstone and granite buildings are usually observed on both, sheltered and exposed surfaces (Fig. 12). However, as will be shown below, these deposits represent fundamentally different weathering phenomena. The black colour of such deposits is not necessarily related to a particular mechanism of its formation.

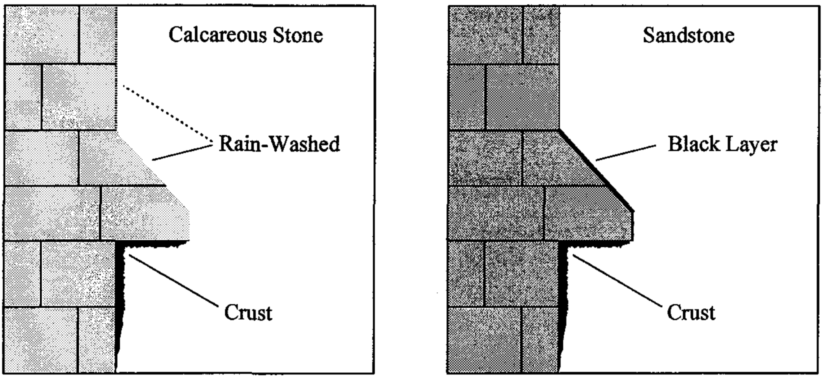

Fig. 12. Typical macroscopic appearance of exposed and sheltered surfaces of calcareous materials (limestone, marble) and sandstone.

Moreover, black discolouration *per se* might not be regarded as damage at all. Since we are more interested in the mechanisms of surface modifications than in their macroscopic appearance, the term "black crust" should be avoided whenever the composition of a crust or deposit is known from microscopic examination or chemical analysis. Even if such information is not available, different types of crust or deposits might be further classified according to their macroscopically visible morphology as deposits either masking or tracing the original material surface (Fitzner *et al*, 1995).

Gypsum crusts are among the most widespread encrustations found on building materials. The formation of sulphation crusts on carbonate stone was previously described by Schaffer (1972) and Kieslinger (1932). According to them, gypsum encrustations are preferentially formed at the rain-sheltered surfaces of carbonate building materials. Also according to Camuffo *et al.* (1982), gypsum crusts occur on surfaces not directly exposed to rainfall which are corresponding to their black areas. In fact, gypsum crusts on buildings in urban environments nearly always appear black. The black colour of gypsum crusts is caused by the embedding of particles originating from a number of different sources including fly ash particles, soot, mineral dust, iron oxides and oxyhydroxides, organic pollutants, and black fungi (e.g. Del Monte *et al.*, 1981; Del Monte and Sabbioni, 1984; Nord and Tronner, 1991;

Urzi *et al.*, 1992; Whalley *et al.*, 1992; Saiz Jimenez, 1993). White gypsum crusts on natural outcrops were observed by Zehnder (1982).

There is no doubt that the formation of gypsum crusts on calcareous stones is the result of the dry deposition of SO_2 to a moisture film on the stone surface followed by the dissolution of calcite and subsequent precipitation of gypsum. Hence, the major damage mechanism is one of chemical weathering. The replacement of calcite by gypsum and the growth mechanism of crusts have been studied in detail, both, for limestone (Schiavon, 1992) and marble (Vergès-Belmin, 1994). It was shown that gypsum crusts on limestone and marble are growing inward which is in contradiction to the growth model of Skoulikidis and Charalambous (1981), who proposed a solid state diffusion model according to which gypsum growth would proceed outward.

Another type of chemical weathering crust on calcareous stones are calcium oxalate crusts. Whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot 2H_2O$) are commonly found on Italian marble and limestone monuments and natural carbonatic outcrops (Del Monte *et al.*, 1987). There has been some controversial discussion on the origin of these crusts in particular with respect to the patina called "scialbatura" which is commonly found on Roman imperial marble monuments (Del Monte and Sabbioni, 1987; Lazzarini and Salvadori, 1989). Biological activity (lichens, algae, etc.) is probably the major source of oxalate crusts (Del Monte *et al.*, 1987), though oxalates may also derive from atmospheric deposition or protective treatments (Lazzarini and Salvadori, 1989; Watchman, 1991).

The formation of gypsum crusts on sandstone is less obvious. However, gypsum crusts are commonly found on calcite-cemented sandstones (e.g. Zehnder, 1982) and nearly calcium-free materials such as quartz sandstone and granite (Whalley *et al.*, 1992; Neumann *et al.*, 1993; Smith *et al.*, 1994). In contrast to calcareous stone, the mechanism of crust formation on sandstone must be different, because both, sulphate and calcium must originate from external sources. One obvious source is the mobilisation of calcium from mortar joints. Another source of calcium is the deposition of particulate matter from the atmosphere, either as gypsum or calcite. Apart from gypsum, the examination of crusts on sandstones and granite by microscopic and chemical analysis shows the presence of a wide range of constituents (e.g. Whalley *et al.*, 1992). Generally, however, the particles embedded in the crusts are similar to those found in gypsum crusts on calcareous stone.

Material loss may occur if crusts are detaching from the stone. Neumann *et al.* (1997) examined gypsum crusts from several buildings built of quartz sandstones. Based on microstructural changes, they have differentiated crusts detaching with and without adherent stone fragments, respectively. On surfaces perfectly sheltered from rain gypsum growth was found to be essentially restricted to growth on top of the stone surface and no material loss is caused by the detachment of these crusts. On surfaces only partially sheltered from rainfall, as typically found in the transition zones from sheltered to exposed areas, substantial material loss is caused by the detachment of crusts with adherent stone fragments. The infiltration of water in these transition zones is sufficient to permit the migration of gypsum into the underlying stone. Due to the limited supply of water, however, the solution cannot deeply penetrate into the stone resulting in a continuous crystallisation and accumulation of gypsum in the pore space close to the stone surface.

Microscopic examination of crusts confirmed that the available pore space just beneath the stone surface is very often completely filled with gypsum. A characteristic feature of the later stage of the damage process is the complete destruction of the original internal fabric which is replaced by a secondary gypsum supported fabric (Neumann *et al.*, 1997). The resulting loss of cohesion was quantitatively studied by Neumann *et al.* (1993). They used the number of grain contacts and the distances between quartz grains as a measure of cohesiveness of the fabric. As can be seen from Fig. 13, the number of grain contacts is significantly lower in crusts compared to the original sandstone. Moreover, Neumann *et al.* (1993) report several examples of crusts in which grain contacts could not be observed at all. At this stage, the quartz grains are embedded in a secondary gypsum fabric. Clearly, stress generated by the crystal growth of gypsum within the confined pore space is the major cause of damage. This damage mechanism is fundamentally different from the chemical weathering process of gypsum growth on calcareous stone.

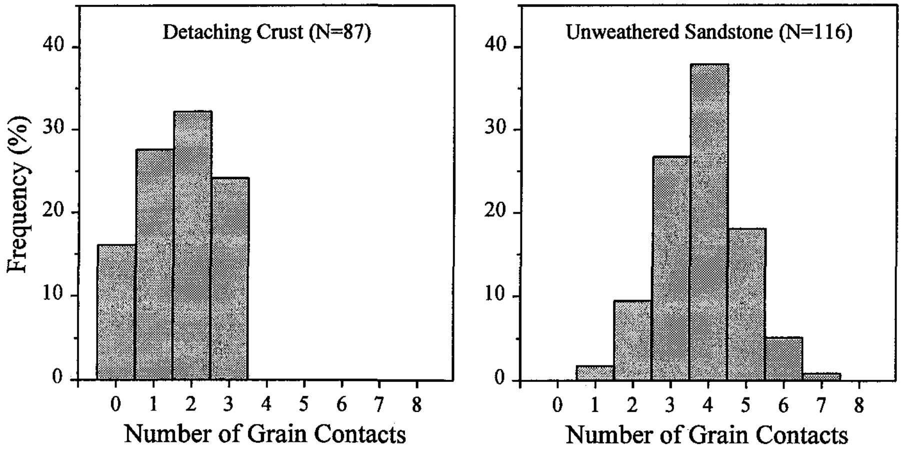

Fig. 13. Frequency distribution of the number of grain contacts per quartz grain in a detaching crust compared to the unweathered sandstone; N is the total number of grains (redrawn from Neumann *et al.*, 1993).

The situation becomes a lot more complicated if a stone surface is exposed to rainfall. If rainfall hits the surface of a porous material, it will be absorbed by capillary transport. As water is freely available at the surface of a porous material, the absorption of water obeys the equation

$$i = A\ t^{1/2} \tag{14}$$

where i is the cumulative infiltration (mass per unit surface area), and A is the water absorption coefficient. Equation (14) does not strictly apply to the case of driving rain penetrating into a porous material because the supply of water is limited by the rainfall rate. A more rigorous treatment of the problem based on unsaturated flow theory is provided by Hall and Kalimeris (1982). For the simple qualitative approach followed here, equation (14) might be appropriate, however.

It directly follows from equation (14) that the rate of infiltration, $u = di/dt$, decreases as $t^{-1/2}$, resulting in very large rates at small values of t. During the initial phase of absorption, the actual infiltration rate is therefore limited by the rainfall rate, V_0, which is schematically depicted in Fig. 14. As the infiltration rate decreases, a point will be

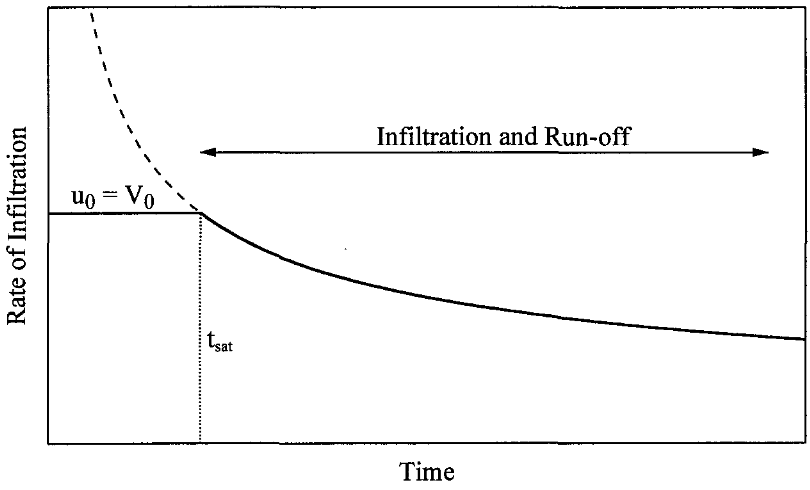

Fig. 14. Supply limited infiltration rate and formation of run-off water.

reached at which the rainfall rate exceeds the infiltration rate. The porous material becomes saturated and the excess water will start to run-off. The time to reach saturation, t_{sat}, depends on the rainfall rate and the water absorption coefficient, A.

Hall and Kalimeris (1982) provide a useful equation for the calculation of t_{sat} for many building materials:

$$t_{sat} = 0.64 \cdot \frac{A^2}{\rho_w^2 V_0^2} \tag{15}$$

Here, ρ_w is the density of water. Figure 15 depicts the saturation times of typical building materials and their dependence on the rainfall rate, calculated using equation (15). Typically, rates of driving rain are rarely exceeding 2–3 mm/h (Schwartz, 1973; Fazio *et al.*, 1995). It can be seen that saturation times are in the order of minutes to several tenth of hours depending on the water absorption coefficient. Hence, there are different modes of action of precipitation. The acidity of rainfall may lead to direct attack on the mineral compounds of a material. Indirect effects include the dissolution and transport of previously deposited material and the corrosion products of dry deposition. Dissolved matter may be either transported into the

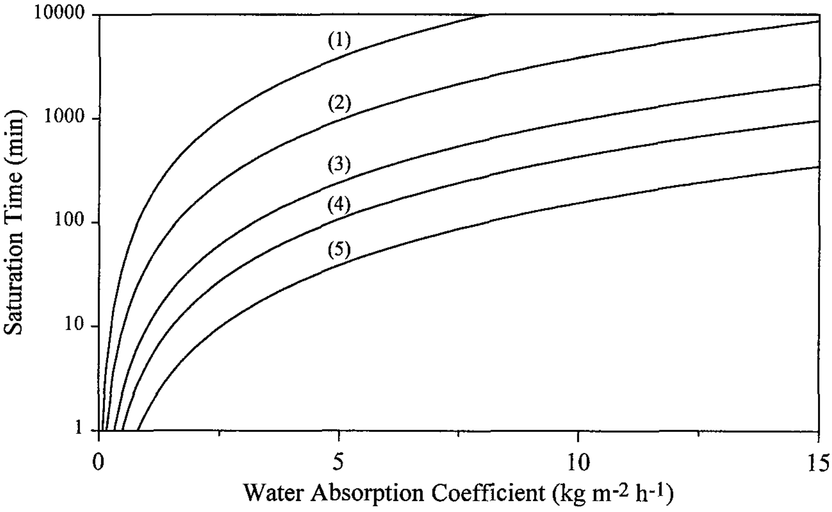

Fig. 15. Dependence of saturation time on water absorption coefficient and rate of driving rain: (1) 0.5 mm/h; (2) 1 mm/h; (3) 2 mm/h; (4) 3 mm/h and (5) 5 mm/h.

porous material, or, may be removed by running water. The significance of these processes is depending on the intensity, duration and frequency of rainfall, its chemical composition, and the properties of the porous material.

The simplest situation that can be considered, is a nearly impermeable material, i.e. a very dense material of low sorptivity such as marble and many limestones. The saturation times of such materials are small and run-off water is the dominant process. This situation corresponds to the surfaces classified as white areas by Camuffo *et al.* (1982). The action of rainfall reduces to the dissolution of calcite and the removal of the reaction products (mainly gypsum) formed due to the dry deposition of acidic species. These processes can cause significant material loss on surfaces exposed to intense rainfall. Lipfert (1989b) provides a review on field exposure studies that were carried out to quantify the material loss of carbonate stones exposed to different environmental conditions. Such data may be used to derive quantitative expressions for the chemical weathering rates of these materials (Lipfert, 1989b; Webb *et al.*, 1992).

The cleansing effect of rainfall is limited due to the relatively low solubility of gypsum. Moreover, the dissolution kinetics might further reduce the maximum amount of gypsum that can be removed with running water. Hence, the cleansing effect depends on both, the frequency and intensity of rainfall and the rate of SO_2 deposition and gypsum formation during dry periods. Gypsum crusts can occur on exposed surfaces if the rate of gypsum formation exceeds the removal rate with running water. In polluted environments, the occurrence of white areas, therefore, is often limited to inclined surfaces, e.g. the top side of cornices. Vertical surfaces, though not sheltered, are less affected by driving rain and the accumulation of airborne particulate matter, and gypsum is also frequently observed on exposed vertical surfaces of buildings in polluted urban areas (Amoroso and Fassina, 1983). Considerable enrichment of gypsum or the formation of crusts on façades exposed to moderate rainfall intensities is particularly often found on calcareous stones of high porosity, such as coarse-grained limestones and calcite-cemented sandstones (Sabbioni and Zappia, 1992; Fitzner and Heinrichs, 1992). Due to the greater saturation times of such materials, rainwater is absorbed and gypsum is transported into the stone. The amount of gypsum in the pore space continuously increases with every wetting and drying cycle, and besides the chemical weathering of calcite, additional damage results from crystal growth of the reaction product (Charola, 1988).

In contrast to marble and limestone, black discolourations often appear more evenly distributed on sandstone and granite surfaces. In particular, their occurrence is not restricted to sheltered areas. Intense black areas are rather found on surfaces frequently wetted by rainfall or run-off. These discolourations often appear as homogeneous black layers firmly attached to the stone surface. In contrast to gypsum crusts, they are tracing the original stone surface and it appears reasonable to adopt the term “thin black layer” as suggested by Nord and Ericsson (1993). Based on microscopic and chemical analysis, black layers might be further classified. In polluted urban environments, black layers mainly consist of insoluble airborne particulates and organic substances (Sabbioni and Zappia, 1992; Nord and Ericsson, 1993; Schiavon, 1993; Schiavon *et al.*, 1995). Microscopic examination confirmed that black layers are homogenous deposits rarely exceeding 200 mm in thickness (Nord and Ericsson, 1993; Begonha and Sequeira Braga, 1996). Black layers, particularly on frequently wetted surfaces, can also originate from biological growth of algae and other microorganisms (e.g. Saiz-Jimenez, 1995; Warscheid and Krumbein, 1996).

Damage mechanisms associated with the presence of thin black layers are still not clear and have been subject to controversial discussion. In many cases, stones covered with black layers show essentially no damage at all. Often, however, the detachment of rather thin scales or flakes is observed. It is very unlikely that damage can be attributed to a single mechanism (Schiavon, 1993). Gypsum may or may not be accumulated in near-surface pores of stones covered with thin black layers. Apparently, gypsum growth and the formation of black layers are different phenomena that can evolve independently. Neumann *et al.* (1997) provide an example for the development of a gypsum crust on a quartz sandstone exposed to rainfall that was originally covered by a thin black layer.

The formation of gypsum crusts on exposed sandstones or granites is only possible if the rate of gypsum formation exceeds the removal of gypsum. Therefore, gypsum crusts on quartz sandstones are usually only observed in polluted areas where the supply with both, calcium and sulphate is sufficient. If gypsum mobilisation by rainfall is predominant, gypsum might be either removed with running water, or, can migrate into the porous material. There are many buildings where the maximum gypsum enrichment is not found at the exposed stone surface, but rather some distance in the interior of the stone. Zehnder (1982) provided several examples from different buildings with gypsum maxima at depths from a few millimetres up to several centimetres. He could further show that the presence of gypsum is correlated with severe damage due to the formation of contour scales.

The transport of gypsum to such great depths requires substantial penetration of water into the stone. In addition, as water evaporates during the drying of the stone, capillary transport back to the surface must not take place. As Zehnder (1982) has pointed out, these conditions are most likely to be met as a result of intense wetting and rapid drying. The evolution of moisture profiles during infiltration

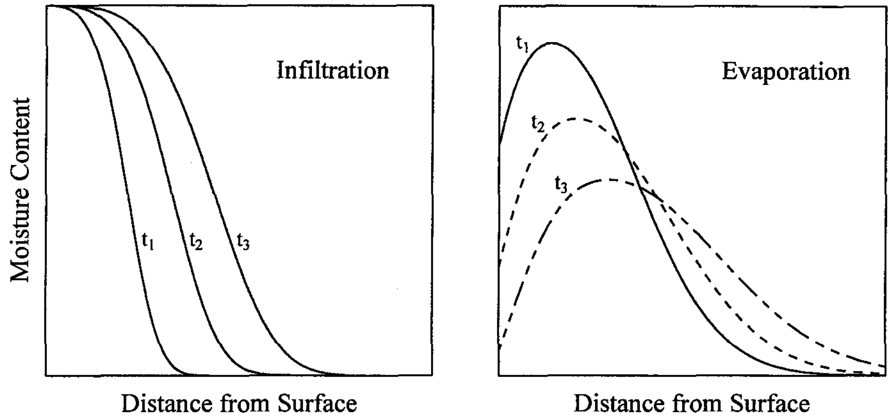

Fig. 16. Moisture profiles at different times, t, during infiltration and evaporation ($t_1 < t_2 < t_3$).

and drying is schematically illustrated in Fig. 16. Snethlage and Wendler (1997) have numerically simulated the dynamics of wetting-drying cycles using the approach for the parameterisation of moisture transport in porous materials proposed by Künzel (1995). They obtained average moisture distributions for several sandstones with maxima at different distances from the stone surface depending on the moisture transport properties of the stones. Hence, the evaporation of water occurs at some distance from the stone surface corresponding to zones of maximum salt enrichment.

As mentioned before, the amount of gypsum that can be transported into the stone is limited due to its rather low solubility. In effect, gypsum accumulation proceeds slowly. The maximum gypsum concentrations found by Zehnder (1982) and others (Wendler *et al.*, 1991; Steiger *et al.*, 1993) rarely exceed 2–3% by weight. Compared to the enormous enrichment of gypsum in crusts, these concentrations are much lower and are far from filling the available pore space. However, even these moderate concentrations exceed the mobility of gypsum in typical materials by about two orders of magnitude (cf. Fig. 3). Hence, the gypsum once deposited is essentially immobilised. Although every rain event will inevitably add to the further accumulation of gypsum, it should be noted that only a small amount of gypsum crystallises out during each drying cycle. It is not clear whether the growth of such a small amount of gypsum can generate significant stress. This would be possible only if the continuous accumulation of gypsum would preferentially occur in confined intergranular spaces. In a laboratory experiment carried out by Wendler and Rückert-Thümling (1992), however, it was shown that continuous accumulation of gypsum caused significant irreversible expansion of a sandstone. It might be concluded that gypsum is an important cause of contour scaling.

Apart from salts accumulated in the ground moisture zones of buildings, gypsum is very often the most abundant salt in building materials. Atmospheric pollution is by far the most important source of gypsum, and due to its low mobility, gypsum tends to be strongly accumulated in porous materials. The discussion so far reveals that besides the chemical weathering of calcareous materials, the growth of gypsum in the pore space of building materials is a major cause of damage. In the absence of calcite, either as a mineral constituent of the material itself or from external sources, acid deposition can also cause the mobilisation of other cations than calcium. The salts then formed show different behaviour. For example, Fig. 17 depicts a salt profile measured in a sandstone monument. The building is located in a rural environment in Southern Germany where the local air

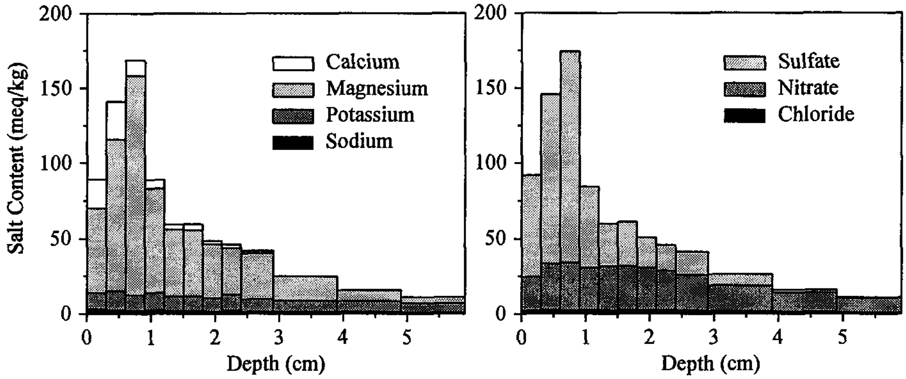

Fig. 17. Salt profile in sandstone from Schloss Weissenstein, Pommersfelden (unpublished results).

pollution level is low and it is expected that there is a significant contribution of acid rain to the total deposition of acidity.

Magnesium, sulphate and nitrate are the major constituents of the salt system, whilst the calcium concentration is of minor importance only. The maximum salt concentration (1.1 wt % total salts) is found at depths of about 6–9 mm. Considering the porosity of the stone and the solubilities in the salt mixture, it can be concluded that apart from gypsum, all other salts will be completely dissolved if rainwater penetrates into the stone. As water evaporates from the stone, salts will crystallise out resulting in a fractionation as discussed before. For the salt mixture given, it can be simply deduced from available solubility data that, apart from gypsum, epsomite ($MgSO_4 \cdot 7H_2O$) will be precipitated first. This is in accordance with the profile in Fig. 17 showing a strong enrichment of magnesium and sulphate at a distance of 6–9 mm from the surface, whilst the remaining ions are more evenly distributed, and are therefore, probably present in dissolved form. Clearly, the profile shown in Fig. 17 only reflects an intermediate state. Depending on the ambient temperature and RH, the drying process may either continue followed by the crystallisation of other solids, or, the system might already be in equilibrium with the surrounding atmosphere. Anyhow, on every wetting-drying cycle, the salts will be completely dissolved and re-distributed. The damage potential of such a hygroscopic salt mixture is obviously much greater than that of an equal amount of gypsum.

It is generally recognised that hygroscopic salts are a major cause of damage in the ground moisture zone of buildings where extreme salt enrichment and rapid destruction are quite often observed. It appears, however, that sometimes their relevance might be underestimated if they are only present in moderate concentrations. Due to their mobility, hygroscopic salts are usually more evenly distributed in building materials, and extreme enrichment and strong gradients as typically found for gypsum are rarely occurring. Therefore, relevant salt concentrations might be present in the interior of a porous material even if there are no visible efflorescences indicating salt damage. Apart from rainfall and condensation, the water necessary to dissolve these salts can also come from hygroscopic moisture uptake.

In effect, damage is not limited to wetting-drying cycles but can also be continuously initiated during dry periods by relatively minor fluctuations of the ambient RH.

6. Conclusions

Building materials exposed to polluted atmospheres are severely affected by acid deposition. The damage mechanisms associated with acid deposition are reasonably well understood on a qualitative basis. It might be even possible to predict the type of damage for a particular material exposed to a given environment. It is much more difficult, however, to predict rates of damage, i.e. to establish a quantitative relationship between the concentration of air pollutants and the rate of damage. The concept and mathematical form of such damage functions were recently reviewed by Livingstone (1997). However, even for the most simple situation that can be considered — formation of gypsum by dry deposition of SO_2 on a rain-sheltered surface of a calcareous stone — a damage function has not yet been established. Damage functions for other situations, i.e. other materials and different exposures, would be considerably more complex.

The major problem arises from the fact that acid deposition can act in two different ways. First, wet and dry deposition of acidity is the major cause of chemical weathering of materials. Second, acid deposition is a major source of salt accumulation, and therefore, physical weathering. These damage mechanisms follow different rate laws. Chemical weathering rates might be sufficiently well described by the actual environmental conditions (pollutant concentrations, deposition velocities, pH and amount of rainfall). In contrast, the actual rate of salt weathering will largely depend on two influences: (1) the present-day environmental conditions (cyclic variation of meteorological variables), and (2) the concentration and composition of the salt mixture in the material given as the integral salt accumulation from past to present. Not much is known, however, about the influence of the concentration of salts and their relative destructive power on the rate of salt damage in different materials.

In view of these uncertainties, it is also difficult to assess how the overall rates of damage would change in response to clean air legislation. Unquestionably that salt damage would still continue with a rate similar to its present rate even if pollutant concentrations were reduced to zero. However, considering that "every mole of sulphur or nitrogen oxides not emitted is a mole not deposited" (Schwartz, 1989), further accumulation of salts can be significantly retarded by reducing emissions. Materials susceptible to chemical weathering such as calcareous materials would benefit even more from further reduction in acid deposition.

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CHAPTER 6

ORGANIC POLLUTANTS IN THE BUILT ENVIRONMENT AND THEIR EFFECT ON THE MICROORGANISMS

C. Saiz-Jimenez

1. Introduction

The Northern Hemisphere is experiencing a series of severe ecological problems with forest decline, acidification of lakes, and accelerated corrosion of monuments, buildings and metallic structures.

Stone buildings, monuments, outdoor-exposed sculptures and objects of art have been degraded over the centuries by natural causes. Wind, rain and frosts contribute to a gradual process of ageing and deterioration. The alteration of stone is not therefore a contemporary phenomenon, but was already known in ancient times, and was a preocupation of Greek and Roman writers.

The process of weathering of a rock begins as soon as it is taken from the quarry and comes into contact with atmospheric agents. However, in the last century, industrial and urban activities have modified the composition of the atmosphere, resulting in a more aggressive environment, accelerating the decay of materials.

Thousands of chemicals are emitted directly or indirectly to the atmosphere because of human activities, but most pollutants emitted into the atmosphere are eventually removed through naturally occurring cleansing mechanisms. These removal and deposition processes represent the final stages of a complex sequence of atmospheric phenomena. Once released into the atmosphere, organic and inorganic airborne pollutants may undergo a variety of complex interactions determined by physical, chemical and photochemical processes occurring during their residence. These processes influence the nature of the capture of the pollutants in a sink or reservoir, where they are transformed, immobilised or encapsulated (Schroeder and Lane, 1988).

Buildings and monuments act as repositories of airborne organic pollutants, which accumulate at the surfaces in zones frequently soaked by rainwater but are not washed out. Obviously, this enriches the substratum and anthropogenic compounds may greatly influence the colonisation and growth pattern of microorganisms in stones located in polluted urban environments when compared with the growth of microorganisms in the same stones placed in rural environments. The industrialised society of the 20th century has thus caused a radical change in the conditions of preservation and conservation of stone, and the atmospheric pollution associated with industrialisation is currently modifying the biological spectrum of microorganisms thriving on stones.

Although it has been reported that a great variety of microorganisms colonise stones in urban environments, and their possible role in biodeterioration processes discussed (Saiz-Jimenez, 1995), the studies on different inputs of organic matter to stone, the use of organic pollutants as nutrients, the interactions between anthropogenic compounds and microorganisms, etc. have barely been investigated. In this chapter, recent findings on the effects of environmental conditions upon colonisation and growth of microorganisms, including the deposition of organic compounds on building stones and their possible utilisation by microorganisms are reviewed.

2. Sources of Organic Pollutants in Urban Environments

Organic compounds in the atmosphere arise from biotic (including anthropogenic components), abiotic (volcanic activity and lithospheric erosion) and extraterrestrial origin (meteorites). Only anthropogenic compounds will be considered in this chapter.

The organic species present in the atmosphere comprise gases, lipids and carbonaceous (insoluble) matter. Among the gases, the short chain alkanes and alkenes, aldehydes, ketones and acids are frequent. They originate mainly from spillage of petroleum-derived products as well as from combustion processes. Apart from methane, which is the major biogenic organic gas, a minor amount of volatiles also evolves from microbial activity and odoriferous plants, as for instance, isoprene and monoterpenes.

As stated by Simoneit and Mazurek (1981), urban aerosols generally consist of a mixture of lipid materials emitted locally along the aged material that has been carried into the urban area by winds. Thus, the urban atmospheric environment contains many organic pollutants which are related to incomplete fuel combustion in domestic heating, industrial plants and vehicular exhausts, such as long-chain alkanes and methyl alkanes (Cautreels and van Cauwenberghe, 1978; Boone and Macias, 1987), monocarboxylic and dicarboxylic acids (Kawamura *et al.* 1985; Kawamura and Kaplan, 1987), polycyclic aromatic hydrocarbons (Leuenberger *et al.* 1988), terpenoids (Simoneit, 1984), etc. In addition to organic compounds, carbonaceous matter (mainly graphitic carbon) is common in urban environments. Table 1 shows

Table 1. Classes of compounds identified in aerosols and particulate matter.

Compounds	Range*	Compounds	Range
n-Alkanes	C_7–C_{40}	Alkylnaphthoic acids	C_{11}–C_{13}
Isoprenoid hydrocarbons	C_{10}–C_{20}	Alkylphenanthroic acids	C_{15}–C_{17}
Isoprenoid ketones	C_{10}–C_{20}	Alkylcyclohexanes	C_9–C_{29}
Alkan-2-ones	C_{10}–C_{32}	Diterpenoid derivatives	C_{16}–C_{20}
Alkanols	C_{11}–C_{28}	Triterpenoid hydrocarbons	C_{27}–C_{35}
n-Fatty acids	C_1–C_{34}	Tricyclic terpane hydrocarbons	C_{19}–C_{29}
Hydroxy fatty acids	C_{10}–C_{26}	Steranes and diasteranes	C_{27}–C_{29}
α, ω-Dicarboxylic acids	C_2–C_{26}	Unresolved hydrocarbons	C_{14}–C_{31}
Alkylbenzoic acids	C_7–C_9	Polycyclic aromatic hydrocarbons	C_{10}–C_{24}
Alkylbenzenedioic acids	C_8–C_{10}	Oxygen-polycyclic aromatic hydrocarbons	C_{10}–C_{16}

* Range denotes number of carbon atoms in the compounds.

the classes of compounds identified in aerosols and particulate matter (Saiz-Jimenez, 1995).

2.1. Hydrocarbons

This class of compounds has been analysed in many urban areas. Typical *n*-alkane distributions range from C_{15} to C_{34} with no carbon number predominance (also termed carbon preference index or CPI). CPI is the sum of the odd carbon number homologues over a specified range divided by the sum of the even carbon number homologues over the same range. This index is an indicator for evaluation of anthropogenic/biogenic contributors in aerosols. Since biogenic *n*-alkanes generally show a strong odd C-numbered predominance, their CPI values are high, whereas *n*-alkanes from petroleum, vehicular exhausts and lubricating oils have a CPI of 1. Thus, the greater the anthropogenic contribution, the more closely the CPI approaches unity. As CPI of *n*-alkanes in urban aerosols is near 1, it was concluded that fuels or partly uncombusted fuels do contribute to these aerosols (Simoneit, 1985).

Aerosols also contain isoprenoid hydrocarbons such as pristane (2, 6, 10, 14-tetramethylpentadecane) and phytane (2, 6, 10, 14-tetramethylhexadecane) which are diagenetic products of phytol and are not primary constituents of most terrestrial biota, thus confirming an origin from petroleum (Simoneit, 1984).

2.2. Acids and Ketones

According to Simoneit and Mazurek (1981), these types of compounds originating from anthropogenic sources are usually only minor components of aerosols. The organic acids (C_1–C_{10}) were detected in many urban aerosols and a similar distribution in motor exhaust from automobiles was found by Kawamura *et al.* (1985). Gasoline and diesel exhaust sampled showed a dicarboxylic acid distribution (C_2–C_{10}) similar to those of air samples, but their concentrations were 28 (gasoline) and 144 (diesel) times higher that the average concentration of atmospheric diacids (Kawamura and Kaplan, 1987). Hence, the data indicate that vehicular emissions are the most important primary source of atmospheric acids. Furthermore, Graedel (1978) reported low molecular weight (up to C_{10}) aldehydes and ketones in diverse anthropogenic emissions.

2.3. Triterpenoid Hydrocarbons

Biological markers are organic compounds present in the geosphere whose structures can be unambiguously linked to the structures of precursor compounds occurring in original source materials (Philp, 1985).

Hopane-type triterpanes are ubiquitous biological markers in fossil fuels and their precursors are widely distributed among organisms. Virtually all crude oils contain the hopane series, which are also found in aerosols. It has been reported (Simoneit, 1985) that the distribution of the $17\alpha(H)$, $21\beta(H)$-hopanes are essentially identical for auto and diesel exhausts, confirming these emissions as the major source of petroleum residues in aerosols.

Gasoline and diesel fuel do not contain these triterpanes, but the same distribution is found in lubricating oils. This indicates that primarily lubricants adsorbed on particulates or as vapour microdroplets impart the molecular indicator signature of petroleum residues to vehicular emissions.

2.4. Polycyclic Aromatic Hydrocarbons

It is generally accepted that airborne polycyclic aromatic hydrocarbons are derived from combustion processes such as the burning of fossil fuel, forest fires and agricultural burning.

Lower polyaromatics (up to benzofluorene) are more abundant in the gas phase while higher polyaromatics are predominantly in the particulate fraction. The higher polyaromatics identified in aerosols are fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, dibenzanthracenes, benzo(ghi)perylene and coronene. The volatile polyaromatics are acenaphthene, biphenyl, fluorene and some heterocyclic species such as dibenzofuran and dibenzothiophene (Simoneit and Mazurek, 1981).

2.5. Carbonaceous Matter

Environmental soot, which is a mixture of various forms of particulate carbon with organic tar and refractory inorganics, is also of importance in aerosols. It has been found that typical aerosols contain 10–30% total carbon. Of this fraction, 20–50% is elemental carbon, less than 5% is carbonate, and the remainder is organic carbon. The colloidal carbon is characterised by a unique morphology defined as aciniform carbon, in which an arrangement of graphitic layers can be observed. This form of carbon is predominant in chimney smoke and engine exhaust, from which the particulate portion of diesel soot is almost exclusively aciniform carbon. About 60% of the carbonaceous soot in the Los Angeles area is graphitic in nature (Simoneit and Mazurek, 1981).

Interestingly, it has been reported that carbonaceous particles consisting of uncombusted coal and oil, coal coke, and intermediates contribute significantly to the interaction with organic compounds. These carbonaceous particles are more sorptive, have high levels of organic matter, and exhibit high specific surface areas. Griest and Tomkins (1984) observed that polycyclic aromatic hydrocarbons were strongly sorbed by and difficult to extract from diesel soot. Carbonaceous particles appear to be responsible for this effect. Chriswell *et al.* (1988) considered that extraction of organic material present in particles is difficult because their matrices contain silica, alumina, metal oxides, and possibly even activated carbon, all of which are excellent adsorbents for organic compounds. These particles appeared to behave not only as carrier of chemicals but also as gypsum nucleating agents (Del Monte *et al.* 1984).

A study of Sagebiel *et al.* (1997) illustrates the importance of diesel vehicles in the production of particulate emissions, as it was reported that 31 diesel vehicles whose age averaged 22 years showed average emissions of 944 mg/km, with one vehicle emitting at a rate of 10,500 mg/km. For comparison, emission rates of total particles were below 6 mg/km for most production catalyst vehicles.

To investigate the possible contribution of diesel soot to organic pollutants and blackening of building stones in urban environments, diesel soot collected from the exhaust of a ten-year-old Sevillian public

Table 2. Main classes of compounds identified in diesel soot.

Compounds	Range*	Compounds	Range
n-Alkanes	C_{14}–C_{31}	Alkylnaphthalenes	C_{10}–C_{17}
n-Fatty acids	C_6–C_{20}	Alkylfluorenes	C_{12}–C_{15}
α, ω-Dicarboxylic acids	C_6–C_{11}	Alkylphenanthrenes	C_{14}–C_{17}
Alkylcyclohexanes	C_{16}–C_{22}	Alkylbenzoic acids	C_7–C_{10}
Alkylbenzenes	$C_{6}{-}_{21}$	Polycyclic aromatic hydrocarbons	C_{12}–C_{16}

* Range denotes number of carbon atoms in the compounds.

bus was analysed by Saiz-Jimenez (1994a). The extract was a complex mixture of compounds, the *n*-alkanes being the majority. Some of the identified classes of compounds are listed in Table 2, which agree with those reported in Table 1. In addition, many other compounds were identified up to a total of around 250, among which nitrogen- (e.g. quinolines), oxygen- (benzofurandiones and dibenzofurans), sulphur-heterocyclic compounds (dibenzothiophenes), phenols, alkan-2-ones and alkanols, were also found.

3. Identification of Organic Pollutants in Black Crusts

3.1. Analytical Methodologies

Sulphur dioxide has long been recognised as the primary gaseous component of air pollution and a correlation exists between sulphur dioxide concentration and sulphatation of carbonatic stones, because oxidation of sulphur dioxide results in sulphuric acid production. In this process, carbonaceous particles are capable of greatly accelerating the destructive action, and behaves as a catalyst — they contain V, Ti, Fe, Mn, Cu — for the oxidation of sulphur dioxide. Aerosols in the form of sulphuric acid droplets also attack building limestones. Sulphuric acid reaction ultimately results in gypsum formation (Saiz-Jimenez and Bernier, 1981; Del Monte *et al.* 1984).

Wet and dry deposition processes combined with gypsum crystal growth give rise to the formation of a hard, grey-to-black crust, in which airborne organic pollutants, carbonaceous particles, aerosols,

Table 3. Resolving power of some analytical techniques.

Method	Compounds resolved
Thin layer chromatography	<10
High performance liquid chromatography (HPLC)	>20
Gas chromatography (packed column)	<100
Gas chromatography (capillary column)	>200
Pyrolysis-gas chromatography (capillary column)	>500

dust, pollen, spores, and every class of particulate matter are entrapped in the mineral matrix. Therefore, organic species present in weathered surfaces are complex mixtures of many classes of compounds entangled in the gypsum matrix. This prevents direct analysis without prior extraction and separation. In order to eliminate mineral interferences, the samples must be extracted with suitable organic solvents and analysed by means of an adequate technique. Table 3 shows the number of resolved compounds in mixtures from weathered stones when different analytical techniques are applied.

From Table 3, it seems evident that gas chromatography (gc) provides the best means of resolving complex mixtures. Some other techniques, such as for instance, column chromatography with gradient elution or preparative HPLC, help to obtain less complex fractions which permit an easier analysis. Since the state-of-the-art for capillary columns and stationary phases is continuously improving (e.g. the introduction of high temperature capillary columns by Lipsky and Duffy, 1986), the number of compounds resolved on capillary columns possibly could be higher that those stated in Table 3.

Most of the modern analytical techniques currently used require solubility and/or volatility of compounds to be separated and analysed. Thus, much of the work with different types of materials has been concentrated on the analysis of organic molecules with a relatively low molecular weight or those readily volatilised by derivatisation (e.g. methylation). In this respect, samples can be extracted with organic solvent and fractionated by column chromatography, prior to analysis, to separate different classes of compounds and facilitate identification.

There are many fractionation schemes according to the nature of compounds to be studied. However, fractions eluted from the chromatography column with solvent mixtures of increasing polarity often contain hundreds of compounds, which are still difficult to resolve by gc. Furthermore, the final fractions, the most polar compounds, contaminate the analytical instruments, as polar species may be lost on cold or adsorbing sites.

In general, fractionation and separation of organic compounds results in tedious and time-consuming analysis. In addition, contamination of samples with compounds introduced during that preparation (e.g. dialkyl phthalates) is highly probable. Furthermore, a great deal of information is missed when unsuitable methods are applied to the analysis of the insoluble fractions of black crusts. However, solvent extraction, in which relatively large amounts of material were analysed by techniques involving gas chromatography in combination with mass spectrometry (gc/ms) was applied as standard method for studying the black crust composition.

For solvent extraction, 20 g of black crust were ground in an agate mortar and extracted in a Soxhlet apparatus. Two extracts were obtained by successive extractions with 200 ml of toluene (8 hours) and with 200 ml of methanol (8 hours). The use of methanol as solvent is reflected in the appearance of both organic and inorganic materials in the extract. The inorganic materials were eliminated by extraction with bidistilled cold water (three times). Both extracts were mixed and evaporated under vaccuum at low temperature (below 40°C) and redissolved in diethylether. Acidic compounds were derivatised by addition of an excess of diazomethane solution in ether, and consequently, carboxylic groups were converted into methyl esters. Extracts were injected in a gc/ms system. Methods and analytical conditions have been thoroughly described elsewhere (Saiz-Jimenez *et al.* 1991).

3.2. Sites Investigated

The organic compounds present in the crusts collected from monuments located in three cities, Dublin (Ireland), Mechelen (Belgium) and Seville (Spain) were investigated. A sample corresponded to black gypsum crusts from the Custom House, an 18th century building in

Dublin, constructed in 1791 with Portland limestone. In addition to damage to the fabric caused by the aggresive atmosphere of Dublin, and the damage caused by the corrosion of ferrous metals, the Custom House has suffered greatly from the effects of three major fires (Saiz-Jimenez, 1991). Crusts were collected from the balustrade removed from the east front during the restoration works accomplished in 1988. The crusts were situated on the back part of the railing, in a sheltered and rain-protected site. The railing and small columns were eroded and free from the black crust, except on the underside of the railing.

The cathedral of Mechelen (13th–15th century), whose building materials and architecture were characteristic of many large historic buildings throughout Flanders, was also selected. The façades built of Balegem stone, a sandy limestone, are covered by a black gypsum crust, consisting mostly of fine-grained equi-dimensional crystals and a smaller amount of elongated crystals. The cathedral of Mechelen is situated on a straight line between Antwerp and Brussels and the heavily industrialised areas north of Brussels, and especially north of Antwerp, are some 15 and 25 km away, respectively. Therefore, Mechelen lies at the centre of one of the world's most polluted areas and downtown traffic passes around most of the cathedral (Fobe *et al.* 1995).

From the cathedral of Seville, the Prince Gate, constructed in 1887 was studied. The entrance to this gate is protected by a fence supported by a small limestone wall and pilasters, which are severely deteriorated due to black crust formation. This is related to the fact that one of the main Sevillian bus terminals, operating for more than 20 years, was just in front and less than 10 m far from this wall. The exhaust gases and particulate matter heavily affected the limestone.

3.3. Solvent Extraction of Black Crusts

After extracting the samples with organic solvents, the extracts were methylated and deposited onto a ferromagnetic wire (358°C) inserted in a pyrolysis unit coupled to a gc/ms system. The solvent was removed before introduction in the pyrolysis unit. In this way, very good chromatograms, without interference from solvents, were obtained. The extractable lipid material consisted primarily of hydrocarbons and fatty acids (as methyl esters), represented by homologous series of *n*-alkanes ranging from C_{13} to C_{40}, and *n*-fatty acids from C_{10} to C_{34} (Table 4). Furthermore, a few diterpenoids, triterpanes, polycyclic aromatic hydrocarbons and dialkyl phthalates, were identified as major peaks.

The range of *n*-alkanes found in black crusts is determined by the analytical procedure. This is due to the technical difficulty associated with the analysis of high molecular weight alkanes (typically > *n*-C_{35}), which are less amenable to chromatographic analysis in conventional capillary gc. It is considered that in the black crusts, in a similar way to oils and derivatives, the *n*-alkane range could be greater than those found in gc studies.

For investigating sources of homologous series of *n*-alkanes, CPI was used. CPI of *n*-alkanes for each sample ranged from 1.0 to 1.7, denoting an exclusive contribution of petroleum derivatives for the Seville crust, and progressive inputs of alkanes of biological origin in the Dublin and Mechelen crusts. A more sensitive method requires splitting the carbon range into low (C_{15}–C_{24}) and high (C_{25}–C_{34}) ends. In this case, CPI for the Irish extract were 0.8 and 1.9, for the Belgian extract 1.1 and 2.1, and for the Spanish extract 0.8 and 1.1, respectively. The lower end is representative of a petrogenic origin, as the typical CPI of petroleum is 1.0, and petroleum residues are a major and usually predominant component of the lipids extractable from aerosols in urban environments (Simoneit, 1986). The high end, in the case of the Irish and Belgian extracts, demonstrated a plant wax signature, confirmed by the dominance of *n*-C_{29}, which indicates a mixed origin from forest and grassland. Furthermore, burning of shrubs, litter, trees, etc. produced similar CPI in the high end (Standley

Table 4. Some series of organic compounds present in black crusts.

Location	*n*-Alkanes	C_{max}	CPI	*n*-Fatty acids	C_{max}	CPI	Triterpanes
Dublin	C_{13}–C_{35}	C_{29}	1.3	C_{10}–C_{32}	C_{16}	2.9	C_{27}–C_{34}
Mechelen	C_{14}–C_{40}	C_{29}	1.7	C_{12}–C_{34}	C_{16}	5.1	C_{27}–C_{34}
Seville	C_{15}–C_{40}	C_{31}	1.0	C_{10}–C_{34}	C_{22}	1.9	C_{27}–C_{35}

and Simoneit, 1987). On the contrary, the high end of the Spanish extract is characteristic of petroleum.

The source of these hydrocarbons from petroleum is confirmed by the suite of biomarkers found in such materials, as for example the triterpanes, and the hump or unresolved complex mixture (UCM) in the chromatograms of the Irish and Spanish extracts. In fact, these samples exhibited a broad envelope of UCM components ranging approximately from n-C_{16} to n-C_{38} alkanes for the Spanish and n-C_{18} to n-C_{32} for the Irish extract, which have been reported to be composed of highly branched and cyclic hydrocarbons, and ascribed to lubricating oil (Simoneit, 1985) and petroleum (Gough and Rowland, 1990).

According to Simoneit (1986), petroleum contains only minor amounts of long-chain fatty acids, and the homologues $<n$-C_{20} and probably in part $<n$-C_{24} are derived from microbial sources and the homologues $>n$-C_{22} from vascular plant wax. Usually, the major homologue for microbial sources is n-C_{16}, as well as the alkenoic acid n-$C_{18:1}$. However, the distribution of n-fatty acids in diesel engine exhaust and in lubricating oil (Simoneit, 1985) is similar to those reported for the crusts, especially the second one with a bimodal distribution at n-C_{16}/n-C_{18} and n-C_{22}.

Later, Mazurek *et al.* (1991) split the CPI homologous series of fatty acids (in this case, the sum of the even carbon number homologues over a specified range divided by the sum of the odd carbon number homologues over the same range) into (1) low molecular weight acids (C_6–C_{11}) from non-specific degradation processes (e.g. microbial metabolism, combustion, thermal alteration and photochemical reaction), (2) intermediate molecular weight acids (C_{12}–C_{19}) from recent biogenic sources (e.g. microorganisms and plant waxes; CPI > 2) or from combustion sources (e.g. vehicular emissions; CPI < 2), and (3) high molecular weight acids (C_{20}–C_{33}) derived from epicuticular waxes of vascular plant foliage. CPI for fatty acids from the Irish extract is 2.9, and when broken down into molecular weight categories, the lower CPI in the C_6–C_{11} range (in this and other samples) could not be calculated because this range hardly can be distinguished from background in the chromatogram, CPI for the C_{12}–C_{19} range is 3.4, and CPI for the C_{20}–C_{33} range is 2.4. For the

Belgian extract, CPI in the whole range is 5.1 (5.8 and 4.6, respectively) and for the Spanish extract is 1.9 (1.6 and 2.1, respectively). From all the three extracts, only the CPI for fatty acids in the Spanish sample agree with those of vehicular emissions, whereas it appears that the fatty acid fractions could have a biogenic origin in the Irish and Belgian extracts.

Diterpenoids are regarded as characteristic molecular markers for conifer resins (i.e. methyl dehydroabietate), and retene is an incomplete combustion product of compounds with the abietane skeleton (Standley and Simoneit, 1987). These compounds are frequent in cities in which residential wood combustion is widely used, and therefore could only be observed in Dublin and Mechelen but not in Seville.

Polycyclic aromatic hydrocarbons are the result of combustion-generated airborne particulate matter, and have been identified, among other sources, in smoke particles from plant burning (Standley and Simoneit, 1987) and diesel engine soot (Yu and Hites, 1981). It is well-known that organic compounds adsorbed onto the particulate phase of diesel exhaust possess direct-acting mutagenicity and can be accounted for by polycyclic aromatic hydrocarbons (Bayona *et al.* 1988). Polycyclic aromatic hydrocarbon mixtures encountered in crust extracts are complex because of the presence of alkyl-substituted compounds, as well as the numerous isomeric parent compounds. Generally, compounds from two to six aromatic rings are widely distributed in the three crust extracts, particularly in the Irish one. In addition, ketones, sulphur and nitrogen-substituted compounds were identified.

Petroleum biomarkers are compounds utilized for defining both the fossil origin and the geological source of the petroleum residues (Simoneit *et al.* 1988). In fact, as crude oils usually contain tricyclic terpanes and hopanes, triterpanes have been proposed as sensitive molecular markers of petroleum pollution. The triterpanes of the black crusts are composed of predominantly the $17\alpha(H),21\beta(H)$-hopane series, which is of a petroleum origin. Tricyclic terpanes make them further possible indicators of petroleum. In addition, series of steranes were also present.

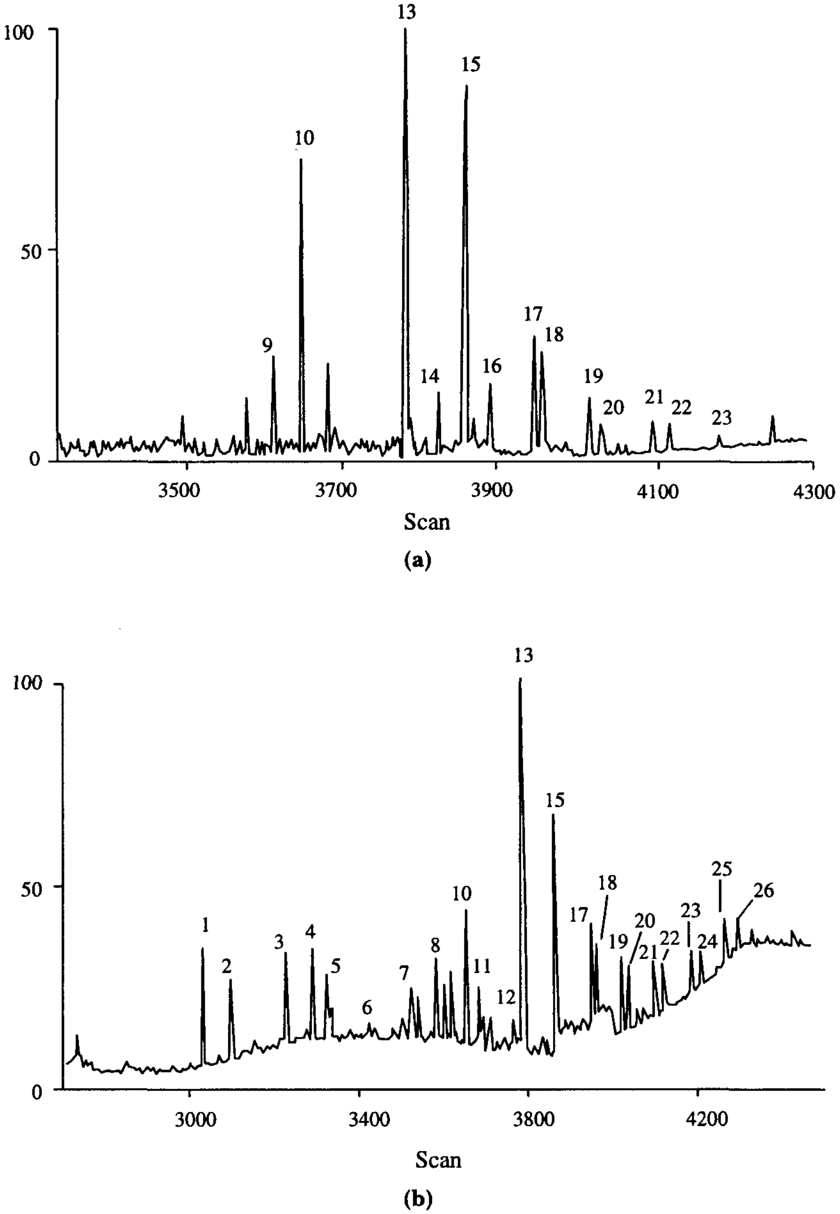

Fig. 1. **(a)** Mass fragmentogram (m/z 191) of the extract of black crust, Custom House, Dublin. **(b)** Mass fragmentogram (m/z 191) of the pyrolysate of the black crust from the cathedral of Seville. Peak numbers refer to Table 5.

The hopanes are relatively easy to detect by using gc/ms and ion monitoring since two major fragment ions, m/z 191 and m/z 148 + R, are formed from the parent ion in the ion source of the mass spectrometer. An example of the distribution of the hopanes in the Irish black crust extract is shown in Fig. 1(a) and the identity of the compounds is referred to in Table 5. Interestingly, the pattern of the biomarkers found in black crusts is similar to those reported

Table 5. Triterpanes and steranes identified in black crusts.

Peak	Compound
1	C_{23} tricyclic terpane
2	C_{24} tricyclic terpane
3	C_{25} tricyclic terpane
4	C_{25} tetracyclic terpane
5	C_{26} tricyclic terpane
6	C_{27} tricyclic terpane
7	C_{28} tricyclic terpane
8	C_{29} tricyclic terpane + 5α(H), 14β(H)-cholestane
9	18α(H)-22,29, 30-trisnorhopane
10	17α(H)-22, 29, 30-trisnorhopane
11	24-methyl-5α(H), 14β(H), 17β(H)-cholestane
12	24-ethyl-5α(H), 14β(H), 17β(H)-cholestane
13	17α(H), 21β(H)-30-norhopane
14	17β(H), 21α(H)-30-normoretane
15	17α(H), 21β(H)-hopane
16	17β(H), 21α(H)-moretane
17	17α(H), 21β(H)-homohopane 22S
18	17α(H), 21β(H)-homohopane 22R
19	17α(H), 21β(H)-bishomohopane 22S
20	17α(H), 21β(H)-bishomohopane 22R
21	17α(H), 21β(H)-trishomohopane 22S
22	17α(H), 21β(H)-trishomohopane 22R
23	17α(H), 21β(H)-tetraquishomohopane 22S
24	17α(H), 21β(H)-tetraquishomohopane 22R
25	17α(H), 21β(H)-pentaquishomohopane 22S
26	17α(H), 21β(H)-pentaquishomohopane 22R

for crude oil (Philp, 1985), automobile and diesel engine exhausts (Simoneit, 1985).

Studies on the organic composition of black crusts have been carried out by other authors with similar results. Nord and Ericsson (1993) found as main compounds of the black crusts from a church in Stockholm *n*-C_9 to *n*-C_{30} alkanes, PAH from three to seven aromatic rings, and some nitrogen- and sulphur-containing polycyclic aromatic species. In the black crusts from historic monuments in Dresden, Machill *et al.* (1997) found *n*-C_{14} to *n*-C_{29} alkanes, *n*-C_{10} to *n*-C_{25} alkanols, *n*-fatty acids from C_3 to C_{24}, α,ω-dicarboxylic acids from C_2 to C_9, some hydroxyacids and aromatic acids, PAH from two to five aromatic rings, sulphur- and oxygen-containing polycyclic aromatic species, and a few diterpenoids and carbohydrate derivatives.

3.4. Analytical Pyrolysis of Black Crusts

Sometimes, the required amounts of samples needed for solvent extraction are not available, and an analytical approach feasible at microscale level and able to supply fairly general information on a wide range of classes of compounds is needed. This approach is analytical pyrolysis, a flash thermal desorption and degradation method, also in combination with gc/ms, which allows the collection of fairly general composition data from microgram quantities of samples. This method was applied to a variety of samples obtained from cathedrals, churches, historic buildings and sculptures in Belgium, Ireland, Italy, Spain and the Netherlands, with the best results (Saiz-Jimenez, 1991, 1993, 1994a, b and 1995; Saiz-Jimenez *et al.* 1991).

Analytical pyrolysis was accomplished as described by Saiz-Jimenez (1991). In this case, only a few micrograms of sample were needed for analysis. The sample was applied to a wire and pyrolysed for 10 seconds using an Fe wire with a Curie temperature of 770°C. This temperature has been shown to be adequate for evaporation/pyrolysis of organic materials within mineral matrices (Saiz-Jimenez *et al.* 1991). However, some changes in the thermal breakdown of molecules can be expected, as the crust contains high percentages of gypsum and other salts, and it has been demonstrated that cations influence the thermal behaviour of organic materials (van der Kaaden *et al.* 1983).

Furthermore, some decarboxylation of organic acids was observed (Saiz-Jimenez, 1991).

This method was applied to the study of the black crusts obtained from different building materials in the same monument, the Pardon Gate of the cathedral of Seville, and justified by the scarce amount of sample available. The Pardon Gate is the main entrance to the Orangery Court, remains of the Moorish mosque begun in 1172. This arch is ornamented with arabesques of plaster, all inserted in a limestone wall, which constitutes the cathedral north front. Four terracotta statues representing Saint Peter, Saint Paul and the Annunciation, and a high relief representing the Expulsion from the Temple were added in the 16th century. The four statues are sustained by an alabaster pedestal. Therefore, four types of building materials exist in the Pardon Gate: limestone, plaster, alabaster and terracotta.

Crusts from all these materials, at a height of about 10 m from the ground, were sampled and analysed by analytical pyrolysis. The pyrogram obtained from the black crust formed on terracotta was identical to those of crusts removed from alabaster, limestone or plaster, thus confirming that the same compounds are present in crusts of different materials exposed to the same polluted environment.

The pyrogram was dominated by homologous series of aliphatic hydrocarbons and a few polycyclic aromatic hydrocarbons. The aliphatic hydrocarbons most probably have a double origin, as they may arise either from uncombusted or partially combusted fuels (*n*-alkanes) or from pyrolytic decarboxylation of fatty acids (*n*-alk-1-enes). The polycyclic aromatic hydrocarbons, less abundant than the aliphatic hydrocarbons, were characterised by the presence of indene, naphthalene, fluorene, phenanthrene and pyrene. These compounds have an environmental significance because although present in oil, they also represent the product of incomplete combustion of gasoline and diesel fuel in vehicles (Boyer and Laitinen, 1975).

As observed by SEM and EDX, the black crusts present in the building materials from the Pardon Gate are composed of gypsum crystals originating from oxidation of sulphur dioxide and reaction of the resulting sulphuric acid with the exposed materials. During the process, aerosols and particulates present in the polluted urban atmosphere are entrapped. The carbonaceous particles contain S, Al, Ca, Fe, Cu, Mn and V as mineral elements, and aliphatic hydrocarbons and polycyclic aromatic hydrocarbons as main organic compounds.

In addition, the black crust obtained from the Prince Gate was investigated. Interestingly, the pyrogram for this crust (taken only 1.7 m from the ground) was different to those available from the Pardon Gate, especially at the end of the analysis programme, characterised by a complex mixture of branched and cyclic hydrocarbons (hump or UCM) which can be seen in the range C_{20}–C_{34} of *n*-alkanes. This was already observed in the chromatogram from solvent extract. The huge hump indicates a severe contamination by fossil fuels. In the pyrogram, a homologous series of *n*-alkenes in the range C_6–C_{35} predominates together with the same series of *n*-alkanes. However, whereas alkenes predominate over alkanes up to C_{20}, the opposite is true for alkanes from C_{21} with a considerable reduction in alkenes as the series progresses. Polycyclic aromatic hydrocarbons up to five rings and alkylbenzenes up to C_{21} were other significant compounds.

No fatty acids were detected in the pyrolysate. Several facts could contribute to this absence, such as the relatively high pyrolysis temperature and the presence of considerable amount of salts. It has been stated that inorganic additives result in the production of unwanted thermal reactions, namely cyclisation and aromatisation reactions of unsaturated fatty acids (Saiz-Jimenez, 1994b and 1995). A decarboxylation process in fatty acids could be expected in the pyrolysis of black crusts, resulting in the formation of alkenyl compounds with one C atom less than the original fatty acid, together with the formation of some other artifacts.

The identification of triterpanes (hopanes and hopenes) and steranes (cholestanes) is of interest in the pyrogram of the black crust from the Prince Gate. They are distributed through the UCM of compounds. Table 5 lists some of the identified compounds from the m/z 191 mass chromatogram [Fig. 1(b)], whereas for instance, in the Pardon Gate crust removed from alabaster only 17α(H),21β(H)-30-norhopane was clearly identified. As all these compounds are found in vehicular emissions, diesel fuel and lubricating oil (Simoneit, 1985), the origin of those encountered in the Prince Gate black crust can directly be ascribed to the vehicular exhausts originated by idle engines in the bus stop.

Interestingly, triterpanes pattern in both solvent extracts [Fig. 1(a)] and pyrolysates [Fig. 1(b)] were similar, indicating that no differences were obtained irrespective of the analytical approach used.

3.5. Simultaneous Pyrolysis/Methylation

In an attempt to solve the bias of data in pyrolysis, mainly the missing of polar compounds, a novel procedure, simultaneous pyrolysis/methylation, was tested. Solvent extraction versus pyrolysis data was briefly discussed in a previous paper (Saiz-Jimenez, 1991). The major classes of compounds identified in solvent extraction and subsequent gc/ms analysis versus conventional pyrolysis are shown in Table 6. From these data, it was concluded that analytical pyrolysis is a fast screening procedure for identification of organic compounds. The method provides basic information about most classes of compounds present in surfaces of building stones, but for a detailed study and specific search for polar compounds, solvent extraction and concentration should be employed. The disadvantage of pyrolysis with regard to solvent extraction is both the loss of information on polar compounds and the formation of thermal degradation products.

Pyrolysis/methylation consists of the derivatisation of samples containing carboxyl and/or hydroxyl groups with an alkylating reagent. Tetramethylammonium salts of organic acids can be converted to methyl esters and the corresponding by-products in the pyrolysis unit, thus the functional groups are directly protected (Challinor, 1989). The application of pyrolysis/methylation to the study of black crusts seems to be very promising as several series of polar compounds, not previously found in conventional pyrolysis, were identified in the pyrolysates. In fact, Table 6 also shows the major classes of compounds identified from a total of 250 in pyrolytic methylation. The carboxylic acids are recovered as the corresponding methyl esters and the hydroxyls as methoxyls. Throughout this chapter, they are referred to as acids and hydroxyls, their original forms, rather than as derivatised methyl esters and methoxyls.

Table 6. Main classes of compounds identified in the black crust of the Custom House, Dublin, according to the analytical procedure.

Class of compounds	Solvent extraction range*	Pyrolysis range	Pyrolysis/methylation range
n-Alkanes	C_{13}–C_{35}	C_5–C_{32}	C_9–C_{29}
n-Fatty acids	C_{10}–C_{32}	–	C_6–C_{26}
α,ω-Dicarboxylic acids	+	–	C_7–C_{17}
Alkylbenzenes	+	C_6–C_{17}	C_6–C_{26}
Alkylnaphthalenes	C_{10}–C_{13}	C_{10}–C_{14}	C_{10}–C_{13}
Alkylphenanthrenes	C_{14}–C_{16}	C_{14}–C_{17}	C_{14}–C_{16}
Diterpenoids	C_{18}–C_{20}	C_{18}	C_{18}–C_{20}
Triterpenoids	C_{27}–C_{34}	C_{27}–C_{35}	+
Polycyclic aromatic hydrocarbons	C_{10}–C_{22}	C_{10}–C_{24}	C_{10}–C_{18}

* Range denotes number of carbon atoms.
+ Present, but range not determined; – not found.

The fatty acid series in pyrolysis/methylation is only limited by the resolution of the chromatographic column. This fatty acid series is absent in conventional pyrolysis. The series of dicarboxylic acids was also absent in conventional pyrolysis, and evidenced in pyrolysis/ methylation up to a range of C_{17}.

The identification of aromatic acids is to be noted. These included benzoic acid, methylbenzoic acids, benzenedicarboxylic acids, methylbenzenedicarboxilic acids, benzenetricarboxylic acids and naphthalenecarboxylic acid. Cautreels and van Cauwenberghe (1978) identified alkanes, polycyclic aromatic hydrocarbons (PAH) and its alkylated derivatives, dialkyl phthalates, fatty acids and aromatic acids in the gas phase of urban air. Aromatic acidic compounds included phenol, cresols, xylenols, benzoic acid, methylbenzoic acids, hydroxybenzoic acids, benzenedicarboxylic acids and naphthalenecarboxylic acid. These compounds were also encountered in the pyrolytic methylation of the black crusts. Kawamura and Kaplan (1987) suggested that benzoic acids and phenols originate from non-biogenic sources, such as fossil fuel combustion.

Some phenols and quinones were encountered in the pyrolysate mixture. They encompass phenol (as methoxybenzene), cresol (as methoxymethylbenzene) and benzenediol (as dimethoxybenzene), ethoxybenzoic acid ethyl ester, probably as such in the sample, and the methylated derivatives of 3-methoxy-4-hydroxybenzoic acid (vanillic acid), phenylprop-2-enoic acid and 4-hydroxyphenylprop-2-enoic acid (*p*-coumaric acid). In addition, fluorenone and anthracenedione were identified. The 4-hydroxyphenylprop-2-enoic acid could be considered as a tracer of conifer pollen, as *Pinus* pollen contain sporopollenin which comprises *p*-coumaric acid (Mulder *et al.* 1992), whilst the phenylprop-2-enoic acid is probably a pyrolysis product of the original acid, in which a dehydroxylation was produced. Vanillic acid can be traced as a product of residential wood stoves (Hawthorne *et al.* 1988).

The PAH mixtures encountered in black crusts are complex because of the presence of their alkylated derivatives. These compounds derive from combustion-generated airborne particulate matter and have been identified, amongst other sources, in smoke from plant burning (Standley and Simoneit, 1987) and carbonaceous particles from fossil fuel combustion (Simoneit, 1985 and 1986). Basically, species from two to four aromatic rings are distributed in the pyrolysate, the same compounds being previously identified in the solvent extracts (Saiz-Jimenez, 1993). In urban environments, lower PAHs up to benzofluorenes are abundant in the gas phase, whereas higher PAHs are found predominantly in the particulate fraction.

Sulphur- and oxygen-containing polycyclic aromatic species, including polycyclic aromatic ketones, were found in the pyrolysate, thiophene, benzothiophene, dibenzothiophene, benzonaphthothiophene, benzofuran, dibenzofuran, benzonaphthofuran and some of their alkylated derivatives being the identified compounds. Methylthiobenzothiazole and some alkylated pyrrols and indoles were representative of nitrogen-containing compounds.

Lee *et al.* (1977) identified similar PAHs in the combustion of three common fuels. The sulphur-containing species were related to coal combustion products. However, Williams *et al.* (1986) identified these compounds in diesel fuels. Sicre *et al.* (1987) reported that dibenzothiophenes are common in crude oils and coal emissions, therefore their presence is not indicative of a specific origin. Benzofurans are probably related to wood or coal combustion (Lee *et al.* 1977). Bayona *et al.* (1987) found indoles in coal tar fractions, and Ramdahl (1983) identified polycyclic aromatic ketones in diesel exhaust, and wood and coal combustion samples.

Diterpenoids were observed in all three analytical procedures described in Table 6. However, in conventional pyrolysis only retene, an incomplete combustion product with the abietane skeleton, was identified. This compound is used as an indicator of residential coniferous wood combustion (Standley and Simoneit, 1987). Dehydroabietic acid derivatives were identified in both solvent extraction and pyrolytic methylation, which further support a coniferous wood origin.

Triterpenoids were also present in pyrolytic methylation, but due to the absence of molecular ions in the mass spectra, they could not be individualised. However, the series of hopanes were identified in both solvent extraction and conventional pyrolysis studies with a powerful mass spectrometry instrument (Saiz-Jimenez, 1991).

All classes of compounds shown in Table 6 have been previously identified in gas phase, aerosols and particulate matter in urban atmospheres. This is of interest as Grimalt *et al.* (1991) reported the close similarity between the organic composition of black crusts from the Holy Family church (Barcelona, Spain), and airborne particulates, collected by glass fibre filtration, and gas-phase organic compounds, obtained by polyurethane foam adsorption. These facts and the finding of carbonaceous particles entrapped in the voids of gypsum crystals demonstrated that the organic compounds present in the black crusts, covering the building stones in urban environments, are the result of a direct input of air pollutants, the buildings acting as non-selective surfaces passively entrapping all deposited aerosols and particulate matter, from whose analysis a source can be traced.

The series of aliphatic and aromatic acids found in the pyrolysis/methylation mixture clearly indicate that this method protects carboxylic groups through the formation of methyl esters, and hydroxyl groups through the formation of methoxyls. This reveals that conventional pyrolysis is a strongly biased method for the identification of compounds containing oxygenated functional groups. A previous report demonstrated that pyrolysis/methylation is an analytical procedure of great sensitivity for investigating organic compounds in inorganic matrices (Saiz-Jimenez *et al.* 1994). No time-consuming solvent extractions, concentrations, derivatisations and other manipulations which imply the possibility of cross-contamination are required to obtain similar data to those obtained by solvent extraction and subsequent gc/ms analysis.

Finally, Table 7 shows a comprehensive list of the major classes of compounds identified in pyrolysis/methylation of black crusts from the Custom House (Dublin), the cathedral of Seville (Spain), and two new monuments, the balustrade of the stairs next to the Count Belliard

Table 7. Classes of identified compounds in pyrolysis/methylation of black crusts and diesel soot.*

Class of compounds	Dublin	Brussels	Rome	Seville	Diesel soot
n-Alkanes	C_8–C_{31}	C_8–C_{30}	C_8–C_{32}	C_8–C_{30}	C_9–C_{32}
n-Alkenes	C_8–C_{27}	C_9–C_{26}	C_8–C_{24}	C_9–C_{30}	C_8–C_{25}
Isoprenoid hydrocarbons	C_{19}, C_{20}	C_{19}, C_{20}	C_{19}, C_{20}	C_{19}, C_{20}	C_{18}–C_{20}
n-Fatty acids†	C_6–C_{26}	C_5–C_{30}	C_5–C_{27}	C_4–C_{28}	C_5–C_{25}
α, ω-Dicarboxylic acids‡	C_7–C_{17}	C_5–C_{17}	C_7–C_{13}	C_5–C_9	–
Alkylbenzenes	C_6–C_{25}	C_6–C_{22}	C_6–C_{23}	C_6–C_{26}	C_6–C_{27}
Alkylcyclohexanes	–	–	–	–	C_{15}–C_{24}
Benzoic acids	+	+	+	+	+
Benzenedicarboxylic acids	+	+	+	+	+
Benzenetricarboxylic acids	+	+	+	+	+
Benzenetetracarboxylic acids	–	–	–	+	–
Polycyclic aromatic hydrocarbons	C_{10}–C_{16}	C_{10}–C_{16}	C_{10}–C_{18}	C_{10}–C_{16}	C_{10}–C_{17}
Thiophene derivatives	+	+	+	+	+
Furan derivatives	+	+	+	+	+
Pyridine derivatives	–	–	–	+	–
Benzonitriles	+	+	+	+	+
Quinoline derivatives	–	–	–	+	–

* C_8 denotes number of carbon atoms; + detected compound; – not detected compound.

† Detected as methyl ester.

‡ Detected as dimethyl ester.

statue (Brussels) and the pillars of the Barberini Palace fence (Rome). For comparison, the compounds present in diesel soot from a Sevillian public bus is shown (Hermosín, 1995). From the data, it was concluded that the black crusts from different European monuments and buildings contain molecular markers that are characteristic of petroleum derivatives. The overprint of some biogenic components of aerosols over petroleum components from anthropogenic emissions (mainly vehicular) can be illustrated by the dominance of hydrocarbons around n-C_{29} (plant waxes) and fatty acids in the range n-C_{12}–C_{19} (microorganisms and plant waxes). Accordingly, the black crusts coating the surfaces of building materials located in urban environments are constituted by a suite of all kind of organic compounds present in aerosols and particulate matter, which are transferred by dry and/or wet deposition. The composition of each crust is governed by the composition of the particular airborne pollutants in the area, but is mainly derived from vehicular emissions, diesel engines having a strong influence. Finally, it is clear that the exposed building materials act as a non-selective surface, passively entrapping all deposited airborne particulate matter and organic compounds which obviously modifies the composition of the materials present in the stone surface.

4. Microbiology of Black Crusts

The study of microbial communities is usually accomplished by using standard culture methods. Microorganisms traditionally are characterised by phenotype (morphology, biochemical tests, lipid composition, etc.). However, it is believed that fewer than 20% of the extant microorganisms have been discovered, and that culture methods are inadequate for studying microbial community composition. Pace (1996) considered that only a small portion, typically far less than 1% of organisms in the environment can be cultivated by standard techniques. There are many reasons for the routine failure of the usual cultivation strategies, the most common is that selective enrichment cultures fail to reproduce the conditions that particular microorganisms require for proliferation in their natural habitat.

Although in the literature many reports on the microbiology of weathered stones in monuments can be found, attention to the microflora of black crusts has barely begun, and only a few studies on the growth of epilithic microorganisms on black crusts (Ortega Calvo *et al.* 1993; Ortega-Calvo and Saiz-Jimenez, 1996) and endolithic filamentous cyanobacterium (*Phormidium* sp.) under black crusts (Saiz-Jimenez, 1991; Saiz-Jimenez *et al.* 1991) can be found. Standard microbiological studies on monuments showed that crust-free stones contained from three to 15 times more CFU than black crusts (Table 8) and that some of the isolated bacteria can degrade pollutants (Table 9). However, when relying on cultural methods to identify species, there is a problem of selectivity and thus the inevitable underestimation of community diversity. Direct exploration

Table 8. Site, description and microbial numbers of stone samples from cathedrals.

Site	Sample code	Description	CFU/g ($\times 10^5$)*
Seville cathedral			
	S1	Pilaster 1, crust-free	8.25
	S2	Pilaster 1, crust-free	7.00
	S3	Pilaster 1, black crust	2.81
	S4	Pilaster 2, black crust	1.29
	S5	Pilaster 3, black crust	0.68
	S6	Pilaster 4, black crust	2.28
Quarry			
	Q1	Ground quarry stone, calcarenite	N.D.†
	Q2	Ground quarry stone, limestone	N.D.
Mechelen cathedral			
	M1	Crust-free. East, 1.5 m height	1.40
	M2	Black crust, same as M1	0.09
	M3	Crust-free. North, 1.5 m height	2.54
	M4	Black crust, same as M3	0.58
	M5	Crust-free. Northeast, 2 m height	1.46
	M6	Black crust, same as M5	0.19

* CFU/g presented are for total heterotrophs.

† Not detected.

Table 9. Characterisation and identification of isolates from phenanthrene-degrading enrichments of cathedral samples.

Isolate	Origin*	Description	Identification
S4A	Sample S4	Gram-negative rods, motile, oxidase-positive, catalase-positive, nitrate-positive, forms PHB, growth with phenanthrene	*Pseudomonas* sp.
S4B	Sample S4	Gram-negative rods, motile, oxidase-positive, catalase-positive, nitrate-positive, growth with phenanthrene	*Pseudomonas* sp.
S4C	Sample S4	Gram-positive rods, arranged in short chains, slightly motile, oxidase-negative, catalase-positive, forms PHB, growth with phenanthrene	*Nocardia* sp.?
S4D	Sample S4	Gram-positive rods, spore-forming, motile, orange pigment, oxidase-positive, catalase-positive, forms PHB, growth with phenanthrene	*Bacillus* sp.
M4A	Sample M4	Gram-negative rods, motile, oxidase-positive, catalase-positive, nitrate-positive, growth with phenanthrene	*Pseudomonas* sp.
M4B	Sample M4	Gram-positive cocci, motile, oxidase-positive, catalase-positive, nitrate-positive	*Planococcus* sp.

* See Table 8.

of the inhabitants of natural microbial communities in the black crusts can be expected to have a significant influence on our understanding of microbial phylogeny and physiology and to ascertain how representative are cultivated species of the phylogenetic diversity within the black crust.

It has been suggested that the presence of an organism on decayed material does not necessarily imply that it has caused the damage observed (Saiz-Jimenez, 1995). The activity of microorganisms in promoting stone deterioration is largely dependent upon the production of corrosive metabolites which can solubilise minerals in a manner similar to chemical agents. Probably, low-frequency isolation cannot be directly correlated with metabolic activity as, for instance, the fungi isolated in culture media may be dormant (spores) and are not necessarily the ones which are functioning in the ecosystem. Because isolation in culture media rich in organic carbon can mask the real fungal distribution in weathered stones and isolate selectively airborne propagules instead of active microorganisms, an approach involving direct study of gypsum crusts was carried out by Saiz-Jimenez (1993). The incubation of the crusts in petri dishes with sterile water revealed a different fungal population to those previously reported by Petersen *et al.* (1988) and De la Torre *et al.* (1991) in weathered stones. In fact, from the Seville cathedral a *Papulaspora*-like fungus with dark chlamydospore balls was the only isolate, with high presence in the tested samples (82%). From Mechelen cathedral the species isolated were *Engyodontium album* (15%), *Botriotrichum piluliferum* (4%), *Ulocladium atrum* (4%) and *Mucor circinelloides* (4%). These fungi most probably use the organic compounds present in the black crusts, which include, among others, aliphatic and aromatic hydrocarbons, fatty acids, triterpanes, etc. (Saiz-Jimenez, 1991). Therefore, it appears that two types of fungal populations can be isolated from stones: those utilising readily available carbon (carbohydrates), which are similar to ubiquitous saprophytic airborne fungi, evidenced by using conventional culture media, and those using petroleum-derivatives originating from deposition of pollutants, capability which probably is present in a relatively minor part of the population utilising carbohydrates.

Although ubiquitous in terrestrial and aquatic environments, the fraction of the total heterotrophic community represented by the hydrocarbon-utilising bacteria and fungi is highly variable, with reported frequencies ranging from 6 to 82% for soil fungi and 0.13 to 50% for soil bacteria (Leahy and Colwell, 1990). Nyns *et al.* (1968) tested a wide range of fungi for their ability to assimilate aliphatic and aromatic hydrocarbons and petroleum fractions. Species of the genera *Fusarium*, *Penicillium* and *Aspergillus* are particularly active in the assimilation of hydrocarbons. Bossert and Bartha (1984) listed 22 genera of bacteria and 31 genera of fungi able to degrade hydrocarbons.

The most remarkable fact is that the list of genera of fungi growing on hydrocarbons reported by Nyns *et al.* (1968) or the most frequent isolates quoted by Leahy and Colwell (1990) agree well with those isolated from weathered building stones and frescoes (Saiz-Jimenez and Samson, 1981; Petersen *et al.* 1988; Karpovich-Tate and Rebrikova, 1990; De la Torre *et al.* 1991; Saiz-Jimenez, 1993). This finding indicates a possible relationship between fungi and organic pollutants derived from oil combustion.

Advances in molecular biology are now providing the means for solving long-standing problems in microbiology. These techniques have been applied to determining the genetic diversity of microbial communities and to identifying several uncultured microorganisms. Muyzer *et al.* (1993) presented a new approach for directly determining the genetic diversity of complex microbial populations. The procedure is based on electrophoresis of PCR-amplified 16S rDNA fragments in polyacrylamide gels containing a linearly increasing gradient of denaturants (DGGE). In this electrophoresis, DNA fragments of the same length but with different base-pair sequences can be separated. This demonstrated the presence of up to ten distinguishable bands in the separation pattern, which were most likely derived from as many different species constituting these populations, and thereby generated a DGGE profile of the total population. Muyzer and Ramsing (1995) reviewed the potentials and limitations of different molecular techniques which are nowadays used to determine the species composition of microbial communities. A specific limitation of the DGGE approach is, that separation of PCR products obtained from very complex mixtures of bacteria such as those which are found in soils might not be possible. Furthermore, only limited sequence information is obtained with the DGGE approach, because separation is reduced for fragments longer than 500 bp. Felske *et al.* (1997) isolated ribosomes from soils and 16S rRNA was partially amplified via RT-PCR using conserved primers for members of the domain Bacteria. Subsequent sequence-specific separation by temperature-gradient gel electrophoresis (TGGE) in combination with taxon-specific probing, leads to the identification of the metabolically dominant portion of the community. TGGE profilings from black crust from different monuments and locations would permit to know whether there is a specific microbial community for this particular niche or the communities diverge due to environmental effects.

5. Biodegradation of Black Crusts

5.1. Aliphatic Hydrocarbon Biodegradation

Although biodeterioration processes have been discussed by some authors (Petersen *et al.* 1988; Saiz-Jimenez *et al.* 1990; De la Torre *et al.* 1991; Ortega-Calvo *et al.* 1991; Warscheid *et al.* 1991), biodegradation of organic compounds in monuments has rarely been investigated. Lewis *et al.* (1988) suggested that bacteria on stone can be extremely versatile and could maintain their activity during nutrient perturbations, operating at low nutrient levels and utilising what the environment has to offer. As a consequence, bacterial populations may be able to maintain their involvement in the process of stone deterioration during periods of nutrient flux. Recently, both biodegradation of polycyclic aromatic hydrocarbons by heterotrophic bacteria, and gypsum crusts by cyanobacteria have been reported (Ariño *et al.* 1995; Ortega-Calvo and Saiz-Jimenez, 1996) and present new insights on the microbial ecology (and physiology) of bacteria in black crusts.

Warscheid *et al.* (1991) studied chemoorganotrophic bacteria from the uppermost layers of sandstones of German monuments. It was shown that most of the isolated bacteria used a wide range of different carbohydrates, amino acids, fatty acids and hydrocarbons. About 40% of the strains were shown to be potential acid producers, whereas the capability of manganese and iron oxidation was only sporadically found. Kerosene, as a representative mixture of different hydrocarbons detectable in polluted atmospheres, was well metabolised by 70% of the bacteria.

Heath *et al.* (1997) considered that a consequence of the biodegradation of petroleum is that the lower molecular weight compounds are removed preferentially to higher molecular weight compounds greater than *n*-C_{30} (triacontane). They found that a *Pseudomonas fluorescens* strain was able to totally degrade alkanes with carbon numbers *n*-C_{20}–C_{25} from a waxy Indonesian oil after 14 days. At the end of the trial, no biodegradation was observed for compounds greater than *n*-C_{45}, which suggested a carbon number cut off for biological degradation between *n*-C_{40} and *n*-C_{45}. However, when the bacteria was acclimated (subjected to a previous growth in high molecular weight alkanes), the utilisation of *n*-C_{60} as a sole carbon source was observed. This was claimed to be the first tentative evidence of an organism able to utilise such high molecular weight hydrocarbons.

In addition, it has been stressed that the degradation of petroleum by bacteria often results in the progressive depletion of chromatographically resolved hydrocarbons (e.g. *n*-alkanes, acyclic isoprenoid alkanes, alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes) relative to the UCM. Hence, the UCM is thought to comprise compounds which are relatively inert to microbial degradation (Gough *et al.* 1992). Biodegradation of UCM compounds by *Pseudomonas aeruginosa* was proven under laboratory conditions (Robson and Rowland, 1988). This bacterium is common in petroleum products and oil emulsions. The degradation rates were *n*-alkanes > *n*-alkenes > highly branched alkenes > highly branched alkanes + regular and tail-tail isoprenoid alkanes. A further study with *Pseudomonas fluorescens* demonstrated that the UCM rate and extent of degradation was influenced by the molecular structure (Gough *et al.* 1992). However, the ability for oil hydrocarbon biodegradation is not extended. Chosson *et al.* (1991) showed that of 73 aerobic bacteria (*Nocardia, Mycobacterium, Corynebacterium, Arthrobacter, Protoaminobacter, Pseudomonas,* etc.), assessed for their ability to degrade steranes and cyclic triterpanes, only seven Gram-positive strains, belonging to the *Nocardia, Mycobacterium* and *Arthrobacter* genera, were able to produce noticeable effects. A *Nocardia* sp. produced the most extensive biodegradation, the preference observed being $C_{27} > C_{28} > C_{29}$.

Refractory petroleum hydrocarbons (e.g. UCM compounds, triterpanes, steranes, etc.) are usually identified in the surface of building stones (Saiz-Jimenez, 1993) and their degradation probably requires specific bacteria belonging to genera which are widespread in soils and well-known hydrocarbon degraders.

5.2. Polycyclic Aromatic Hydrocarbon Biodegradation

Phenanthrene concentrations at contaminated sites, usually associated with wood treatments, coking plants and gas works (Wilson and Jones, 1993) and urban environments (Sturaro *et al.* 1993) are among the highest of individual PAHs; therefore the selection of phenanthrene to estimate the activity of PAH-degrading bacteria and subsequent PAHs degradation in building stones seems an appropriate choice.

Polycyclic aromatic hydrocarbon-degrading bacteria have been used previously as indicators of the microbial activity in polluted environments. For instance, Bogardt and Hemmingsen (1992) detected and enumerated the phenanthrene-degrading bacteria in petroleum-contaminated sites; and phenanthrene-utilising and phenanthrene-cometabolising microorganisms have been evidenced in estuarine sediments (Cerniglia, 1993). For this reason, it was considered that these bacteria could be present on weathered stones in urban environments subjected to heavy air pollution, and a sampling was performed in the cathedrals of Mechelen (Belgium) and Seville (Spain).

Table 10 shows the sites, code samples and extents of phenanthrene mineralisation. Microbial numbers (see Table 8) revealed that most samples had a significant heterotrophic microbial population. Seville and Mechelen samples from crust-free zones contained significantly more heterotrophic microorganisms than samples of black crusts obtained from the same place. Quarry stones had no detectable heterotrophic population (Ortega-Calvo and Saiz-Jimenez, 1997).

Phenanthrene was readily mineralised to CO_2 by the natural microbiota in samples from the cathedrals. Both the rate and extent of mineralisation showed no statistical differences between crust-free or black crust zones for either the Seville or Mechelen sites.

Mineralisation in the crust-free samples S1 and S2 from the cathedral of Seville started rapidly with no apparent lag phase and

Table 10. Mineralisation of phenanthrene in samples from cathedrals.

Sample code*	% Mineralised	Sample code	% Mineralised
Seville		*Mechelen*	
S1	35.0 ± 2.1	M1	23.3 ± 1.4
S2	26.9 ± 2.3	M2	3.2 ± 0.2
S3	15.3 ± 1.7	M3	37.6 ± 9.7
S4	21.4 ± 2.3	M4	28.9 ± 2.7
S5	18.0 ± 1.4	M5	24.5†
S6	28.1 ± 1.6	M6	19.5

* See Table 8.

† Values from non-duplicate measurements.

reached a final extent of 35.0 and 26.9% of substrate mineralised after 100 days. An acclimation period of ten days and a lower rate and extent of mineralisation characterised the mineralisation in the black-crust sample S3, where only 15.3% of the compound was converted to CO_2 in 100 days. This sample was obtained from the same place as samples S1 and S2. Mineralisation in samples of black crusts from other pilasters also occurred after an acclimation period but differed in the rates and extents. In these samples, the percentage of phenanthrene mineralised to CO_2 in 100 days ranged from 18.0 to 28.1%. Sample Q1, from a quarry, showed a reduced activity, close to background levels.

Mineralisation of phenanthrene in black crust samples from the cathedral of Mechelen also occurred at lower rates and extents than the corresponding crust-free samples from the same place, and also correlated with microbial numbers. Thus, 37.6% of the compound was converted to CO_2 in crust-free sample M3, which had a total heterotrophic population of 2.54×10^5 CFU/g, whereas the extent of mineralisation in the corresponding black crust sample M4 was 28.9%, with a microbial population of 0.58×10^5 CFU/g. The extent of mineralisation tends to increase as the CFU increases. Mineralisation in a black crust samples, M2, was drastically reduced when compared to other samples, as only 3.2% of phenanthrene was mineralised after 100 days.

Bacteria that were able to grow in media with phenanthrene as the sole source of carbon were isolated from some stone samples with and without black crusts. A short description of each isolate obtained from enrichment cultures is given in Table 9. From sample S4, two Gram-negative rods identified as *Pseudomonas* sp., and two Gram-positive rods, a *Bacillus* sp. and a tentatively identified *Nocardia* sp., were obtained. From sample M3, a Gram-negative rod was identified as *Pseudomonas* sp. and a Gram-positive coccus as *Planococcus* sp. All isolates except *Planococcus* sp. showed capability of growth with phenanthrene.

To investigate the effect of different types of stone materials on the mineralisation of phenanthrene by individual isolates, *Bacillus* sp. S4D, *Pseudomonas* sp. S4B and *Pseudomonas* sp. M3A, which showed the fastest growth, were tested. The bacteria mineralised phenanthrene in liquid culture, at an initial concentration of 0.1 μg/ml, both with and without black crust or crust-free stone samples. The presence of stone samples caused a delay of the phase of maximum mineralisation in the three strains. The final extent of mineralisation was always higher in cultures amended with black crust. However, the influence of stone samples on maximum rates of mineralisation was different depending on the isolate. While *Bacillus* sp. S4D mineralised the substrate at a maximum rate irrespective of whether the medium contained stone or not, the presence of stone induced different maximum rates of mineralisation in the two *Pseudomonas* sp. isolates. Interestingly, the higher rate of mineralisation for each *Pseudomonas* sp. strain occurred according to the origin of the strain (crust-free or black crust sample). Maximum rates of mineralisation by *Pseudomonas* sp. M3A, isolated from crust-free stone, were 0.42 and 0.59 ng/mL/h in the presence of black crust and crust-free stone, while the mineralisation rate in stone-free controls was 0.94 ng/mL/h. *Pseudomonas* sp. S4B, isolated from black crust, mineralised phenanthrene at maximum rates of 0.29, 0.13 and 0.42 ng/mL/h in the presence of black crust, crust-free stone, and stone-free controls, respectively.

The concentration of phenanthrene in solution decreased drastically due to adsorption by the stone, 3.0 and 6.3% of the total phenanthrene being present in the aqueous phase of black crust and crust-free stone suspensions. Those values are in general substantially below the final extents of transformation to CO_2 with black crust and crust-free stone (24.8 and 19.4% for *Bacillus* sp. S4D, 24.6 and 10.6% for *Pseudomonas* sp. M3A, and 21.3 and 6.3% for *Pseudomonas* sp. S4B), indicating that at least part of the adsorbed compound was degraded.

It has been found that black crusts contain toxic compounds such as phenols, benzoic acids, lead, etc. (Fobe *et al.* 1995) which can inhibit bacterial growth. This could explain the decrease of the bacterial population, between three- and ten-fold, with respect to crust-free zones (Table 6). However, these compounds do not inhibit PAH utilisers. On the contrary, a clearly stimulatory effect in ^{14}C-phenanthrene mineralisation was found in cultures of *Pseudomonas* sp. S4B in the presence of black crust suspension, which indicates the presence in the crust of nutrient elements required for an adequate growth and to the adaptation of the bacteria to the polluted environment from which they were isolated.

From literature data, it appears that non-volatile PAHs are degraded by a variety of bacteria, yeasts and fungi (Cerniglia, 1993) which generally belong to autochthonous flora. The PAH-utilising bacteria most frequently reported include several species of *Pseudomonas* and a few of *Arthrobacter*, *Acinetobacter*, *Alcaligenes* and *Streptomyces*. *Pseudomonas* strains are also the most frequent isolates from building stones.

Biodegradation by natural surface and sub-surface soil microorganisms appears to be the process primarily responsible for the removal of PAHs in a multiphase soil system. The biodegradability of two- and three-ring PAHs is extensive, whereas that of four- to six-ring PAHs is considerably less significant (Wilson and Jones, 1993). It has been shown that building stones also contain bacteria able to utilise PAHs. This kind of microflora is not only restricted to fuel-contaminated soils or sediments, PAH-contaminated wastes, etc. but can also be found in urban environments, where the bacteria have adapted to specific site conditions which include high PAH concentrations for long periods. In fact, the Seville public bus service started to operate in the early 1960s, and some of the stops were located just in front of the sampling zone, at about 10 m from it. The city of Mechelen is located on the industrial axis between the major cities of Antwerp and Brussels. Refineries, electrical power plants and non-ferrous industries make this area the most important emitter of industrial SO_2 and

NO_x in Belgium. High concentrations of PAHs are found in the black crust coating the limestone of this cathedral (Saiz-Jimenez, 1993; Fobe *et al.* 1995).

The data indicate that microbial degradation of phenanthrene is common in weathered stones from European cathedrals both in crust-free stones and black crusts. Although the experiments performed in this work required the removal of the samples from the cathedral walls, the rapid and significant phenanthrene mineralisation observed strongly suggests that microbial transformation reactions also occur *in situ.* Mineralisation of organic compounds is characteristic of growth-linked biodegradation and part of the phenanthrene was converted to cell components and degradation products that could remain in the stone. It is also possible that the particular conditions prevailing in the stone niches promote the selection of microorganisms able to transform, either by growth-linked reactions or by co-metabolism, other anthropogenic compounds that have been so far considered as recalcitrant.

Due to its lipophilic nature, phenanthrene is associated to lipids deposited on the stone surface or remains adsorbed to airborne carbonaceous particles. Microorganisms may be able to transform phenanthrene either as such or after spontaneous or microbiologically-induced desorption in the water present in the porous stone. However, it can be expected that phenanthrene entrapment in the weathering black crust during gypsum crystal formation may cause some decrease in bioavailability, and this therefore contributes to its persistence in the stone.

The data herein reported suggest that on the surfaces of building stones, there is an active microflora of PAH-degraders. Therefore, biological activity plays a role in the fate of organic compounds deposited on building stones located in urban (polluted) environments.

5.3. Gypsum Crust Biodegradation

Another biodegradation process in black crusts was due to cyanobacteria. Observations of a wide range of monuments in different enviromental conditions indicate that black crusts covering building stones are colonised by phototrophic microorganisms

(Ortega-Calvo *et al.* 1991 and 1993). In general, the presence of phototrophic microorganisms is more apparent on the north façades of buildings than on the south, because the latter dry out more readily. These organisms are also frequently found on black crusts where they form large patches of green, brown and black cyanobacterial/ algal mats, disfiguring buildings. These patches largely consist of biofilms — cells and other materials immobilised on the substrata and embedded in an organic matrix. Biofilm may also contain significant amounts of adsorbed inorganic materials derived from the substratum (quartz, calcium carbonate and clay) and detritus (dead cells, microbial by-products, etc.). The slimy surface favours the adherence of airborne particles (dust, pollen, spores, oil- and coal-fired carbonaceous particles) giving rise to hard crusts and patinas which are difficult to remove.

The biofilms formed on black crusts are usually characterised by the abundant presence of Chroococcales (*Gloeothece, Gloeocapsa,* etc.). *Gloeothece* is a unicellular cyanobacterium capable of fixing nitrogen aerobically and producing a complex sheath with high amounts of sulphate (Tease *et al.* 1991).

Black crusts deposited in petri dishes with only the addition of sterile water doubled in four weeks the biomass when inoculated with the cyanobacterium *Gloeothece* sp. The result shows that the mineral content of the crusts is enough to support cyanobacterial development. The finding suggest that gypsum might play a role in the cyanobacterial colonisation of blackened monuments in urban environments.

Under laboratory conditions, it was proven that the gypsum present in a black crust from the cathedral of Seville, can be used as a source of sulphur by the cyanobacterium *Gloeothece* sp. (Ortega-Calvo *et al.* 1994). The sulphate released to the medium due to gypsum dissolution was progressively incorporated into the carbohydrate sheath and used for balanced growth.

The sulphate-bonding capacity of the sheath in *Gloeothece* sp. causes a particularly high demand for this anion. This makes sulphur nutrition a relevant aspect in the physiology of this cyanobacterium, as demonstrated by Ariño *et al.* (1995). In fact, when deprived of sulphur, bleached *Gloeothece* sp. cells contain a disintegrated photosynthetic apparatus and accumulations of different kinds of reserve material. Such characteristics are absent in sulphate-sufficient diazotrophic cultures. The inability to obtain from the culture medium an adequate supply of sulphur for protein synthesis, and therefore, for balanced growth induces in *Gloeothece* sp. the immobilisation of fixed carbon in the form of glycogen, polyhydroxybutyrate and cyanophycin. In other words, *Gloeothece* sp. reacts to sulphur starvation by notable changes in its ultrastructure related to alteration in the overall physiological processes, including sheath synthesis, nitrogen metabolism and photosynthesis. The addition of sulphate to a sulphate-deficient medium restored the regular activity of the cyanobacterium.

6. Conclusions

The data herein reported indicate that microorganisms are also able to remove some of the most abundant components of black crusts, such as gypsum and polycyclic aromatic hydrocarbons. Although the use of microorganisms is not foreseen as a method for cleaning façades due to some obvious limitations (dimension of monuments, time needed, wetting of weathered surfaces, economy, etc.), it must be emphasised that nature develops strategies for biodegradation of pollutants in urban environments. In fact, the continuous input of inorganic and organic compounds modifies the chemical composition of building stones, resulting in the selection of microorganisms with specific nutrient requirements or with a defined metabolic capability. Although we are still far from a complete understanding of the physiological diversity of microorganisms and their interactions in the surface of stone monuments, biodegradation of deposited chemicals is envisaged as an important process, in addition to biodeterioration. There is a scope for molecular techniques and particularly for molecular microbial ecology studies which can fill the current gaps in our knowledge on the organisation of microbial communities in monuments and their effect on building materials.

Acknowledgements

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CHAPTER 7

AIR POLLUTION DAMAGE TO METALS

J. Tidblad and V. Kucera

1. Introduction

It has been known for several centuries that air pollutants emitted by burning of fossil fuels have a serious impact on metals exposed in the built environment. In addition to the loss of mechanical strength and failure of protective coatings, the release of heavy metals to the environment is of concern. Calculations of the economic impact of sulphur pollutants on technical materials have indicated that the costs for corrosion damage to materials including metals are substantial.

There are many parameters that can influence the atmospheric corrosion of metals, the degradation process is a complex interplay between chemical, physical and biological parameters. The present treatment focuses on air pollutants and their effect on the built environment, i.e. the aspects specific to the urban situation. It is, however, important to recognise that atmospheric corrosion is a process that occurs even in the absence of pollutants and that the interplay between natural and anthropogenic factors determine to which extent urban conditions affects and accelerates the "natural" or background atmospheric corrosion.

The present treatment serves as an overview of the effects of acidifying air pollutants to metallic materials. It is divided in two main sections and three additional sections. Section 2 describes the general role of atmospheric pollutants in the corrosion process. Despite the general characteristics of the pollutants, every metal is unique and a selection of metals is described separately in Sec. 3. The quantification of effects, in particular the assessment of life times and calculation of corrosion costs deserves a special treatment given in Sec. 4. Finally, the trends in corrosion, in Europe as well as the developing countries are given in Sec. 5. This chapter is not a review. Instead of a complete list, references have been selected that are suitable for further reading including general references on atmospheric corrosion (Kucera and Mattson, 1987; Kucera and Fitz, 1995; Leygraf and Graedel, 2000) and are cited once at the most appropriate place.

2. Effects of the Environment

The most important pollutants acting as corrosive agents are sulphur and nitrogen compounds, including secondary pollutants and particulates. It has clearly been demonstrated that pollutants enhance the natural corrosion process for several metallic materials even if it has so far been difficult to quantify the direct contribution of individual pollutants other than sulphur dioxide (SO_2) in the weathering process.

Depending on the way pollutants are transported from the atmosphere to the corroding surface, two types of deposition processes are recognised in atmospheric corrosion — dry deposition and wet deposition. Wet deposition refers to precipitation whereas dry deposition refers to the remaining processes, including gas-phase deposition and particle deposition.

2.1. *The Multi-Pollutant Situation*

In many European countries, the concentration of SO_2 has decreased significantly in the last decades while the concentrations of nitrogen pollutants, ozone (O_3) and particulates remain at high levels. Nitrogen dioxide (NO_2) has also decreased significantly but not as much as SO_2. Traditionally and with right, SO_2 has been regarded as the most important corrosion stimulator. With the reduced levels, SO_2 is no longer the only main pollutant. In addition to the added effects of many individual pollutants, synergistic effects of i.a. SO_2 in combination with NO_2 or O_3 need to be considered. This complex pollution situation with effects of a number of important single-pollutants in combination with several synergistic effects, described in the following, is named the "multi-pollutant situation". The general acceptance of the new multi-pollutant situation was recently manifested in the multi-effect, multi-pollutant Protocol to Abate Acidification, Eutrofication and Ground-level Ozone adapted in 2000 in Gothenburg within the Convention on Long-Range Transboundary Air Pollution of the United Nations Economic Commission for Europe.

2.2. Climate

Climate has both indirect and direct effects on atmospheric corrosion of metals. Indirect effects include for example the less mixing and higher concentration levels of pollutants present when there is a temperature inversion. The present treatment only describes direct effects. The dominating part of the research activities has been performed in Europe and North America and therefore the effect of acidifying pollutants has mainly been investigated in regions situated in temperate climate.

Atmospheric corrosion is an electrochemical process and proceeds only when the surface is sufficiently wet, the degradation process may be considered as discontinuous. This is illustrated in Fig. 1 where it is seen that the instantaneous corrosion rate varies strongly with time, several orders of magnitude. The time of wetness (TOW) is a commonly used concept for metals that refers to the time when corrosion occurs, i.e. when a moisture layer is present. This concept is useful when describing the degradation process and when classifying different climatic regions from a corrosion point of view but is difficult to calculate from readily available meteorological data. Therefore, recently developed dose-response functions include annual averages of temperature and relative humidity, which is more easily available.

Dry deposition of pollutants is greatly influenced by temperature (T) and relative humidity (Rh). T and Rh are important since they are the main factors that determine the thickness of the moisture layer in absence of rainfall. The corrosion rate increases with Rh, starting

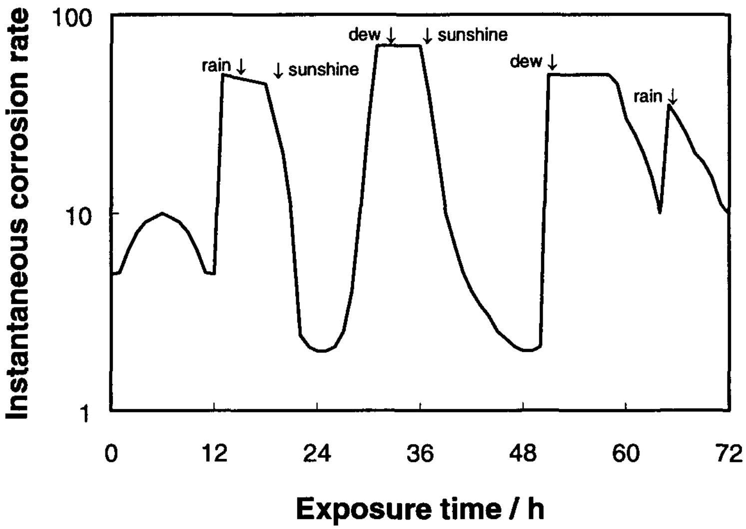

Fig. 1. Instantaneous corrosion rate during a few days of exposure (adapted from Kucera and Mattson, 1987).

from a critical humidity value, where the adsorbed water layer begins to act as an electrolyte. At low temperatures, the corrosion rate increases with increasing annual temperature since the fraction of time above the water freezing point also increases. At higher temperatures, the corrosion in non-marine areas decrease with increasing temperature, which has been attributed to periods with a surface temperature above the ambient temperature, partly related to sun radiation. An elevated surface temperature leads to a faster evaporation of moisture after rain or condensation periods and to a decrease of the thickness of the adsorbed water layer and, consequently, to a decrease of the time when the metal surface is wet. Figure 2 show an example of the temperature effect for zinc based on a dose-response function presented in Sec. 3 (equation 2).

2.3. Gaseous Pollutants

Trace gases of importance for atmospheric corrosion include O_3, H_2O_2, SO_2, H_2S, COS, NO_2, HNO_3, NH_3, HCl, Cl_2, HCHO and HCOOH.

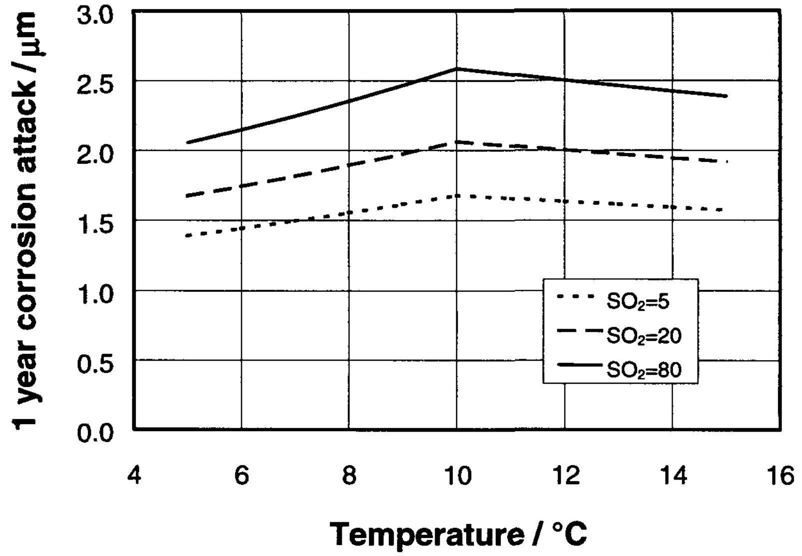

Fig. 2. Corrosion attack of unsheltered zinc vs. temperature calculated from equation (2) with Rh = 75% and a constant wet deposition term, 0.029Rain[H^+], corresponding to 0.6 µm. Curves are shown for the SO_2 concentrations 5, 20 and 80 µg/m^3.

The present treatment focuses on SO_2, NO_2, O_3 and HNO_3 — pollutants that are especially important in urban environments. Recently, carboxylic acids have also earned some attention due to the increased use of methanol and ethanol as alternative fuels. Especially formic acid is a strong acid, which makes the potential effect high. However, data is scarce both on estimated future pollutant levels and atmospheric corrosion effects.

SO_2

In the field of atmospheric corrosion, SO_2 is the single most investigated gaseous pollutant. Its detrimental effect on materials in general has long since been an indisputable fact. Sulphur compounds emitted to the atmosphere were suspected to be the cause of acidification even towards the end of the 19th century. Systematic laboratory exposures in the 1930s demonstrated the corrosive effect of SO_2 on metals. This was also later proven by field exposures and SO_2 was for a long time considered to be the main corrosive pollutant. Even with decreased levels, it is important to remember that SO_2 is still one of the main actors in the new multi-pollutant situation, although not as dominant as in the past.

SO_2 is dissolved in the moisture layer forming sulphite and, after oxidation, sulphate:

$$SO_2(g) + H_2O \rightarrow H^+ + HSO_3^- \rightarrow \ldots \rightarrow 2H^+ + SO_4^{2-} \qquad (1)$$

This process results in an acidification of the moisture layer, which enhances the corrosion process. Sulphate is also frequently present in corrosion products. The SO_2 deposition rate depends mostly on the material, it is often higher for sensitive materials, and varies between 0.01 and 2 cm/s.

Figure 3 shows a plot of one-year corrosion values of carbon steel, with selected cities in Europe highlighted. Worth noting is that the SO_2 pollution levels and corrosion rates today in most European cities are significantly lower (see Sec. 5). Quantitative relationships, i.e. dose-response functions, expressing the corrosion attack as a function of SO_2 and other parameters exist for several metals (see Sec. 3).

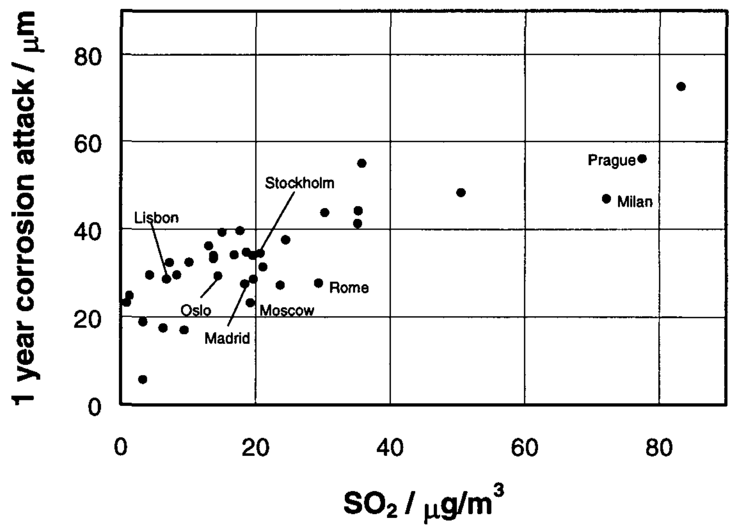

Fig. 3. Corrosion attack of unsheltered carbon steel exposed in the UN ECE exposure programme during the period September 1987 to August 1988 vs. SO_2 concentration.

Synergistic effects of NO_2 and O_3 in combination with SO_2

In contrast to SO_2, the effects of NO_2, and especially O_3, are not well documented (Arroyave and Morcillo, 1995; Tidblad and Kucera, 1996). Field exposure programmes have failed to detect effects attributable to NO_2 or O_3 with the exception of O_3 and copper (see Sec. 3.4). Laboratory exposures of several metals including zinc, copper and nickel have led to the following picture regarding synergistic effects.

The term "synergistic effect" means that the corrosion attack for a material exposed to a mixture of gases is greater than the sum of effects from individual single-gas exposures. Significant synergistic effects have been found in the laboratory for both O_3 and NO_2, however, the relative magnitude of the effects depends on the metal. For both O_3 and NO_2, the synergistic effect is attributed to the promotion of equation (1), i.e. the oxidation of S(IV) to S(VI). The reaction between SO_2 and O_3 is most likely stoichiometric while the reaction between SO_2 and NO_2 needs further investigation. With few exceptions,

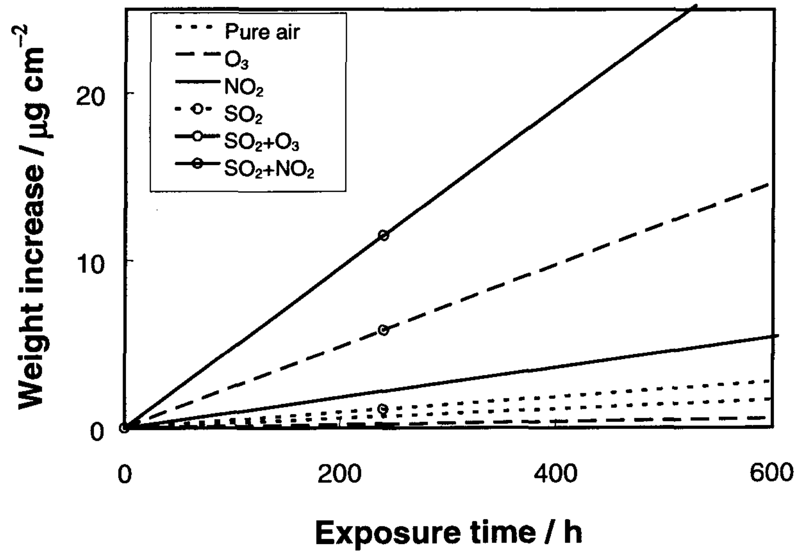

Fig. 4. Weight increase of nickel exposed in air at 70% Rh based on results after 240 hours and assuming a linear time dependence. The influence of additions of O_3 (100 ppb), NO_2 (100 ppb) and SO_2 (90 ppb) including combinations are shown.

there seem to be synergistic effects. The synergistic effects increase with relative humidity for most metals. However, at high relative humidities, aluminium and iron show no SO_2 + NO_2 synergism. When comparison is possible, the synergistic effect of SO_2 + O_3 is stronger than SO_2 + NO_2, except for nickel, which is illustrated in Fig. 4.

HNO_3

Nitric acid (HNO_3) is a secondary pollutant formed by the oxidation of NO_2. It can reach appreciable concentration levels in urban areas — reports are usually in the interval 1–7 $\mu g/m^3$ but in some cases the concentration can be above 10 $\mu g/m^3$. HNO_3 is a strong acid with a high deposition velocity that is almost independent of the humidity, which makes it relatively more harmful for dry and warm climates. The magnitude of its effect relative to other pollutants such as SO_2 is so far not investigated for metals.

*2.4. **Particles***

Particles normally increase but may in some cases decrease the deterioration rates of metals. The effect of particles on corrosion can also be either direct or indirect. Anthropogenic particles can be divided into primary and secondary. The primary particles are directly emitted from combustion, have a relatively short life span and deposit near the source. Secondary particles are smaller, less than 2 μm, long-lived, and are the result of chemical reactions amongst other pollutants i.a. SO_2, NO_2, volatile organic compounds and ammonia. Compared to the many effects, described in the following, that particles can have on the atmospheric corrosion, there is a lack of quantitative assessments especially the comparison to effects of gaseous pollutants.

Droplets of sulphuric acid resulting from the oxidation of SO_2 can be neutralised by ammonia-forming particles of ammonium sulphate. Similarly, particulate ammonium nitrate can form through the neutralisation of HNO_3. The particles thus enhance the corrosion by providing corrosion stimulators, especially sulphate is frequently found in corrosion products. Also, when water is adsorbed and then evaporates, gaseous ammonia is released to the atmosphere resulting in an acidification of the aqueous layer that may increase the corrosion rate.

Particles may in some cases also decrease the corrosion rate if they are basic by neutralising the surface water film formed on the degraded material.

Salt containing particles play an important role in atmospheric corrosion and this is related to their ability to increase the time of wetness. They are hygroscopic and starts to absorb water when the relative humidity exceeds a critical level, determined ideally by the equilibrium properties of a saturated solution of the salt. In practice, however, the particles deposited on the surface are a mixture of different compounds resulting in a difficulty to define a critical relative humidity. The ionic content of the particles prolongs the time of wetness also by reducing the freezing point of the adsorbed water below 0°C.

2.5. Wet Deposition

SO_2 and NO_2 both contribute to the increased acidity of wet deposition, in addition to their direct effects. The effect of wet deposition is relatively well quantified for many metals. Dose-response functions based on field exposures that includes the effect of acid rain exists for several metals. On the other hand, similar to particles, the effect of wet deposition can be either detrimental or beneficial, depending on the conditions. In principle, the wet deposition can have two effects on the corrosion process. First, it transports chemically active compounds present in the rain to the surface, thereby increasing the corrosivity of the moisture layer. Second, it washes away compounds previously deposited on the surface, with the opposite effect. Thus, for a specific material and environment the choosing of a sheltered exposure condition rather than unsheltered may, or may not, increase the corrosion rate as is illustrated in Table 1, where it is shown that aluminium has a higher corrosion rate in sheltered position in contrast to the other metals.

The effect of wet deposition has traditionally been regarded as minor compared to the effect of dry deposition. However, as is illustrated in Fig. 5, the effect depends strongly on pH and amount

Table 1. Corrosion attack in mm after eight years of exposure in the UN ECE exposure programme in unsheltered and sheltered positions. Intervals are shown corresponding to lower and upper quartiles (25- and 75-percentiles).

Metal	Unsheltered	Sheltered
Weathering steel	37–59	27–54
Zinc	9.2–18	2.2–3.4
Copper	3.4–5.3	1.8–3.5
Bronze	2.9–5.4	1.6–3.0
Aluminium	1.0–1.7	1.1–3.1

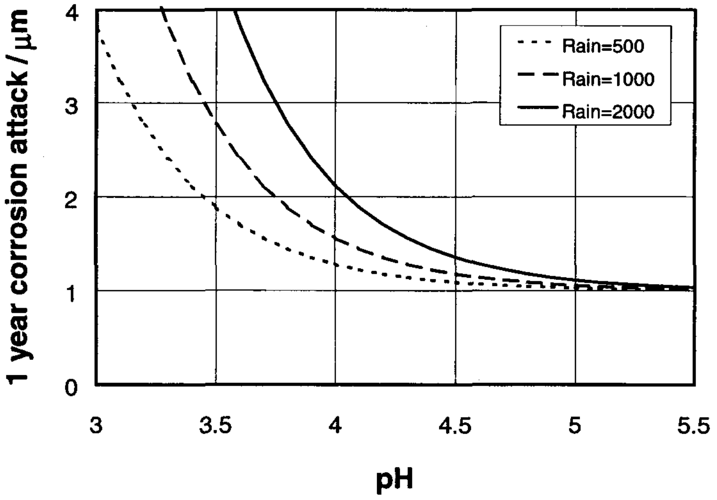

Fig. 5. Corrosion attack of unsheltered copper vs. pH of precipitation calculated from equation (3) and a constant dry deposition term, $0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh{\cdot}e^{f(T)}$, corresponding to 1.0 μm. Curves are shown for the precipitation (Rain) values of 500, 1000 and 2000 mm.

of precipitation. At about pH 4.5 and lower, the effect cannot be neglected.

In addition to compounds deposited on the surface, corroded metal ions are removed by the rain-wash. This release of metals to the environment is an environmental concern due to the potential effect that the heavy metals can have on ecosystems. However, when assessing the impact it is important to recognise first that the metal release is significantly lower than the total corrosion rate, which also includes metal ions left on the corroded surface in the corrosion products, and second that only part of the released metal is biologically active. Also, the metal runoff depends on the amount of precipitation reaching the surface, which means that the amount of precipitation as well as the inclination of the surface is of outmost importance when assessing run-off values.

3. Effects on Metallic Materials

In its unprotected form, examples of use for carbon steel include mounting and fittings and forged objects. Cast iron has been used in fences and gates. The main use is, however, in its protected form, which makes the economic importance of unprotected steel relative low. Zinc is commonly used as a pigment in zinc-rich coatings and in hot dip galvanising. An alternative use is rolled zinc sheet for roofing and rainwater drains. In buildings, aluminium is mainly used as a roof and facade material. By 1897, the San Gioacchino church in Rome was already covered with aluminium. The main uses of copper include roofs and window ledges. Historic and cultural monuments made of cast bronze are common especially in statues.

3.1. Effects on Metals in General

A typical metal exposed to dry air spontaneously forms a metal oxide of thickness 1 to 5 nm. Thus, it is the nature of the thin metal oxide, whether it is passive or active, stable or unstable, protective or not protective, that governs the atmospheric corrosion behaviour of that metal, rather than the properties of the base metal. The relative humidity when adsorbed water have properties equal to those of bulk water varies from 50% to 90% depending on the metal and this interval coincides with that of the "critical relative humidity" above which corrosion rates starts to be significant (see Sec. 2.2). Atmospheric corrosion of metallic materials is an electrochemical process in which the overall reaction can be divided into an anodic and a cathodic reaction. Under most atmospheric conditions the anode reaction, i.e. metal dissolution, is the rate-limiting step. With time, a film of corrosion products form that usually hinders the transport of ions, which lowers the anodic reaction rate and, hence, the atmospheric corrosion rate. The initially formed corrosion products are oxides, hydroxides, and even oxyhydroxides. During prolonged exposure, however, a variety of corrosion products may form including compounds originating from the atmosphere, i.e. sulphate, nitrate and chloride. The atmospheric corrosion of metals is a complex process and the extent of deterioration as well as the mechanism varies considerably depending on the metal.

For several metals that are frequently used in buildings, including objects of cultural heritage, dose-response functions on damage have been obtained. The functions are of outmost importance for development of systems for classification of corrosivity of environments, for mapping of areas with increased risk of corrosion, and for calculation of cost of damage caused by deterioration of materials. A dose-response function links the dose of pollution, measured in ambient concentration and/or deposition, to the rate of material corrosion.

Metals dealt with specifically in this chapter include ferrous metals (Graedel and Frankenthal, 1990), zinc and galvanised steel (Graedel, 1989a; Odnevall, 1994; He, 2000), copper (He, 2000; Graedel *et al.*, 1987; Strandberg, 1997), bronze (Strandberg, 1997) and aluminium (Graedel, 1989b).

3.2. Ferrous Metals

The corrosion rate of carbon steel is generally high, about 20–60 mm after one year of exposure in non-marine areas, the value to a great extent depending on the SO_2 concentration (see Fig. 3). Weathering steel behaves in a different way than an ordinary carbon steel at prolonged exposure and the corrosion rate is stabilised at fairly low levels since a protective rust layer forms during the first two to four years of exposure. The decrease of the SO_2 influence with time for unsheltered weathering steel is a known fact for this material, which is illustrated in Fig. 6. The practical implication is that weathering steels are a very useful material for unsheltered exposure in SO_2

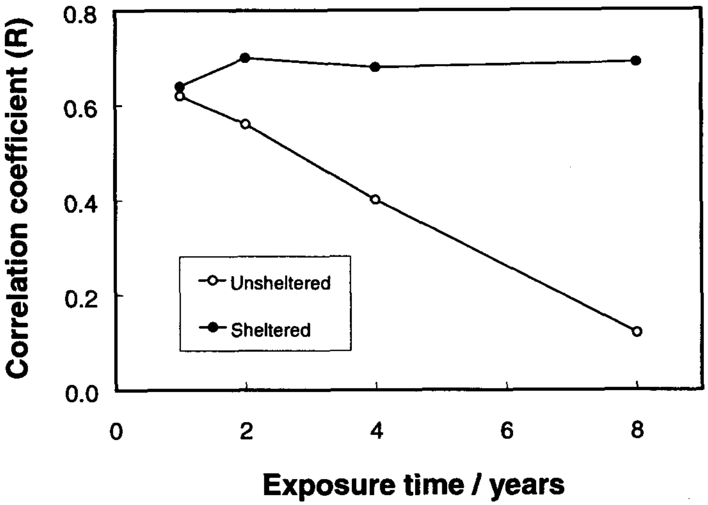

Fig. 6. Correlation coefficient, R, vs. exposure time. R is calculated by comparing SO_2 concentration with corrosion attack of weathering steel exposed in unsheltered or sheltered position in the UN ECE exposure programme.

polluted atmospheres. They have, however, similar corrosion rates as carbon steel in sheltered positions as the creation of a protective rust layer needs regular washing and drying at rain events.

3.3. Zinc and Galvanised Steel

As for many other metals, SO_2 is the most important corrosion stimulator. In addition, wet deposition may result in dissolution of protective corrosion products, which leads to an increase of the deterioration rate. In marine areas, the deposition of chlorides is also a determining factor. The corrosion attack after one year of exposure is about 1–4 μm in non-marine areas.

Zinc is the only one of the common engineering metals for which a carbonate plays an important role in atmospheric corrosion. After an initial formation of zinc hydroxycarbonate, a zinc hydroxysulfate is formed in the urban environment. Deposition of chlorides may eventually also lead to the formation of a zinc chlorohydroxysulfate.

Zinc were exposed in the UN/ECE materials exposure programme and a dose-response function

$$ML = 1.4[SO_2]^{0.22}e^{0.018Rh}e^{f(T)}t^{0.85} + 0.029Rain[H^+]t \qquad (2)$$

was obtained where ML is the mass loss in g/m^2, $[SO_2]$ is the SO_2 concentration in $\mu g/m^3$, Rh is the relative humidity in %, f(T) is a function of temperature in °C, equal to $0.062(T-10)$ when T is lower than 10°C and $-0.021(T-10)$ when T is higher than 10°C, t is the time in years, Rain is the amount of precipitation in mm/year and $[H^+]$ is the hydrogen ion concentration in precipitation in mg/l.

3.4. Copper and Bronze

The corrosion chemistry of copper is complex. The corrosion products consist of a mixture of corrosion products where cuprite (Cu_2O) and basic sulphates, including anthlerite and brochantite constitute the dominating part on surfaces exposed long-term in the urban environment. The formation of cuprite is especially difficult to quantify in terms of environmental parameters and the formation rate can initially be very high especially in rural areas, which have high O_3 concentrations. Copper is the only metal where it has been proven by field exposures that O_3 as well as SO_2 have an important role. After longer exposure times, the relative importance of cuprite decreases in favour of sulphate and the degradation characteristics become similar to those of bronze. The corrosion attack on copper and bronze after one year of exposure is about the same, 1–2 mm, or slightly lower compared to zinc.

Copper is one of the metals that were exposed in the UN ECE materials programme and a dose-response function

$$ML = 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh \cdot e^{f(T)}t^{0.78} + 0.050Rain[H^+]t^{0.89} \qquad (3)$$

was obtained where ML is the mass loss in g/m^2, $[SO_2]$ is the SO_2 concentration in $\mu g/m^3$, $[O_3]$ is the O_3 concentration in $\mu g/m^3$, Rh is the relative humidity in %, f(T) is a function of temperature in °C, equal to $0.083(T-10)$ when T is lower than 10°C and $-0.032(T-10)$ when T is higher than 10°C, t is the time in years, Rain is the amount of precipitation in mm/year and $[H^+]$ is the hydrogen ion concentration in precipitation in mg/l.

Bronze used for sculptures usually contain copper, 1–10% tin, 1–10% zinc and 0–6% lead. Bronze is also one of the metals that were quantified in the UN/ECE materials programme as:

$$ML = 0.026[SO_2]^{0.44}Rh \cdot e^{f(T)}t^{0.86} + (0.029Rain[H^+] + 0.00043Rain[Cl^-])t^{0.76} \qquad (4)$$

where ML is the mass loss in g/m^2, $[SO_2]$ is the SO_2 concentration in $\mu g/m^3$, Rh is the relative humidity in %, f(T) is a function of temperature in °C, equal to 0.060(T−11) when T is lower than 11°C and −0.067(T−11) when T is higher than 11°C, t is the time in years, Rain is the amount of precipitation in mm/year, $[H^+]$ is the hydrogen ion concentration in precipitation in mg/l and $[Cl^-]$ is the chloride ion concentration in precipitation in mg/l. Figure 7 shows observed versus predicted values based on the dose-response function.

3.5. Aluminium

The corrosion attack on aluminium is generally lower compared to the other metals, about 0.1 to 0.2 μm after one year of exposure in non-marine areas. The low corrosion rate is due to a protective

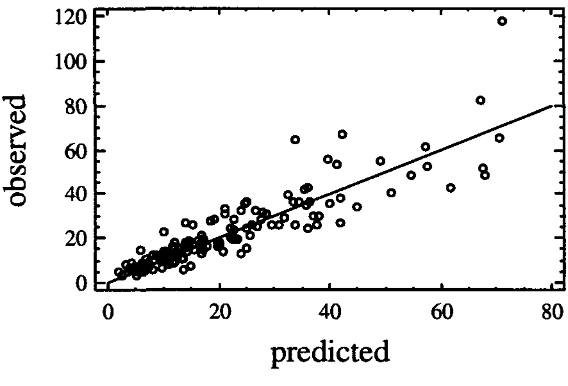

Fig. 7. Observed vs. predicted values for mass loss of unsheltered bronze using equation (4).

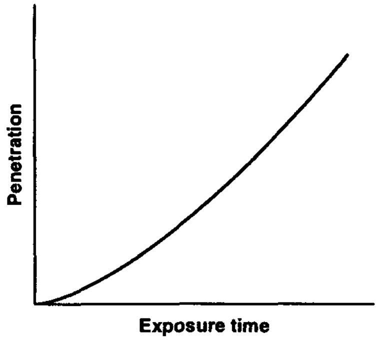

Fig. 8. Sketch of corrosion-time curve for rain-sheltered aluminium in a heavy industrial atmosphere (adapted from Kucera and Mattson, 1987)

aluminium oxide film that forms initially, γ-Al_2O_3. The film may grow and also be transformed into other compounds, such as hydrated aluminium oxides, hydroxides and sulphates, during the atmospheric corrosion process. As for many other metals, the corrosion rate of aluminium is affected by SO_2 to a great extent but aluminium is particularly sensitive to chlorides, which may result in increased pitting formation. Sulphate species dominate in corrosion products formed in urban areas.

Looking at Table 1, aluminium differs from the other metals by having higher corrosion attack values in sheltered position compared to unsheltered. A possible time development in sheltered position is illustrated in Fig. 8 where particles may accelerate corrosion by adsorbing moisture and acidifying compounds from the atmosphere thus producing an acid medium on the surface. Due to the non-existing cleaning by rain, these conditions prevail for long periods and the corrosion rate may increase with time initially.

4. Life Time Assessment and Cost Calculations

In order to be able to calculate costs, a damage function needs to be obtained. A physical damage function links the rate of material corrosion due to the pollution exposure given by the dose-response function to the time of replacement or maintenance of the material.

Performance requirements determine the point at which replacement or maintenance is considered to become necessary. If the performance requirements can be described in terms of a critical degradation level it is possible to transform a dose-response function into a damage function (Kucera *et al.*, 1996; Tidblad *et al.*, 1999).

For assessment of direct costs of corrosion damage caused by air pollutants, a model has been developed and used first in three cities in Europe: Stockholm, Sarpsborg and Prague, and subsequently also for a rough estimation for whole Europe (Kucera *et al.*, 1993; UN ECE Workshop, 1997). The estimated total cost savings were 9.5×10^9 \$/year for SO_2-induced corrosion in Europe resulting from the implementation of the second Sulphur Protocol within UN ECE. The model is shown in Fig. 9. The estimated economic damage can be calculated according to the equation

$$K_a = K \cdot S \cdot (Lp^{-1} - Lc^{-1}) = K \cdot S \cdot f \qquad (5)$$

where K_a is the additional cost for maintenance/replacement, K is the cost per surface area of material, S is the surface area of material, L_p is the maintenance interval (life time) in polluted areas and L_c is the maintenance interval in clean areas. The maintenance frequency, f, is the fraction of material that is subject to actions each year as a result of increased pollution. Equation (5) has to be applied for each material individually. Furthermore, each component in equation (5) can, in principle, have a spatial dependence, i.e., the cost, exposed areas and lifetimes may each depend on the geographical location. In order to make a cost estimation, each block in Fig. 9 needs to be addressed. Depending on the available data the treatment of individual boxes will be more or less comprehensive.

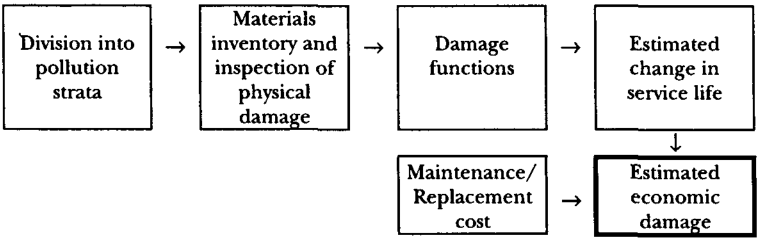

Fig. 9. General approach for assessing cost of corrosion damage (Kucera *et al.*, 1993).

5. Corrosion Trends

Trend effects were assessed as part of a UN ECE exposure programme on materials (ICP Materials) and the following is brief summary of the findings (Tidblad *et al.*, 1999). The aim of the trend exposure was to elucidate the environmental effects of pollutant reductions achieved under the Convention on Long-Range Transboundary Air Pollution and identify extraordinary environmental changes that result in unpredicted materials damage. The trend exposure consisted of repeated one-year exposure of steel and zinc on the 39 test sites during the period 1987–1995.

Figure 10 shows an overview of the trends during the period 1987 to 1994. There are comparatively few trend exposures of steel and zinc while pollution data are available each year. In order to present the results on a common scale, all values are compared to the initial value,

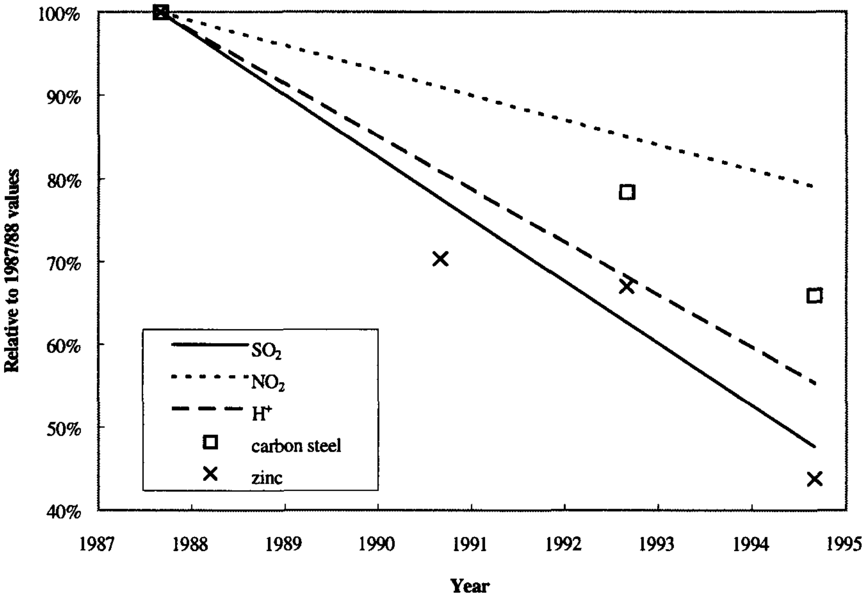

Fig. 10. Trends of SO_2, NO_2, acidity (H^+), and corrosion of unsheltered unalloyed carbon steel and zinc. All values are expressed relative to the initial (1987/1988) value. For environmental data the average trend during the eight-year period is indicated instead of the individual annual averages.

corresponding to the 1987/88 period (100%). Of the environmental parameters measured in the network of urban and rural sites of ICP Materials, only SO_2, NO_2 and H^+ exhibit trends. All of these are decreasing with SO_2 having the strongest trend and NO_2 the weakest. For O_3, no specific trends were observed. The decreasing trend in the concentration of acidifying air pollutants has resulted in decreasing corrosion rates of the exposed materials. Both carbon steel and zinc show decrease of corrosion rate in unsheltered as well as in sheltered positions.

Figure 11 shows a summary of the analysis of unsheltered and sheltered carbon steel and zinc separating the relative contributions of dry and wet deposition assuming that effects of dry deposition is attributed to SO_2 while effects of wet deposition is attributed to H^+ deposition.

SO_2 is the largest single contributing factor to the decreasing corrosion trends. The decreasing H^+ in precipitation is a contributing factor, its effect is, however, much smaller than that of dry deposition. The decrease in corrosivity is generally larger than expected from

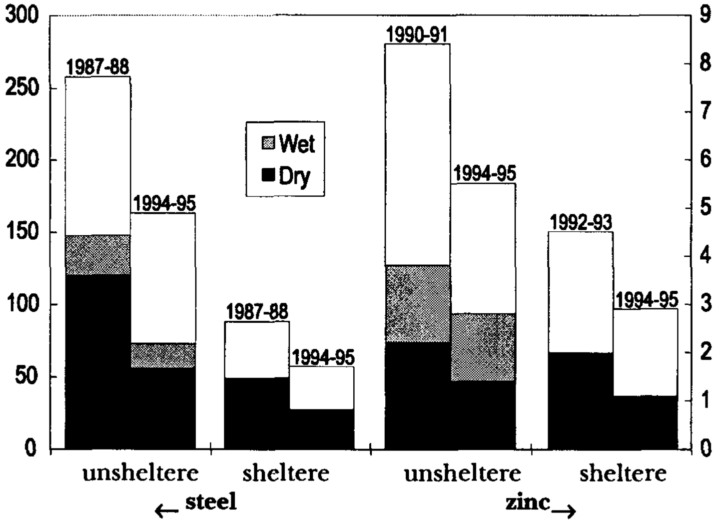

Fig. 11. Average mass loss of unalloyed carbon steel and zinc in g/m^2 for unsheltered and sheltered positions. Each bar consists of parts corresponding to dry and wet deposition as well as a part not directly related to SO_2 and H^+ load.

the drop of SO_2 and H^+ concentrations. This part cannot be directly related to a specific pollutant and reflects the multi-pollutant character of the process of material degradation.

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CHAPTER 8

THE EFFECT OF AIR POLLUTION ON GLASS

J. Leissner

1. Introduction

Glass products that are used outdoors undergo degradation which is of considerable practical importance. Loss in clarity or transmission of ordinary window glass or of stained glass windows is one example. Lighting fixtures that decline in output as a result of weathering mean lost energy. Solar reflectors and collectors that employ glass components must continue to perform at a high level of efficiency if they are to be practical energy collecting systems, which justify the enormous capital outlay in construction. Glass panels that lose their gloss are no longer aesthetically appealing; worse yet if they fail mechanically because of environmentally induced changes.

Historical stained glass windows are among the most important items of cultural heritage of Europe. However, mediaeval stained glasses and their paintings suffer heavy deterioration and are often completely destroyed by environmental corrosive influences. Many parameters such as humidity, temperature changes, inadequate conservation treatments, microorganisms, gaseous pollutants and synergetic interactions contribute to the deterioration of these objects.

There is no doubt that this is a corrosion process of the glass. The main reason lies in the much lower durability of the chemical composition of historic stained glasses compared to contemporary glasses.

2. The Corrosion Process

Glass can be chemically attacked by environmental agents or airborne contaminants may adhere to the glass surface. The deterioration of stained glass windows for example takes place, since manufacture, both indoors and outdoors although when storing the glasses in a museum environment the corrosion rate can be slowed down — a rather unsatisfactory protection measure because stained glass windows gain their sphere of harmony only in their original architectural setting. Additionally major problems occur with the paint layers which mainly consist of a lead silicate glass. These are affected by weathering in the same manner as the stained glass, but the weathering resistance can be better or worse than the glass substrate. Even when the paint is relatively stable, the underlying corroding glass will loosen the paint layers into flakes. Sometimes stained glass is very durable, but the black stain from enhanced corrosion results in a complete loss of the painting. A negative image of the painting is typically observed.

In general, weathering is the interaction of a glass surface with chemical agents in the atmosphere which can lead to three different effects on the glass:

- loss of transparency and gloss
- loss of paint layers
- loss of glass material

The reasons and basic reactions of corrosion will be explained in the following sections.

2.1. Chemical Composition and Structure of Glass

Glass is normally regarded as a hard, brittle and transparent material. The properties of glass however are mainly due to its chemical composition and manufacturing process. The main component of glass is silica (sand), the network former. In order to make a workable glass various compounds, such as network modifiers (alkali and earth alkali compounds) and colourants (metal oxides) are added and result in a marked effect upon the structure and properties of the resulting material (Scholze, 1988; Vogel, 1979).

Glass which was made during the Middle Ages usually has mainly a low content of silica and a high content of potassium and calcium plus some other minor compounds, often phosphates, magnesia and alumina, etc. (Newton and Davison, 1989). The higher the content of silica, the higher the chemical durability and temperature required to melt the glass. The basic molecular structural units for a glass are the silicon atoms which are surrounded tetrahedrically by oxygen (Scholze, 1988). These SiO_4^- tetrahedrons form a three-dimensional irregular non-crystalline network (Fig. 1).

By adding the network modifiers (calcium and potassium), this network is loosened because oxygen bridges are opened and new ionic bonds are formed (Fig. 2). This results in a higher corrosion

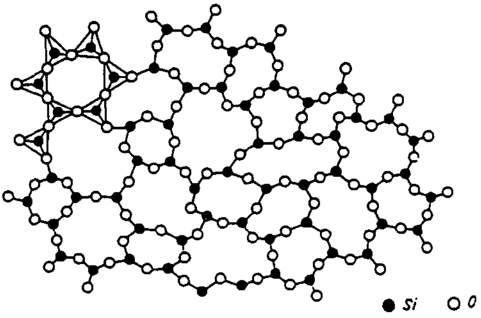

Fig. 1. Two-dimensional network of pure silica glass.

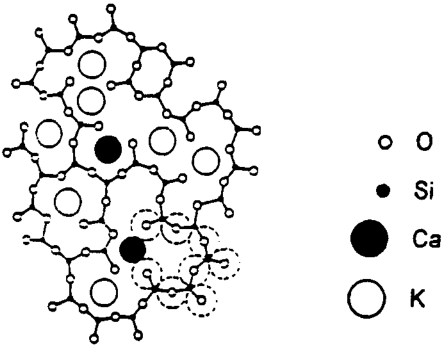

Fig. 2. Two-dimensional network of a mediaeval glass.

sensitivity. Medieval glass is a multi-component material of various oxides and its composition can vary significantly from glass to glass. This can be seen in stained glass windows where relatively good preserved glasses are side-by-side with heavily corroded ones.

2.2. *Principle Corrosion Reactions*

There are many parameters which contribute to the deterioration of glass, therefore the complex corrosion process is not completely understood even today. An enormous number of publications have dealt with its investigation. The most prevalent corrosive agent is water and the existence of water is in nearly all cases necessary to initiate corrosion. In the literature, three basic reaction paths for corrosion are described: corrosion under neutral, acidic or alkaline conditions (Scholze, 1988; Fitz, 1991; Marschner, 1985; Sanders and Hench, 1973; Müller, 1992).

The first step is the adsorption of water onto the glass surface (as illustrated in Fig. 3), the quantity being a function of relative

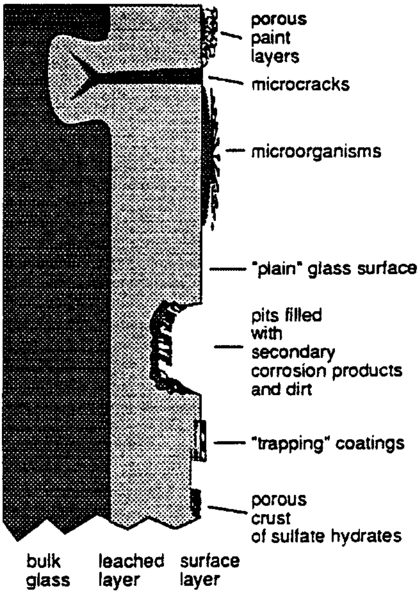

Fig. 3. Schematic representation of the weathering process.

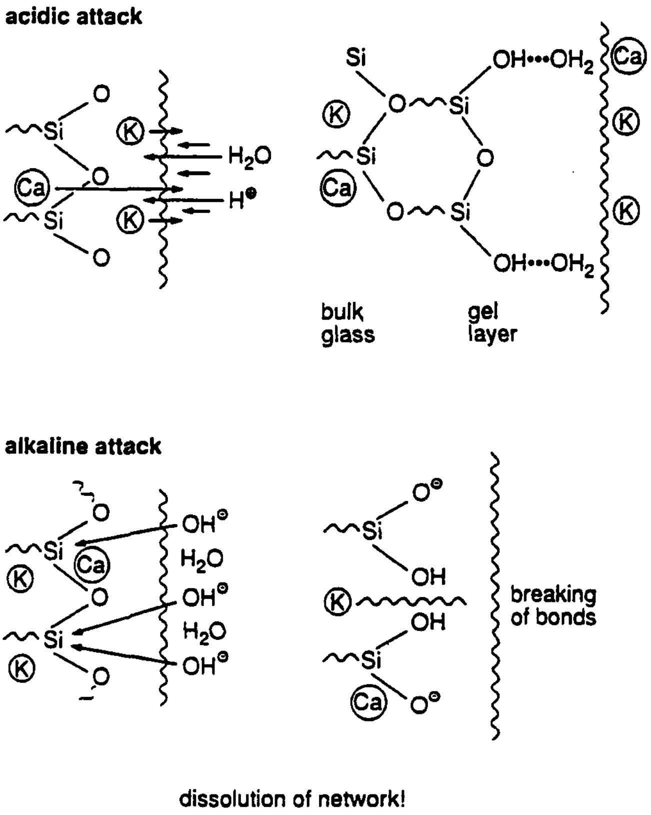

Fig. 4. Scheme for the main glass corrosion reactions.

humidity and glass type. Water then reacts with the glass surface through a sequence of steps involving an exchange of ions (leaching) and etching (first order reaction). In leaching, the network-modifier ions such as potassium and calcium are exchanged against protons deriving from acidic compounds, typically acetic acid or sulfuric acid. This process leads to the formation of a gel-layer which plays an important role for the preservation of stained glass windows. In Fig. 4, the reactions are seen schematically.

The presence of water is necessary for glass to react with compounds from its environment. Under normal conditions, it can be assumed that there is always a certain amount of water at the glass surface. The quantity of water depends mainly on the surface properties, the temperature and the relative humidity. When this water layer on the glass surface is thick enough, it is able to dissolve gases from the atmosphere.

Acid pollutant gases such as sulphur dioxide or nitrogen dissolve on the glass surface and initiate the ion exchange reactions. The reason for the deterioration of stained glass is the increased levels of environmental pollution. The higher the content of alkali and earth alkali ions in the glass, the larger the number of sites which are available for ion exchange reactions. These alkali and earth alkali ions can then migrate towards the surface resulting in a voluminous gel layer of silica. This layer can reach about 100 μm in thickness, for example, in mediaeval glasses. Further reactions take place in this gel layer, which can cause cracks and flaking when accompanied by drastic temperature and relative humidity changes.

The remaining exchanged ions are either washed off by rain or form corrosion products, as for example, gypsum and syngenite resulting in a more or less dense and thick corrosion crust, which will result in a decreasing transparency.

There is another mechanism for corrosion for stained glasses, which have flaws and are not exposed to rain that washes off corrosion products. Under neutral or alkaline surroundings, dissolution of the glass network can occur which means that the strong silicon oxygen bonds are broken; the silica network is totally disrupted and the glass structure is destroyed. In the initial stage, this will be indicated by a cloudy surface that eventually becomes roughened and covered with tenacious reaction products. Hollow glasses of the 17th and 18th century are particularly affected by this type of corrosion. These have a very high potassium content and a very low calcium content, and are called weeping glasses (Fitz, 1991).

$$\mathrm{Si{-}O^{-}K^{+} + H_2O \rightarrow Si{-}OH + K^{+} + OH^{-}}$$
$$\mathrm{Si{-}O{-}Si + OH^{-} \rightarrow Si{-}OH + Si{-}O^{-}}$$

2.3. Different Stages of Surface Corrosion

Surface corrosion can be detected in different stages in stained glass windows. Nearly all medieval glasses are affected by the type of corrosion described above, although sometimes the glass seems to be unaltered. However, if the glass is put under a microscope the changes can be seen clearly. Figures 5(a) to (e) illustrate main alterations of stained glasses and show the progressing surface corrosion as seen under the electron microscope. The glasses are model glasses and exhibit identical corrosion behaviour and similar chemical composition to medieval stained glasses.

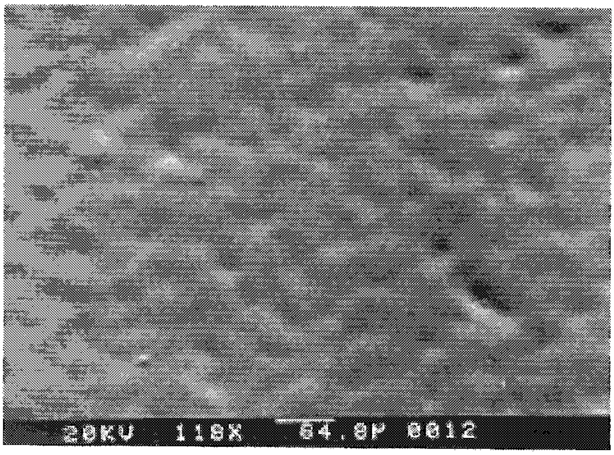

Fig. 5(a). Firepolished new glass surface.

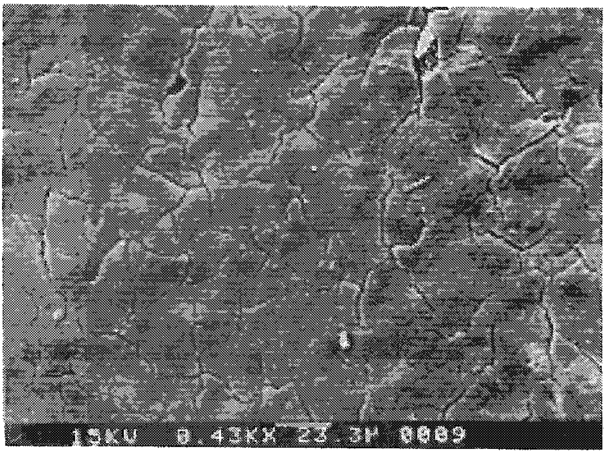

Fig. 5(b). Micro cracking of gel layer on glass surface.

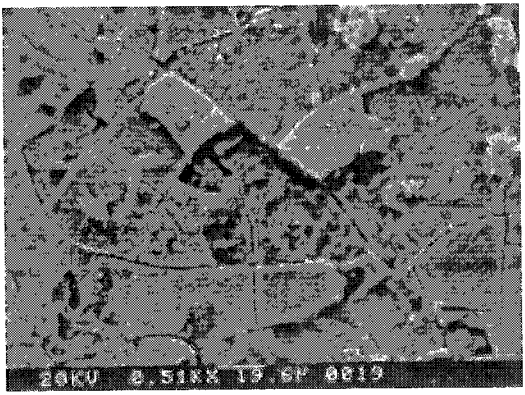

Fig. 5(c). Loss of gel layer parts.

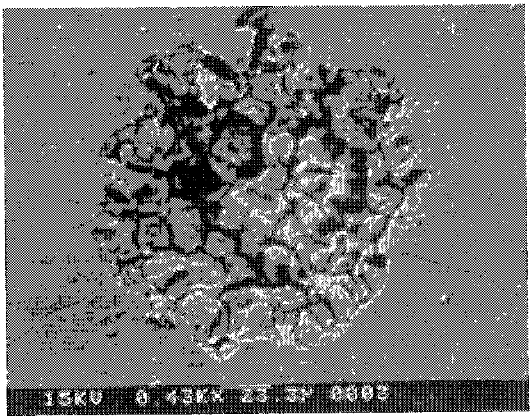

Fig. 5(d). Initial stages of pit formation.

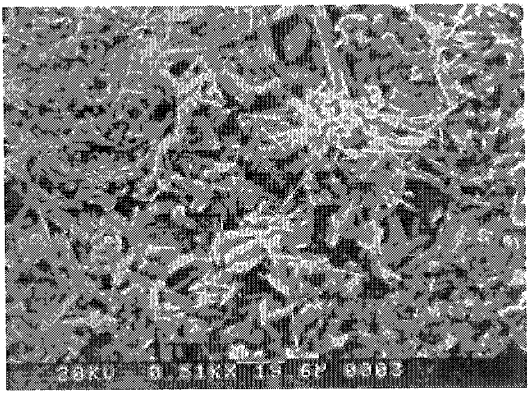

Fig. 5(e). Dense corrosion crust.

2.4. Corrosion Enhancing Factors and Effects

Besides the major influence of composition of the glass, there are other factors which affect the type and rate of glass decomposition:

- *manufacturing process of the glass*
  surface properties
  homogeneity of the glass
- *time of exposure*
- *environmental conditions*
  water (humidity, condensation, precipitation)
  temperature changes
  air pollution
  UV light-causing oxidation processes
  deposition (dust, soot, grease)
- *previous (conservation) treatments*
  cleaning treatments (mechanical and chemical)
  heat treatments for paint consolidation
  inadequate application of coatings
- *attack of microorganisms*
  lichens, fungi, algae, bacteria
- *vibrations*
  road, rail, air traffic, minor earth movements

As already mentioned, water is a primary agent which enhances corrosion, but nevertheless, air pollutants such as sulphur dioxide, nitrogen oxides and ozone in combination with water increase the corrosion rate drastically. On the one hand, they enhance the ion exchange reactions and on the other, they react with the released alkali and earth alkali ions. It is assumed that the first step is the reaction of carbon dioxide with the primary products of corrosion by converting the hydroxides, produced by the attack of water on glass, to carbonates. This step is responsible for the calcite frequently found in the weathering crust of glass. It contains mainly gypsum and syngenite formed through the reaction with atmospheric sulphur compounds. The crust may be up to 1 mm thick, white brownish or even blackish, very soft and powdery, or extremely hard and flinty.

The effect of water and air pollutants are very much linked to time and temperature. The higher the temperature and the time of exposure, the higher the corrosion and its rate. Cycles of temperature change and condensation and drying especially contribute to faster corrosion. Condensation may occur on the inside of church windows especially when heating is installed. These condensation/drying cycles can result in the formation of minute, discrete droplets which then dry out. Any alkali extracted from the glass by the droplets remains as patches on the surface to form nuclei so that the droplets in the next phase of condensation occur at exactly the same spot. Solutions of high pH could then build up at each droplet site causing attack at those points — this may be an explanation of the origin of pitting (see Fig. 5(d) and Sec. 2.2).

Another mechanism for the formation of pits and corrosion phenomena may be the attack by microorganisms (Krumbein *et al.*, 1991; Weissmann and Drewello, 1996; Perez y Jorba *et al.*, 1984; Perez y Jorba and Bettembourg, 1989; Müller, 1992). Much of the action of microbiota could be assigned to water supply via the fungal mycelium. It is suggested that fungi serve as transport agents of water and are thus hydrating forces comparable to the action of a thread of wool. In addition to the supply of water bacteria and fungi act as physical agents and as chemical agents through the formation of various acids, among which citric and oxalic acids are the most prominent ones. Lichen, algae, fungi and bacteria can metabolise, leach, accumulate and redeposit calcium, potassium, magnesium, manganese, etc. Obviously organic growth on both sides of the window glass occurs in warm humid environments where a minimum supply of biological essential elements and nutrients is available. The attack of microorganisms can lead to special etching patterns, biopitting, dealkalisation, staining (darkening) and depositions like calcium oxalate.

The darkening phenomena of windows is not yet understood. It is suggested that the UV light causes oxidation/reduction reactions of manganese and iron oxides which are then deposited along the micro fissures of the gel layer and lead to complete intransparency (Perez y Jorba and Bettembourg, 1989; Müller, 1992).

Inadequate previous conservation treatments, as for example, mechanical or chemical cleaning can damage the glass surface by creating scratches where corrosion processes or enhanced leaching of ions can be initiated (Fuchs *et al.*, 1991).

3. Main Analytical Tools to Examine Corrosion Effects on Glass

The degradation mechanisms and rates depend quite critically on the initial surface and on the evolution of leached layers, gel layers, and reaction product layers as the dissolution process proceeds. Characterisation of these surfaces has brought into play nearly every surface characterisation tool known to material science. For those glasses that develop substantial surface layers, characterisation by scanning electron microscopy, atomic force microscopy, photoelectron spectroscopy, and diffuse reflectance infra-red spectroscopy has proved useful (Salem *et al.*, 1994a and b). Depth profiling techniques such as secondary ion mass spectrometry and sputter induced optical emission spectroscopy allow measurement of diffusion profiles through the glass surface layers. Success in measuring hydrogen concentrations in the hydrated layers has also been obtained by resonant nuclear reactions methods and by Rutherford backscattering.

3.1. SEM/EDX

The Scanning Electron Microscope (SEM) is often the first analytical instrument used when a "quick look" at a material is required and the light microscope no longer provides adequate solution. In the SEM, an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area [see Figs. 5(a) to (e)].

3.2. Infra-red and Raman Spectroscopy

Infra-red and Raman spectroscopical methods are gaining importance in investigation of surface layers of glasses. Infra-red reflection techniques allow especially effective examination of the

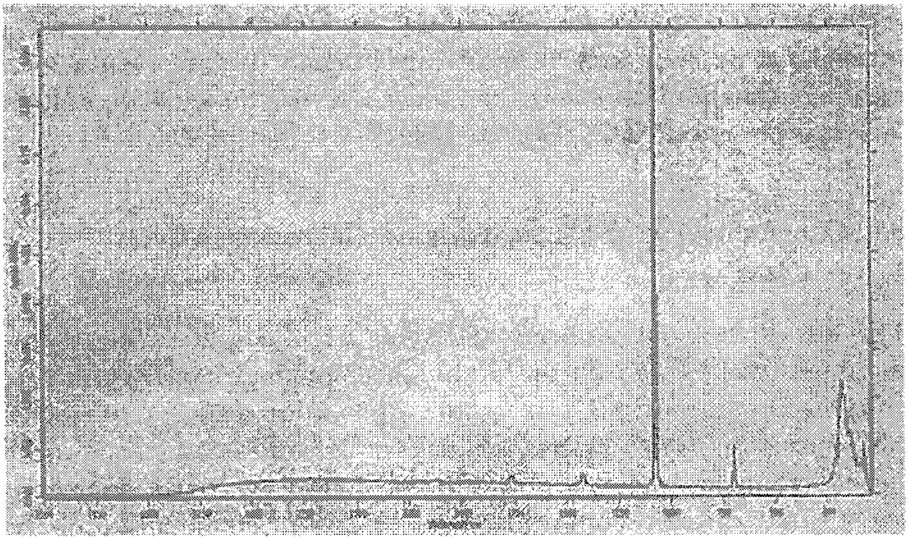

Fig. 6. Raman spectrum of sodium carbonate on a corroded glass surface.

surface. The characteristic vibrations of silicate glasses lie in three regions between 33,000 and 3800 cm^{-1}, 800 and 1200 cm^{-1} and around 500 cm^{-1} and can be recorded by infra-red and Raman spectroscopy. The vibration bands in the infra-red spectra are very strong so that normal glasses are not transparent to infra-red radiation (Fuchs *et al.*, 1988 and 1991a) . Therefore infra-red spectra cannot be recorded in the transmission mode when the glasses are thicker than a few millimetres. A watery gel layer will be formed due to the corrosion process which can be seen by the growth of the OH absorption band at about 3300 cm^{-1}. The corrosion crust also consists of gypsum and syngenite or carbonate crystals (see Fig. 6) which can ideally be identified by the sharp absoprtion bands in the Raman spectrum.

4. Evaluation of Environmental Impact

In conservation research, it is important to evaluate the aggressivity and corrosivity of environments. Basic investigations of the interaction between materials and the environmental stress at the very spot or building structure of interest can render detailed understanding of the deterioration phenomena and corrosion mechanisms. The corrosion relation between specific stress situations and resulting decay processes may be essential for the design of adequate protective measures. The assessment of the combined corrosive effects induced by climatic influences, pollution related parameters and synergetic effects is also of high interest for judgements concerning the protective features of existing conservation concepts.

In the field of stained glass conservation, the state of the art is characterised by transferring standard analytical methods from the fields of climatology and environmental engineering into conservation research. Measurements of single parameters such as temperature, humidity, condensation effects, pollutant concentrations, precipitation and run-off water, examination of microbiota — the spectra of relevant environmental parameters as well as the efforts of analyzing them can be extended at will (Oidtmann *et al.*, 2000).

Up to now, knowledge about the precise meaning of these influences and the resulting impact on the material is fragmentary. To cope with this restrictions, an alternative and integrating concept for total stress level assessments was desirable so the type of sensitive material found in stained glass windows seemed a useful surrogate. Studies using the original materials of the stained glass windows are restricted by the heterogeneity of the assets, the complexity of altered surface layers and, in most cases, the exact history of historic pieces which may not be well documented.

Therefore a solution to these problems is offered by using simulation materials, known as *glass sensors* (Fuchs *et al.* 1988, 1991a and b; VDI-Richtlinie, 1992; Leissner and Fuchs, 1992a), which show qualitatively the same corrosion phenomena, but within a much shorter time. A reliable comparability between different objects and environmental situations can be obtained. Glass sensors are based on low durable potassium-calcium silicate glasses similar to mediaeval stained glasses with a high sensitivity to corrosive stresses. Their easy-to-handle technique enables the detection of combined impact potential. Due to the sensitivity of the dosimeter glass, judgements about corrosive stresses and damage risks can be made within 12 months.

The principle of the *Glass Sensor Method* is the registration of the combined impacts of the environment. The surface of the glass sensor interacts with its immediate atmosphere causing alterations in the surface layer:

- leaching of potassium and calcium
- formation of a gel layer
- formation of a corrosion crust

The degree and kinetics of this alterations as well as the crystallisation of the corrosion crust correspond with the total stress level during the exposition, and intergrates all effective environmental influences as well as their synergetic interactions. The changes can be determined by different analytical routine methods, the data being collected before and after exposure of the glass sensors. The two major corrosion effects, the leached gel layer and the increasing crystalline corrosion crust (K-Ca sulfate hydrates) cause an increase in the intensity of the OH absorption band, in the infra-red spectrum of the exposed glass sensor. The higher the increase in the OH absorption band, the higher the corrosive stress. Additional microscopical investigations allow additional qualitative and semi-quantitative estimations about the degree of corrosion.

The *Glass Sensor Method* is a very valuable tool in the field of stained glass conservation, e.g. to estimate the effectiveness of protective glazings (a widely accepted protection measure). As a case study, three differently ventilated types of protective glazings (internal ventilation, no ventilation and an external ventilation) were investigated with glass sensors (Leissner and Fuchs, 1992b; Romich *et al.*, 1999). The results (Fig. 7) showed clearly that the best outcome is obtained with an internally ventilated protective glazing, whereas the external ventilation shows no protective effect (position 2 has nearly the same corrosive stress as the outdoor position 4). The worst case is with the non-ventilated protective glazing — here the situation for the position 2 is even worse than without protective glazing and will lead to an enhanced corrosion progress. The height of the bars in Fig. 7 represents the corrosive stresses to which the different sides of a stained glass window are exposed (position 1 = front side of original stained

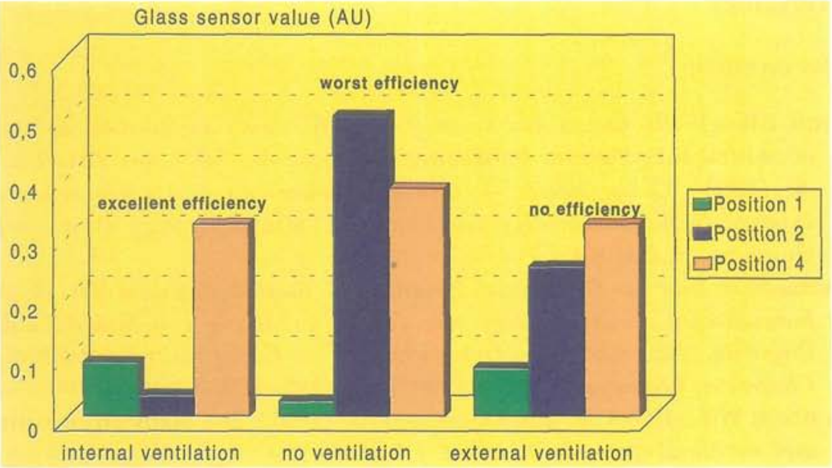

Fig. 7. Efficiency of different ventilation types of protective glazings.

glass window; position 2 = reverse side of original stained glass window, gives information about achieved protective effect; position 4 = reverse side of protective glazing facing outdoor conditions). Up to now, a large number of protective glazings have been investigated by glass sensors which resulted in the general trend, that internally ventilated protective glazings are more effective than externally or non-ventilated types. Nevertheless, every stained glass window and its protective glazing stand in a unique situation concerning overall climate situation, size of slots, indoor climate, etc. and therefore needs its own evaluation of the achieved protective effect.

5. Conclusions

The corrosion process of glass is a very complex mechanism. Many factors which promote corrosion are well known but not all the influences are understood. Since environmental pollution is a major factor for the enhanced corrosion process, it is necessary to protect the historic windows with highly efficient protective glazings and to evaluate the environmental stresses to which they are exposed in order to save them for the future generations.

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CHAPTER 9

THE EFFECTS OF OZONE ON MATERIALS — EXPERIMENTAL EVALUATION OF THE SUSCEPTIBILITY OF POLYMERIC MATERIALS TO OZONE

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and S.E. Espenhahn

1. Introduction

Much of the debate on the deleterious effects of ozone (O_3) in the boundary layer has focused upon vegetation and human health. The effects of O_3 on materials have been largely ignored until recently. Materials can be defined in a number of ways: for convenience, we define materials as the inorganic and organic components of things that humans use in their day-to-day life, for example, clothing, buildings, vehicles, etc. Here, we focus upon polymeric materials and rubbers in particular, and the effects of O_3 on them.

Research into the effects of O_3 on materials is hardly new: some of the older literature goes hand-in-hand with the development of understanding of the generation and abundance of photochemical oxidants (e.g. Bradley and Haagen-Smit, 1951). However, despite the fact that early attempts at limiting O_3 concentrations were targeted at materials effects, further research between the 1960s and 1990s was extremely limited. The research into the effects of O_3 on various materials has been reviewed and this research gap highlighted (Lee *et al.*, 1996; PORG, 1997). The lack of research partly reflects a perception that this is a solved problem. For example, the effects of O_3 on fabrics were understood some time ago and measures put into place in the manufacturing process to mitigate against damage. In the case of polymeric materials and in particular, rubber, antiozonants were incorporated into natural and synthetic rubbers to prevent the well-known effects.

This chapter summarises part of a research programme put into place by the U.K. Department of Environment Transport and the Regions. The research comprised two essential elements: basic research, and analysis of results in terms of economic assessment derived from the basic research and emissions and modelling scenarios of future atmosphere. The latter part, the assessment, is not considered here but is described by Holland *et al.* (1998). The experimental programme and results described here synthesise a number of particular experiments that will be described in more detail in forthcoming publications.

In Sec. 2, the basic experimental philosophy and design is described. In Sec. 3, the results of accelerated exposure of rubber and elastomeric materials are described and discussed. Finally, in Sec. 4, conclusions are drawn.

2. Experimental Design

2.1. Experimental Philosophy and Strategy

The experimental design of the programme centred around the use of so-called "open-top chambers" or OTCs, which have been used widely in biological research into the effects of air pollutants on plants and trees (e.g. Fowler *et al.*, 1989). Basically, the chambers resemble large greenhouses with open tops within which controlled levels of pollutants are injected. These OTCs provided a means of accelerating exposure of materials to O_3 and are described in more detail in

Sec. 2.3. However, before exposing materials over the course of months in the OTCs, a screening exercise was undertaken to identify those materials that were more susceptible to O_3 by exposure in the laboratory to higher concentrations of O_3. This system is described in Sec. 2.2. Finally, materials were also exposed in the field at national monitoring network sites for O_3 to investigate the uniformity of effect (particularly on natural rubber) for the same dose but for slightly different "pollution climates". For example both urban and rural sites, characterized by different balances and concentrations of gaseous pollutants, were chosen.

2.2. The High Ozone Exposure Chambers

Accelerated tests were carried out at the Tun Abdul Razak Research Centre (TARRC). A nominal O_3 concentration of 500 ppb was maintained in a darkened aluminium lined test room operating at a temperature of 20–25°C and a relative humidity of 50–80%. O_3 levels were measured up to two times a week using electrochemical and ultraviolet (UV) methods. Tests at much higher concentrations of 5000 ppb O_3 were conducted in a commercial Hampden 603 O_3 cabinet operating at 25°C.

2.3. The Open-Top Chambers

The controlled exposure of materials to a range of O_3 concentrations was carried out in OTCs at the Centre for Ecology and Hydrology (CEH), Edinburgh (shown in Fig. 1). The octagonal glass-sided OTCs create a controlled environment in which conditions are close to those of the field. Impregnated charcoal filters remove the major pollutant gases, nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and O_3, from the air supplied to the chambers via ducted fan units. This large flow rate of air ($30\ m^3\ min^{-1}$) minimises the warming effect of the chamber to approximately +1°C relative to ambient. The horticultural 3 mm glass normally used was replaced in one of the chambers with UV transmitting glass (Sanalux) on the southeast to northwest facing panels for the "4× ambient +UV chamber". The chambers were fitted

Fig. 1. Open-top chamber facility at ITE, Edinburgh.

with detachable roofs to prevent any precipitation reaching the experimental material. All the paint panels and the rubber frames were mounted on a free-standing framework (Dexion) within the chambers. The rubber experiments were shaded from direct sunlight using horticultural green netting (50% shading).

Rather than injecting known amounts of O_3 in order to determine dose-response relationships, a system was devised to mimic the concentration fluctuations in the real environment by "tracking" the ambient concentrations and enhancing these concentrations in the chambers by 2× ambient, 4× ambient and 4× ambient +UV with one chamber assigned to each O_3 concentration. In addition, one chamber was run at ambient concentrations of O_3 as a control. The computer controlled system monitored the O_3 concentration in the ambient chamber, then adjusted the O_3 concentration to achieve the multiple of the measured ambient concentration, i.e. 2× and 4×.

After development of a computer controlled feedback system, and testing to ensure pre-defined target O_3 concentrations could be achieved, the system was commissioned.

O_3 was generated by electrical discharge in oxygen and fed via electronic mass flow controllers under computer control to the individual chambers. O_3 was injected into the filtered air flow, then into the OTC via a polyethylene manifold. The large air flow-rate produced effective mixing of the O_3 within the chamber.

Air was continuously pumped from each of the OTCs via a series of solenoid valves. Each chamber was individually sampled in rotation; during each 90-second sampling cycle a 45-second purging of the air was followed by a 45-second monitoring period during which the O_3 concentrations were recorded every 0.1 seconds and an average calculated.

The average O_3 concentration in each OTC was then compared to the appropriate multiple of the measured ambient concentration enabling the computer programme to calculate the required flow rate for the mass flow controller to track the pre-defined multiple concentration. O_3 concentrations were monitored using a Thermo Electron O_3 analyser (TECO 49C). The system included appropriate fail-safe controls that automatically stopped the programme if the O_3 analyser failed, in the event of power failure, and if the O_3 concentrations were outside the pre-set maximum and minimum concentrations.

3. Exposure of Rubber and Polymeric Materials to Ozone

3.1. Introduction

Rubbers having an unsaturated carbon-to-carbon main polymer chain are highly susceptible to O_3 degradation, so that scission across the double bond may easily take place. On stretched surfaces, this attack results in the formation of cracks, the density of which increases with the applied extension. The reaction is rapid with many general purpose diene rubbers and, without protection, surface cracks can become evident within even a few days exposure to atmospheric levels of O_3. The damage detracts from appearance and more seriously can reduce product service life through premature tearing, fatigue, loss of sealing stress and diminished impermeability.

O_3 attack is generally accepted as a major weakness of commodity elastomers such as natural rubber (NR) and its closest synthetic competitor, styrene-butadiene rubber (commonly known as SBR), but satisfactory protection can be provided by the addition of antiozonant materials or by blending with other rubbers having a higher inherent resistance to O_3 cracking. However, there are many applications, for example in healthcare, where antiozonants cannot be used and in these cases protection, often during storage, depends on suitable packaging of the product. Furthermore, an increasing number of applications, including many non-tyre automotive components, are now based largely on O_3-resistant rubbers in order to avoid the use of antiozonants and guarantee crack-free resistance, irrespective of the severity of exposure.

Work conducted at the TARRC and elsewhere has demonstrated that O_3 resistance can be defined in terms of two distinctive physical characteristics (Lake, 1970): the first is a threshold strain, typically around 5% in most unprotected rubbers, below which no cracking will occur irrespective of the O_3 concentration used; the second is that the rate of growth of an isolated crack above the threshold is constant with time and linearly dependent on the O_3 concentration. Antiozonant materials raise the threshold strain or reduce the rate of crack growth, or in some instances, both. These findings were obtained at O_3 concentrations considerably higher than those experienced in product service, not only to obtain results more quickly but also to ensure constant exposure conditions and to avoid interaction from other forms of environmental deterioration. Qualitative agreement has been found with ambient O_3 conditions but the relationship between crack growth and O_3 concentration has not been previously examined quantitatively at low and more typical severities, mainly because of the absence of test chambers able to function reliably at O_3 concentrations around ambient.

The principal objective of this part of the work was to assess the effect of controlled changes in O_3 concentration upon crack growth behaviour, the resistance of a range of antiozonant-protected rubbers and the behaviour of a small group of rubber products.

3.2. Test Materials

A series of rubber mixes of known composition were prepared at TARRC. All ingredients were based upon 100 parts by weight of raw rubber (phr). These were as follows:

Control compounds for crack growth measurements

The first compound examined (later known as Compound 2) was an unfilled (gum) natural rubber vulcanised to contain polymerised 2,2,4-trimethyl-1,2-dihydroquinoline as an antioxidant; this is not an antiozonant for NR but is necessary to guard against thermal oxidative degradation. The rubber also contained 5 phr of N330 type carbon black (an effective UV absorber) to reduce the risk of photo-oxidation. Compounds without antioxidant and with an alternative non-staining phenolic antioxidant (Compound 3) were also prepared.

Protected rubbers to assess efficacy of added antiozonant materials

Protection was conferred by a commonly used antiozonant, NN'-dioctyl-p-phenylenediamine (DOPD) added at 0, 1, 1.5, 2, 2.5, 3, 3.5 and 4 phr; the small increments were used to determine the level of protection needed for different O_3 concentrations. Three other compounds were prepared with a commonly used antiozonant system of N-1,3-dimethylbutyl-N'-p-phenylenediamine (6PPD) and a paraffin wax, in this case Sunproof Improved (Uniroyal). The level of wax was held at 2 phr and the level of 6PPD varied at 1, 2 and 3 phr. 6PPD is an example of a crack growth rate-reducing antiozonant that needs the additional assistance of a surface wax bloom to ensure static O_3 resistance, whereas DOPD is the best known antiozonant capable of enhancing threshold strain. The proprietary materials used were Santoflex 6PPD (Flexsys) and, for DOPD, UOP 88 (Universal Oil Products).

The base NR formulation, which in this instance contained 45 phr N330 black for reinforcement is representative of compound used in a wide range of applications, including tyre components, bearings and mountings, and belting covers. NR has been used as the base polymer because of its widespread use in these products but it is also representative of other ozone-susceptible elas-tomers in need of antiozonant protection, including SBR and polybutadiene.

Synthetic rubber

A chloroprene rubber (CR) formulation was examined because CR (an unsaturated rubber) has an inherent ozone resistance that is derived from a very low rate of crack growth (compared with NR or SBR). It can undergo cracking but is sufficiently resistant to be used in many outdoor applications calling for a measure of weathering resistance.

In one compound, 2 phr octylated diphenylamine was used as antioxidant. In the other, this was joined by 3 phr of a diaryl-p-phenylenediamine (Wingstay 100, Goodyear).

The base black-filled formulation, with suitable protection, is typical of CR compounds used in applications ranging from bearings to weather stripping.

NR/EPDM blends

Ethylene-propylene-diene copolymer (EPDM) is the leading example of a completely O_3-resistant rubber because of the absence of main chain unsaturation. Black-filled NR/EPDM blends were prepared and compared with unprotected NR and EPDM controls. EPDM and its blends are used in applications calling for O_3 resistance that does not depend on surface protection. Applications range from hose covers and tyre sidewalls to gaskets and seals.

All test mixes under (a) to (d) were moulded into standard 2 mm thick vulcanised sheets from which test pieces could be cut. The vulcanising conditions for all NR compounds were 40 minutes at 140°C in a steam-heated press. The conditions for CR were 30 minutes at 153°C.

3.3. Test Piece Evaluation

Test pieces were inspected at various intervals during exposure.

Crack lengths, within the surface and along the cut edges, were measured with a graticule having a resolution of 0.1 mm. An average was taken of five to ten crack lengths on both faces of test strips unless fewer cracks were involved. The mean of the two averages was only used where the two faces had similar crack appearances. Difficulties in measurement increase with crack size and crack density through interference and the merging of cracks, but by this time there should be sufficient crack growth to establish the rate of cracking.

Attempts were made to measure the depth of cracking because this is often more critical to the life of the product than crack length within the surface. It was found to be very difficult and necessarily involved destruction of the test pieces. Therefore, as an alternative, stress retention was measured on exposed dumb-bells. The cracked test pieces were stretched to a test extension of 100% and the stress measured after 1 minute relaxation. The stress, or relaxed modulus as it is commonly called, is a measure of the residual effective cross-section of the test piece and therefore falls as crack depth increases. Previous work had shown that the method is not suitable for test pieces having completely isolated cracks and therefore is best used for test pieces exposed at extensions above the threshold strain of the rubber, for example 10% in the case of the unprotected test compound. Tensile strength measurements are more sensitive to isolated cracks than stress retention but were not used here because several duplicate test pieces are necessary to allow for the higher inherent scatter of strength measurements.

For protected rubbers, time to first crack was determined by ×7 magnification with, where necessary, a distinction is made between surface and edge cracks.

A typical test frame for assessment of crack growth is shown in Fig. 2. Two test strips are held at 7.5% extension, one further dumb-bell is held at 10% extension (for modulus measurements) and another is held at 120% extension. The latter is used to measure the effect of any significant differences in air flow-rate over the rubber surface. At high extensions, the crack density is high and previous experience with pieces indoors has shown that the rapid consumption of O_3 may deplete the concentration of O_3 at the surface layer, such that crack growth rate falls unless the O_3 is replenished. Relaxed

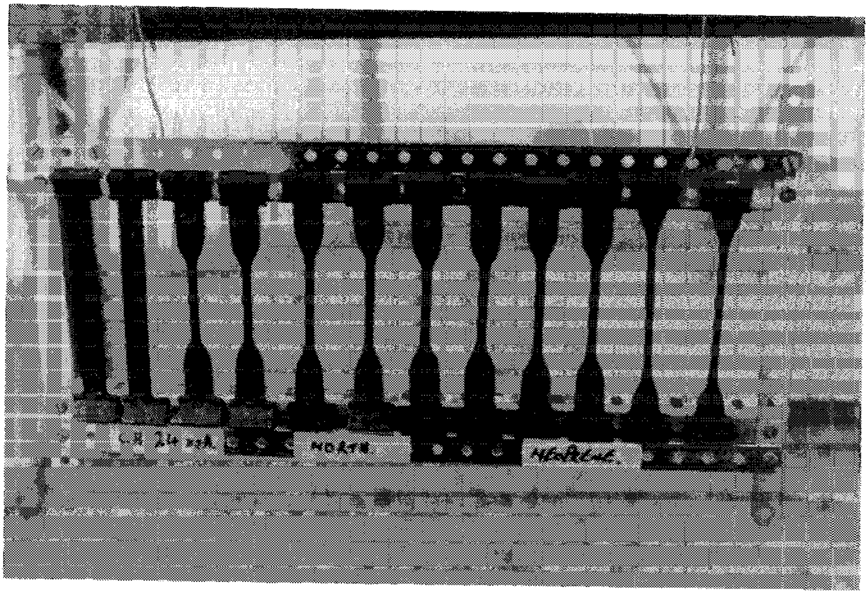

Fig. 2. Frame of rubber test strips (in this case neoprene from Expt. 4) at elongations of 20, 40 and 100%.

modulus measurements showed no discernible effect of flow rate on crack growth in the OTC exposures, as might be expected, where turbulent diffusion is large and the surface resistance (i.e. r_c) is not constrained in an overall deposition velocity term.

3.4. Results

Crack growth measurements

Crack size is not solely dependent upon O_3 concentration and time of exposure. Crack growth is most rapid just above the characteristic threshold strain; in this region only a few surface flaws are large enough to reach the tearing energy needed for crack initiation and therefore the resulting crack density is low, with much reduced chance of interference between neighbouring crack sites. Crack growth is also sustained because the rate of O_3 depletion in the air layer above the surface is much lower than it is when crack density is high (Lake, 1970). Exposure time is significant too because cracks will eventually merge irrespective of the crack density and some may be sufficiently long to rupture the test piece. O_3 cracking may also be affected by stress relaxation if the rubber is in the vicinity of the threshold strain. In addition, surface cracking can result from other forms of deterioration, including surface hardening or embrittlement, photo-oxidation and, in some elastomers, static fatigue. Furthermore, nonlinear crack growth behaviour has been found in some rubbers.

It is therefore important that the test rubbers and straining conditions used in the study are fully characterized, initially under accelerated laboratory conditions.

Figure 3 confirms that a linear relationship initially exists between crack length and exposure time. The test extension of 7.5% is just above the threshold strain of the main test rubber (compound 2), which is estimated to be between 3 to 5% extension. For the 10 mm wide strip used for most of the work, the linearity continues up to a crack length of 5 mm (i.e. half the width): thereafter the rate of growth decreases markedly because of crack interference. Crack density increases markedly above the threshold strain and interference reduces the maximum crack length for linearity.

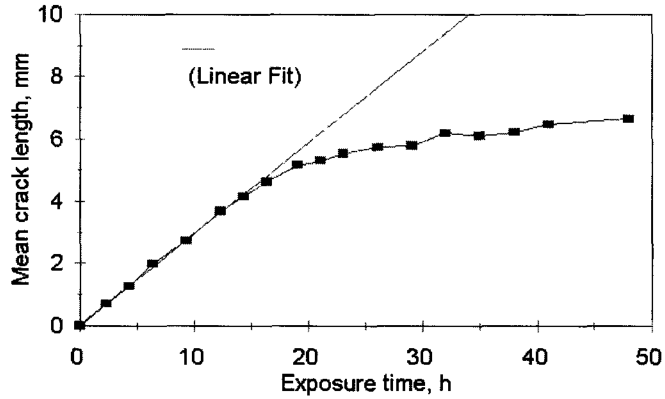

Fig. 3. Dependence of crack growth on exposure time (compound 2, 10 mm strip at 7.5% strain, 500 ppb O_3).

Exposure in the open-top chambers

Two series of tests were conducted in the four CEH OTCs. The first was primarily to assess consistency in crack growth at three positions within each chamber. This exercise demonstrated that there were no significant differences provided steps were taken to eliminate direct sunlight. The rates of crack growth in the chambers operating at ×2 and ×4 ambient O_3 concentration were also closely consistent with predictions from accelerated test measurements, clearly demonstrating that the linearity between crack growth and O_3 concentrations extended to near-ambient severities (Fig. 4).

The crack growth rate in the control chamber (No. 20) was lower than predicted and despite the presence of carbon black there was evidence of photo-oxidation, although other factors might also be involved in the extra time period needed for reasonable crack growth in this chamber. If surface modification or ageing had occurred in this instance, exposure of the returned test piece to an accelerated O_3 test might be expected to show differences with the behaviour of fresh test pieces. This is clearly the case in Fig. 4, with the crack growth rate of the previously exposed test piece (shown as "X" in the figure) only being a quarter of that of a new test piece.

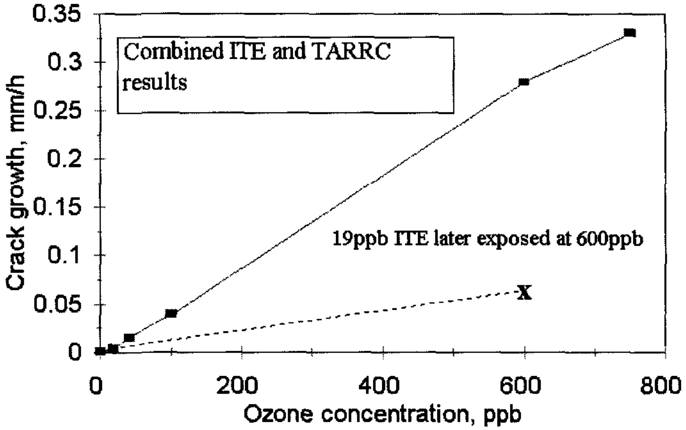

Fig. 4. Correlation between rate of crack growth and O_3 concentration up to 750 ppb (compound 2 at 7.5% strain, first series).

Better agreement among the four test chambers was found in the second series of tests, both for mean crack length (Fig. 5) and for relaxed modulus (Fig. 6); the latter figure showing combined results from the first series of exposures in the OTCs and from the TARRC O_3 room. The dependence of relaxed modulus on the product of O_3 concentration and time is also shown for compound 3 in Fig. 7. Light

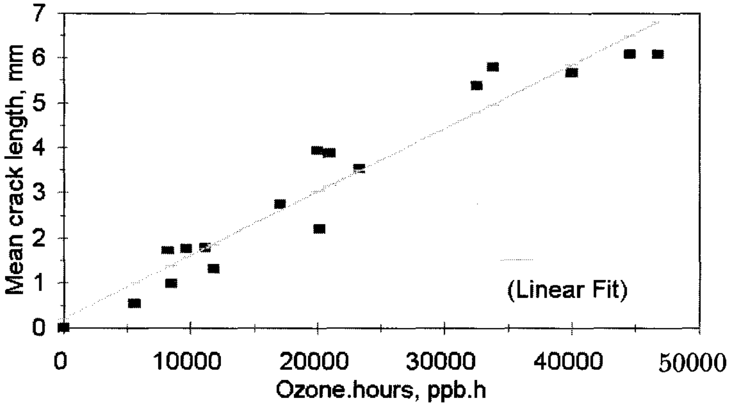

Fig. 5. Correlation between cracking and exposure in CEH (ITE) chambers. First series, compound 2 at 7.5% strain.

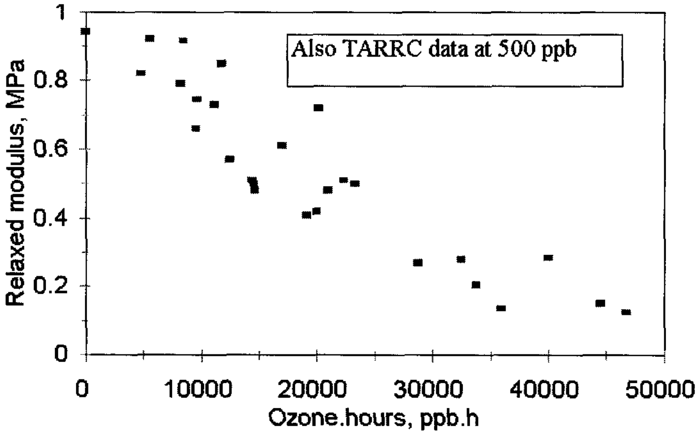

Fig. 6. Correlation between relaxed modulus and O_3 time product for CEH chambers (compound 2 exposed at 10% strain, first series).

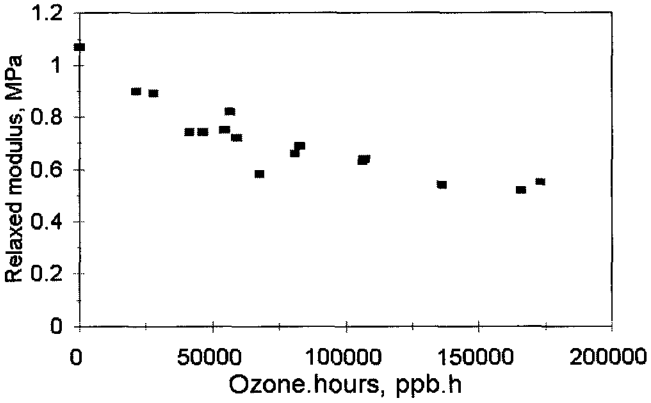

Fig. 7. Correlation between relaxed modulus and O_3 time product for CEH chambers (compound 3 exposed at 10% strain, first series of exposures).

ageing was not evident for compound 3 and the difference suggests that trimethyldihydroquinoline (TMQ) may be capable of promoting photo-oxidation despite the presence of a UV absorber.

Tests with protected and ozone-resistant rubbers

Antiozonant-protected vulcanizates

Test frames returned from CEH after up to a year's exposure in the test chambers were examined and compared with exposures of the same compounds at TARRC under higher O_3 concentrations. In terms of crack appearance, the outdoors exposure at TARRC was a good match with the more closely controlled exposure at ambient O_3 concentration in CEH's Chamber 20, indicating that the OTC is representative of normal environmental conditions.

Table 1 summarises how the severity of exposure affects antiozonant activity at 20% extension, a typical specification test strain. The results at 500 and 5000 ppb O_3 confirm previous findings that more antiozonant is required as the test O_3 concentration is raised. The CEH and other TARRC results support this trend and also confirm that the relationship is nonlinear. Even indoors at O_3 concentrations that are much less than those outdoors, 3 phr DOPD is required for protection

Table 1. Effect of O_3 concentration on antiozonant level for crack-free protection at 20% extension for one year.

Antiozonant (phr)	Indoors (office)	Outdoors at TARRC	CEH ×1 ambient	CEH ×2 ambient	CEH ×4 ambient	500 ppb at TARRC	5000 ppb at TARRC*
Control	X	X	X	X	X	X	X
DOPD 1	X	X	X	X	X	X	X
1.5	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X
2.5	X	X	X	X	X	X	X
3	X	–	–	X	X	X	X
3.5	–	–	–	–	–	X	X
4	–	–	–	–	–	–	X
6PPD, 1; wax, 2		–	–	–	–	–	X
6PPD, 2; wax, 2	–	–	–	–	–	–	X
6PPD, 3; wax, 2	–	–	–	–	–	–	X

*: Test terminated after 24 hours.
X: Cracked.
–: No cracking.

whereas only 4 phr becomes necessary for 500 ppb O_3 and less than 5 phr for 5000 ppb O_3 (Fig. 8). The difference between Chamber 20 and Chamber 24 (with its four-fold O_3 concentration) is equivalent to no more that 0.5 phr antiozonant. This is also apparent for the enhancement of threshold strain (Table 2).

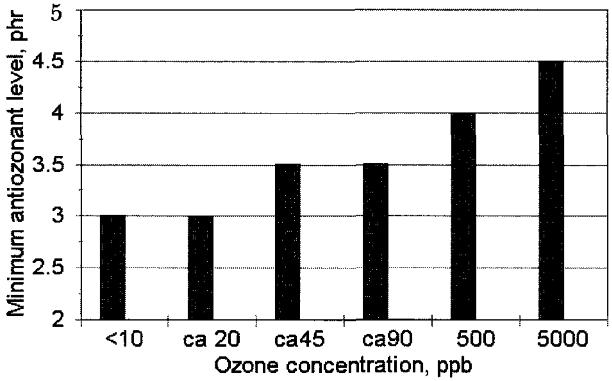

Fig. 8. Estimated level of DOPD antiozonant for crack-free protection at 20% strain for at least one year (combined CEH open-top chamber and TARRC results).

Table 2. Effect of O_3 concentration on estimated threshold strain of antiozonant protected natural rubber.

Antiozonant (phr)	Outdoors at TARRC	CEH ×1 ambient	CEH ×2 ambient	CEH ×4 ambient	500 ppb at TARRC
Control	5–10	5–10	5–10	5–10	5–10
DOPD 1	<10	<10	<10	<10	<10
1.5	<10	<10	<10	<10	<10
2	10–20	10–20	10–20	10	10
2.5	10–20	10–20	20	10–20	10
3	20–40	20–40	20	20	10–20
3.5	>40	>40	>40	40	20
4	>40	>40	>40	>40	20–30
6PPD, 1; wax, 2	>40	>40	>40	>40	10–20
6PPD, 2; wax, 2	>40	>40	>40	>40	20–30
6PPD, 3; wax, 2	>40	>40	>40	>40	30–40

Further tests were made on a reduced time scale in the CEH open-top chambers (Table 3). This second batch was included to assess the influence of the time of year in the efficiency of protection since it is known that antiozonant protection can be "conditioned" by prior exposure to a relatively low O_3 concentration (as might occur in Winter). However, the O_3 levels at the start of the two series of tests were about the same. Even so, the level of resistance was slightly lower during the second series and one likely contributing factor is the known loss in antiozonant activity during sample storage.

The 6PPD/wax protective system was effective at all three 6PPD levels in the first series of exposures. Wax blooms are less sensitive to comparatively small levels of O_3 than they are to changes in temperature, which in these tests were small with temperatures always below the solubility limit of Sunproof Improved.

Table 3. Estimates of antiozonant level for one year's crack-free protection of natural rubber.

Severity	DOPD (phr)
For 10% extension	
Indoors	2.5
Outdoors	3
60 ppb O_3	3
100 ppb O_3	3
500 ppb O_3	3
5000 ppb O_3	3.5
For 20% extension	
Indoors	3
Outdoors	3.5
60 ppb O_3	3.5
100 ppb O_3	3.5
500 ppb O_3	4
5000 ppb O_3	5
For 40% extension	
Outdoors	3.5
60 ppb O_3	3.5
100 ppb O_3	4

Chloroprene rubber

An initial exercise was to determine whether the crack growth of the unprotected CR compound was linearly related to the time of exposure. This was confirmed for a test extension of 10% at approximately 500 ppb O_3 (Fig. 9). The rate of crack growth determined at this concentration and a slightly higher one showed a linear dependence on O_3 concentration (Fig. 10). This plot indicates that at 100 ppb O_3 (the concentration region for Chamber 24 over the

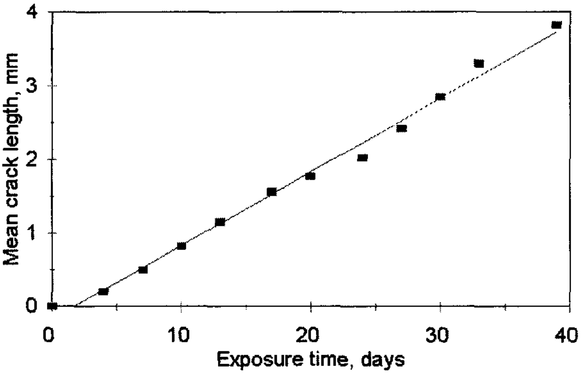

Fig. 9. Linear dependence of crack growth in chloroprene rubber (unprotected CR compound, 10% strain, 500 ppb O_3).

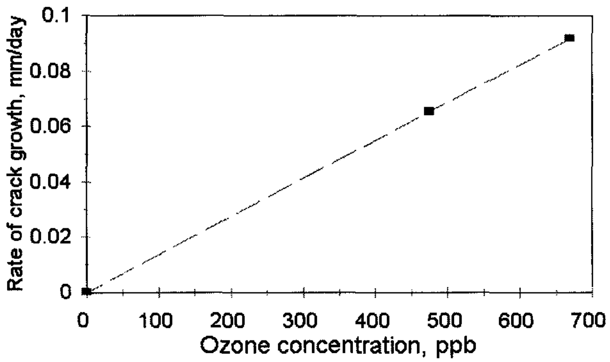

Fig. 10. Dependence of crack growth of chloroprene rubber on O_3 concentration (unprotected CR compound exposed at 10% strain).

year's exposure) the mean crack size should be at least 3 mm. Yet no cracks were detected on the test pieces returned to TARRC, with crack-free protection also being evident at 20% strain. Only at 40% extension did the CR compound suffer any serious cracking. This greater-than-predicted resistance suggests that the octylated diphenylamine antioxidant may be able to exert a small antiozonant effect at low severities and thus give rise to a nonlinear relationship. Assuming the linearity of crack growth with time is maintained, the results at 40% strain also suggest nonlinearity because the crack length in Chamber 24 is at least 20 times longer than in Chamber 20 and five times longer that in Chamber 23. An indication of a small antiozonant activity is a marked conditioning effect at low O_3 concentration. Test pieces exposed for a year outdoors at TARRC continued to show some resistance when inserted in the O_3 room at 500 ppb, a reduction being seen in both the rate of cracking and more significantly in the density of cracks.

The fully protected CR compound was completely resistant at all O_3 concentrations examined (including 5000 ppb).

NR/EPDM blends

None of the NR/EPDM compounds underwent any cracking in the CEH and TARRC tests. Resistance was even found at 100% extension after several months at 500 ppb O_3.

4. Conclusions on the Exposure of Rubber and Polymeric Materials to Ozone

(1) The rate of crack growth of unprotected natural rubber, measured in terms of crack length, is directly proportional to O_3 concentration at the severities used in the CEH test chambers, i.e. between ambient and four times ambient. The increase in crack length is also linearly related to the time of exposure until crack interference occurs. These findings confirm earlier work conducted at very much higher O_3 concentrations far removed from those experienced around rubber products. The results for crack length and for relaxed modulus or stress (as a measure of crack depth)

can be plotted as a function of the product of O_3 concentration and time; this parameter is therefore a convenient means of expressing severity and may be a suitable basis for a dose-response function. These tests are the first to be undertaken at conditions much closer to ambient O_3 concentrations and show that the linear relationships found at very much higher concentrations still apply at close to ambient conditions of O_3.

(2) A more complex relationship exists between resistance and O_3 concentration for fully or partially protected rubbers, a consequence of the separate activity of antiozonants and the ability of some of these to enhance the threshold strain for crack initiation. A significant level of antiozonant is needed even for the very low O_3 concentrations found indoors, but only a relatively small increase is required for protection at outdoor concentration. In terms of crack-free protection for at least one year, the difference between the three O_3 conditions in the OTCs is equivalent to about 0.5 phr of DOPD antiozonant.

(3) There is evidence that the proportionality between crack growth and O_3 concentration extends to unprotected rubber products but resistance is also strongly influenced by packaging, variations in strains and the risk of photo-oxidation in light coloured surfaces. If light ageing is evident, any increase in O_3 concentration will be proportionately more severe than predicted since crack growth can occur before photo-oxidation ensues. Similar conclusions might apply to a rubber that may become more resistant to O_3 cracking simply through stress relaxation.

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CHAPTER 10

THE SOILING OF BUILDINGS BY AIR POLLUTION

J. Watt and R. Hamilton

1. Introduction

When Blake wrote of "dark, satanic mills", he evoked a widespread perception of an industrial cause and effect — buildings blackened by atmospheric pollution due in large part to industrialisation. The "green and pleasant land", in contrast, is mostly associated with an equally strong impression of a clean rural environment. Britain's early industrialisation and development of urban manufacturing centres meant that atmospheric pollution had reached a level that was noticed by contemporary scientists by as early as the second half of the 19th century (Camuffo, 1992). These effects persisted or intensified for the next hundred years, until the 1950s, when a series of intense London smogs galvanised Parliament into producing a series of Clean Air Acts, though by this time the frequency of London fogs had decreased significantly from the numbers reported in Victorian times (Brimblecombe, 1987). The acts ended the burning of coal in homes and factories in most large towns and cities, with a switch to electric power produced in large rural power stations, together with greater use of oil and gas burners, which were much cleaner.

In the years that followed, many buildings and cities were cleaned and a wide variety of colours and textures have re-emerged from under the layers of blackness. Yet it has become apparent that in spite of the huge reduction in smoke resulting from the prohibitions placed on burning coal in cities, for both domestic and industrial purposes, buildings are continuing to become dirty. The massive reductions in the levels of suspended particulate material and sulphate clearly do not contain the whole story. Other mechanisms, especially the role of traffic pollution, must now be investigated. This chapter reviews the work undertaken to date. It looks at experimental and theoretical approaches to estimating the rate of soiling for a number of materials, at the trends in air quality and at their implications for the future, including economic and cultural factors.

Soiling is a visual nuisance resulting from the darkening of exposed surfaces by deposition of atmospheric particles. The size of this nuisance depends strongly on the perception of the individual and on the general conditions of the local environment. Generally, people are much more sensitive to the soiling effect in relatively clean environments than in areas with large dust loads, such as in industrial regions.

To give this nuisance a more objective character, the Workshop on Research Strategies to Study the Soiling of Buildings and Materials (Haynie and Spence, 1984) defined soiling as:

> *A degradation that can be undone by cleaning, washing and painting and that can be measured as the reflectance contrast of a surface with deposited particles by comparison to the reflectance of the base substrate.*

Soiling results mainly from the deposition of atmospheric particles and may be caused by both natural and anthropogenic mechanisms. Increased frequency of cleaning, washing, or repainting of soiled surfaces becomes a considerable economic cost and can reduce the useful life of the soiled material. By requiring surface degradation, the above definition would exclude deposited ambient dust, which although a major cause of complaint due to its high visibility, does not produce a permanent effect. It is caused in general by coarse particles, which deposit by gravitational settling, most efficiently on horizontal surfaces. These particles do not travel far and are relatively easily removed by wind and rain. Various methods exist to quantify dustfall, such as BS Dust gauges and glass-slide soiling (Brooks and Schwar, 1987; Moorcroft and Laxen, 1990; Vallack and Shillito, 1998), and there is perhaps some overlap with studies of soiled horizontal surfaces. Terrat and Joumard (1990) showed that a simple plate method (a measurement of the number of particles deposited on a flat plate of inert material), as well as the measurement of reflectance and transmission of light, were capable of quantifying soiling deposit in a town. These simple plates would seem to be more suitable for areas with high particle pollution and the optical methods may be more suitable for less polluted areas. Martin and Souprounovich, (1986) reported an exposure study to examine the soiling of building materials in Melbourne, Australia. They used reflectance measurements on a range of materials exposed both horizontally and vertically and attempted to address the difference between what has been defined as dustiness and soiling by making two measurements, before and after removal of loose grime with a brush and water. There was no attempt to derive a soiling rate, however and particle composition was not determined (apart from a determination of % solubles).

There have been a number of interesting recent papers that have examined the sources and effect of coarse particles within museums (Brimblecombe *et al.*, 1999; Yoon and Brimblecombe, 2000). These have shown that many particles emanate from visitors to the museums, often brought in by clothing and shoes and re-suspended within the museum. The role of this material in damaging the collections housed within the galleries are not well understood but would seem to be largely analagous to the nuisance dusts described in this section and they have therefore been excluded from the soiling discussions.

2. Soiling and Material Damage

The separation of soiling from other atmospheric damage to buildings and materials is, to some extent, artificial. There is a considerable amount of available information that supports the fact that exposure to acid-forming aerosols has been found to limit the life expectancy of paints by causing discolouration, loss of gloss, and loss of thickness of the paint film layer. Various building stones and cement products are known to be damaged from exposure to acid-forming aerosols.

However, it should be noted that the extent of the damage to building stones and cement products produced by pollution, beyond that expected as part of the natural weathering process, is uncertain. Some investigators have suggested that the damage attributed to acid-forming pollutants is over-estimated and that stone damage is predominantly associated with relative humidity, temperature, and, only to a lesser degree, air pollution. One area in which stone damage and soiling do overlap considerably is the formation of black crusts, especially on limestone and sandstone buildings (DelMonte *et al.*, 1981). These encrustations often develop in urban stone structures in areas protected from rainfall. They have been shown to be combinations of carbon and gypsum, the latter believed to be formed by interaction with the parent building stone. The consequent roughening of the surface has been postulated to increase soot deposition (Camuffo, *et al.*, 1983). These crusts are therefore a considerable part of the blackening of many buildings, and yet they are also very destructive since they eventually spall off and destroy the surface of the stone.

There is in practice no real boundary between decay and soiling, although the study of the various effects of air pollution has often had to be separated for analytical convenience. Black crusts may therefore be considered to form an area of study on their own and are excluded from the study of soiling mechanisms discussed in this chapter, which relates to processes that take place on flat, non-reactive surfaces. Here the reflectance of the surface is related to the reflectance of the deposited particles and the fraction of the surface covered by particles. One model also considers the depth of cover.

Attempts have been made to calculate damage functions for the erosion of buildings (Lipfert, 1989) but these do not include the effects of spalling black crusts as they are based on calculation of steady-state loss mechanisms from various materials and erosion regimes.

One other area of potential overlap between soiling and building damage concerns conservation practice (Torraca, 1988.) Cleaning is the first step in conservation of stone surfaces and it is vital to the success or failure of the whole process. Stone fabric may often be in poor condition due to lack of proper maintenance in previous years and rapid mechanical cleaning, for example by sand blasting, may exacerbate the damage by increasing the number of cracks and introducing salts into fissured and porous surfaces. Specialised cleaning techniques, though more expensive, should be used to reduce this damage.

3. The Nature of Atmospheric Particles

The major contribution to all processes of soiling of buildings is the deposition of particulate matter. In contrast to individual gaseous pollutants, which are considered in other chapters, particles are not single, well-defined substances but are a complex mixture arising from a large number of sources. This is not the place to attempt to review the enormous literature that already exists in the field but it is necessary to discuss the major characteristics of particulate pollution as it affects the soiling of buildings. The major influences on soiling processes are determined by the size and chemistry of the particulate matter, which are largely determined by its source. Techniques to measure particle concentration and to estimate the source contributions are briefly discussed, with special reference to carbonaceous particles because of their importance to soiling.

There is no single comprehensive method of characterisation of airborne particles, which can be assessed by many methods which determine one or more characteristic. It is unlikely that there will ever be a single comprehensive study of airborne particulate pollution, which completely measures their number, size distribution, morphology and composition, thus making it difficult to accurately quantify the impacts of particulate air pollution. There is still great uncertainty in the assessment of background concentrations of particles, and spatial and temporal patterns of concentration are not well understood.

In spite of these difficulties, there are some broad classifications that can be made in terms of size, which are also helpful when considering the origin and fate of airborne particulate material. Three groups of particles (sometimes called "modes") have been defined.

The *nucleation mode*, the group with the smallest particle size, consists of ions and nuclei (often of the dimensions of molecular clusters), and the particles into which they grow as a consequence of the condensation of vapours upon them. Particles arising from gas to particle conversion (e.g. sulphuric acid droplets from the oxidation of sulphur dioxide) are initially formed by condensation onto a nucleus. The size range of particles in this mode extends from that of molecular clusters — say, 0.001 μm in diameter — to about 0.1 μm. Condensation nuclei are usually present in very large number concentrations in urban atmospheres, but because of their small size they make a relatively small contribution to the total mass concentration.

The *accumulation mode* consists of particles which have grown from the nucleation mode by further condensation of vapours upon them or by coagulation. Their size range is usually taken to be from about 0.1 μm to about 1 μm. They are relatively persistent, since the processes which remove particles from the atmosphere (e.g. diffusion, washout and sedimentation) are least efficient for particles in this size range.

The *coarse* mode consists of particles greater than about 1 μm in diameter. Many of them originate from mechanical processes such as erosion, re-suspension and sea spray. Soil dust and most industrial dusts come within this category, as do pollens, mould spores and some bacterial cells.

The *fine particle mode* is a term used to indicate the combined nucleation and accumulation modes.

The composition of particulate matter is dependent on source, chemical transformations in the atmosphere, long-range transport effects and removal processes. Measurements tend to be of average concentrations, which may conceal important extreme or episodic events. Diurnal and seasonal trends may be apparent but a great deal of research remains to be undertaken before a complete understanding is achieved.

3.1. Primary Particulate Matter

Primary particulate material, including anthropogenic emissions (especially significant in the current context), is emitted directly to the atmosphere from a source. The major sources of primary particulate material are:

- Petrol and diesel vehicles, the latter being the source of most black smoke.
- Controlled emissions from chimney stacks.
- Fugitive emissions. These are diverse and uncontrolled, and include the re-suspension of soil by wind and mechanical disturbance; the re-suspension of surface dust from roads and urban surfaces by wind, vehicle movements, and other local air disturbance; and emissions from activities such as quarrying, road and building, construction, and the loading and unloading of dusty materials.

Emission inventories have been developed and are a useful technique in the assessment of the relative contributions of specific sources to the overall particulate load. Most useful in estimating anthropogenic emissions of particulate material, emission inventories provide an indication of trends in emissions and the proportional importance of activities that result in particulate release. Black carbon is very important in the context of soiling of buildings and is almost entirely emitted by vehicles (Hamilton and Mansfield, 1991).

3.2. Secondary Particulate Matter

Secondary particles result from the reaction of two gases or vapours, forming a substance that condenses onto a nucleus. The major sources are the atmospheric oxidation of sulphur dioxide droplets to sulphuric acid, and the oxidation of nitrogen dioxide vapour to nitric acid. Hydrochloric acid vapour (refuse incineration and coal combustion are major sources) is also present in the atmosphere, and both this and nitric acid vapour react reversibly with ammonia (largely associated with agricultural sources) to form ammonium salts (Allen *et al.*, 1989). Sulphuric acid reacts irreversibly in two stages to form either ammonium hydrogen sulphate or ammonium sulphate. Such ammonium salts are formed continuously by the oxidation of sulphur and nitrogen dioxide, whenever there is sufficient ammonia for neutralisation. They are therefore part of a large-scale pollution phenomenon affecting both urban and rural areas. Most of the accumulation mode particles in the United Kingdom atmosphere consist of ammonium salts.

3.3. Particle Mass Concentrations

A number of techniques have been used to measure particle mass concentration and the soiling experiments described below have related to several of them:

- Black smoke is associated with the smoke stain technique (BSI 1747 Part 11, 1993) developed in the 1960s.
- Total suspended particulate (TSP) or suspended particulate matter (SPM) describes all airborne particles. TSP is determined gravimetrically using a high-volume sampler and is expressed as $\mu g/m^3$.
- PM_{10} defines the fraction of particulate matter which passes through a selective inlet of specific size with a 50% cut-off at 10 μm aerodynamic diameter [10 μm is therefore the mass median aerodynamic diameter (MMAD)]. $PM_{2.5}$ has a MMAD of 2.5 μm.

The black smoke method has been the longest established particle measurement technique in the U.K. The reflectance of the stain produced by air drawn through a white filter paper is measured using a reflectometer. A standard calibration curve is used to convert the reflectometer measurement into a nominal mass concentration of the airborne particles (known as the "black smoke concentration"). The method is cheap and simple, but it has a number of disadvantages, the worst of which is that the standard calibration curve was established for particulate material of the type that existed in U.K. urban areas up to the early 1960s. The validity of the results depends upon the fraction of carbonaceous (i.e. black) material in the sample, which is now very different (Muir and Laxen, 1995; Muir and Laxen, 1996; Horvath, 1996). The amount of particulate elemental carbon (PEC), which is emitted at proportionally different concentrations from different sources (Hamilton and Mansfield 1991), has changed dramatically. Indeed, the proportion of each component has changed with time, with diesel vehicles becoming the main contributors of PEC in cities that have controlled domestic and industrial emissions from coal. Figure 1 shows that the contribution of coal to urban smoke in the U.K. has decreased substantially since the introduction of smoke-free zones in the Clean Air Act (1956), and diesel emissions have greatly increased in significance. Despite this, the Black

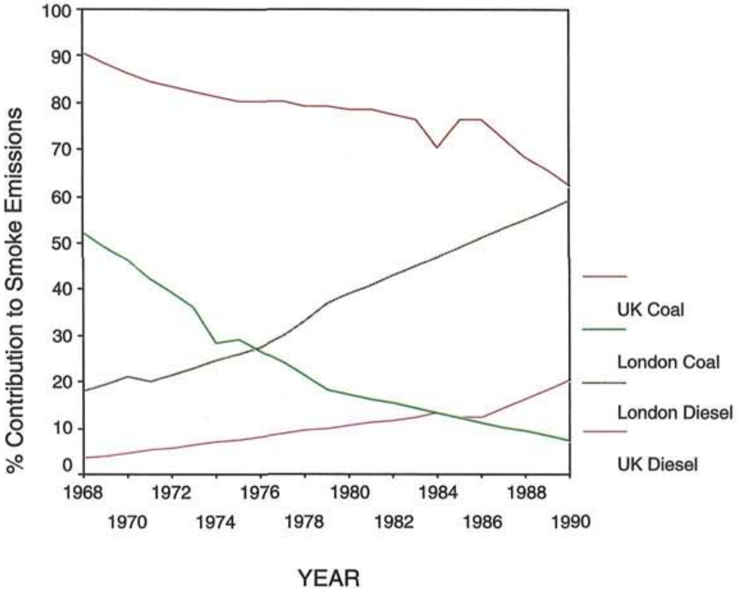

Fig. 1. Contributions of coal and diesel fuel to smoke in the U.K. (Kendall *et al.*, 1994).

Smoke method is currently being used at 222 sites in the U.K. (Broughton *et al.*, 1998) to provide a long-term dataset. There have been attempts to re-calibrate the Black Smoke results to the modern aerosol (Muir and Laxen, 1995; Muir and Laxen, 1996; Horvath, 1996). The greater blackness of the current aerosol is, of course, one of the factors that is contributing to the continued soiling of buildings.

Measurements of TSP or SPM have succeeded and/or complemented the measurement of black smoke. The most widely used method collects particles using a high-volume sampler onto a preweighed glass fibre filter for gravimetric analysis in the laboratory. Variable characteristics of the sampler inlet and variable collection efficiencies of larger particles in different wind speeds and conditions have led to the development of a number of further methods of mass determination.

- Dichotomous samplers, which separate the fine and coarse fractions, are used in the United States.

- In 1992, the U.K. Automated Urban Network (AUN) started to use tapered element oscillating microbalance (TEOM) instruments to provide a continuous reading of PM_{10} (using a pre-heating to 50°C, which influences some of the particles captured).

The relationship between these different measures of particle mass is not straightforward, since the situation is complicated by the changing nature of the particulate pollution. PM_{10} mass concentrations are higher than those of black smoke at co-located AUN sites, and remain seasonally variable and highly site-specific. Measured particle mass concentrations are also dependent on the measuring technique employed. Results from different samplers operating simultaneously or under different conditions do not always agree even where they are nominally capturing the same particles.

3.4. Chemical Composition of Particles

Airborne particles comprise three main categories of compounds:

- Insoluble minerals or crustal material,
- Hygroscopic inorganic salts, and
- Carbonaceous material.

Background particulate concentrations are strongly dependent on the local geology and soil type, distance from the sea, amount and type of vegetation cover, season and local weather conditions.

It is possible to make some general statements about the classification of the type of aerosol being considered, e.g. urban, rural or marine, which contain common chemical components at relatively similar concentrations. The UK Quality of Urban Air Review Group produced an estimate of the typical urban airborne particulate matter composition which synthesised the analytical work available at that time for the U.K., shown in Fig. 2 (Quality of Urban Air Review Group, 1993).

3.5. Carbonaceous Compounds

Carbonaceous matter represents approximately 40% of total particulate matter and represents at least half of the fine fraction. There are

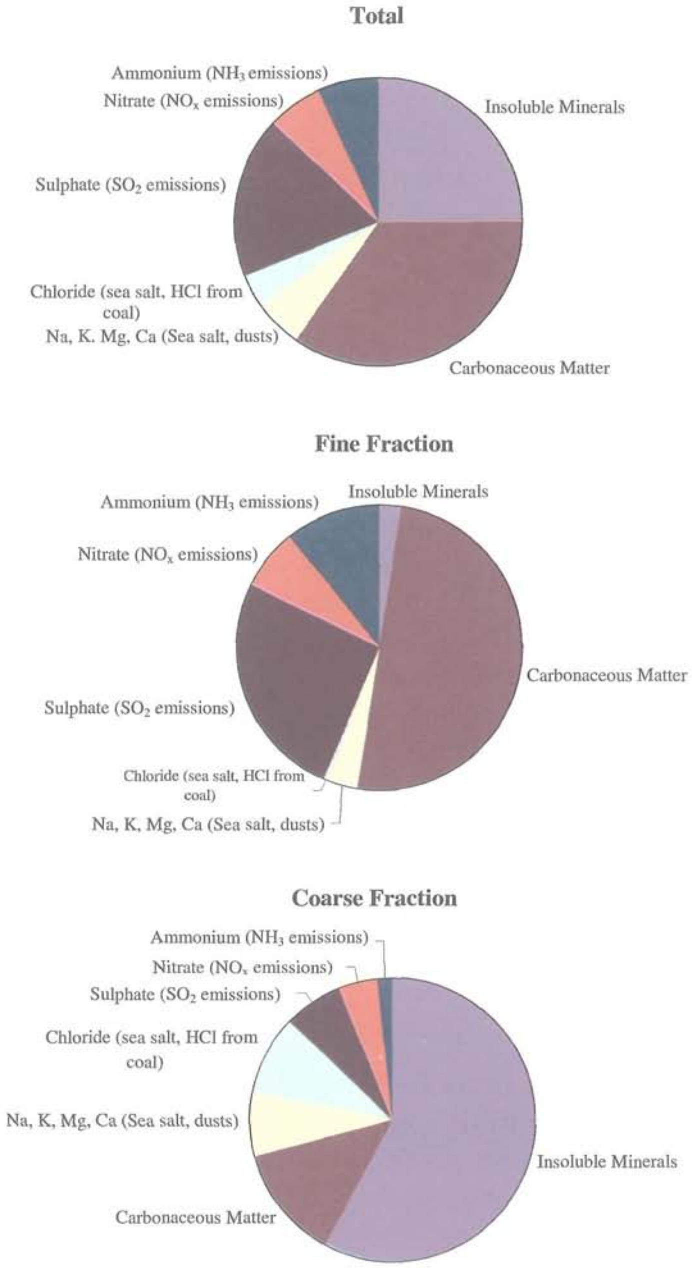

Fig. 2. Typical composition of fine and coarse fractions of particulate matter in the U.K. (Quality of Urban Air Review Group, 1993).

three forms in which carbon compounds are found in particulate matter:

- Carbonate
- Organic carbon
- Particulate elemental carbon (PEC).

Carbonate constitutes approximately 5% of the total mass of particulate, mainly in the coarse mode, and is mainly comprised of soil-derived minerals, construction material and re-suspended dust.

Elemental carbon

Particulate elemental carbon (PEC) is the black component of smoke responsible for soiling of materials and the absorption of light. Light absorption by particles is almost exclusively caused by PEC (Horvath, 1993) and is the most influential factor in the measurement of smoke concentration using the black smoke reflectance method. PEC also has strong adsorptive properties due to its large surface area and the availability of one extra valence electron per exposed carbon atom at particle surfaces. Elemental carbon provides an effective catalytic site for atmospheric reactions such as the formation of sulphuric and nitric acids and acts as a carrier for condensed vapours. PEC measurements taken in the U.K. indicate levels of ~6% in Leeds (Clarke *et al.*, 1984) and ~3% in Birmingham (Harrison, and Jones, 1995). It mainly derives from vehicle emissions, especially diesel combustion (Hamilton, and Mansfield, 1991).

Organic carbon

Organic carbon constitutes 60–80% of the total particulate carbon. A large number of organic compounds have been detected in urban particles. These may be divided into two major source groups — primary condensates and oxidised hydrocarbons. Primary condensates — alkanes (C17–C36), alkenes, aromatics and polyaromatics — originate directly from the incomplete combustion of fossil fuels and are adsorbed onto the surface of particulate matter. Oxidised hydrocarbons may either be attached to the particles as primary condensates or may be produced as the result of atmospheric oxidation reactions. Such compound groups include acids, aldehydes, ketones, quinones, esters, phenols, dioxins or dibenzofurans. These compounds may have an important role in source apportionment of inputs of carbon to soiled layers and black crusts on the built environment and they may also be important in increasing adhesiveness of particles once deposited. As far as direct measurement of soiling is concerned, however, it is the light absorption of elemental carbon that is most important (Hamilton, and Mansfield, 1991).

Source contributions to atmospheric fine carbon particle concentrations

Carbon particles in the atmosphere may be derived from more than 70 different air pollution source types (Gray and Cass, 1998; Hamilton and Mansfield, 1991). The main sources arise from the burning of fossil fuels, with additional contributions from contemporary carbon particles from woodsmoke, cooking and even cigarettes. There are also carbon components in some fugitive emissions such as tyre and brake dusts. Gray and Cass (1998) developed a Lagrangian particle-in-cell air quality model to predict primary carbon particle concentrations over long periods of time. An extensive inventory of fine particle carbon emissions was assembled for the Los Angeles area, which is summarised in Table 1. The air quality model was used to determine source class contributions to both fine primary total carbon and fine elemental carbon concentrations at seven receptor (air monitoring site) locations. It was found that diesel engine applications, including both highway and non-highway applications, dominated black elemental carbon particle concentrations at most monitoring sites. Proportions varied with location.

Miguel *et al.* (1998) confirmed the importance of heavy-duty diesel vehicles to the production of black carbon aerosol. They measured polyaromatic hydrocarbon (PAH) and black carbon emissions in the Caldecott tunnel in the San Francisco Bay Area, making comparisons between different bores of the tunnel, which permitted mixed traffic or light vehicles only. The black carbon measurements in the truck-influenced bore were about five times greater than those found in the tunnel that had only light vehicles, despite the latter

Table 1. Fine particle (< 2.1 micron) carbon emissions in central portion of California coast air basin surrounding Los Angeles, 1982.

Source type	% Total carbon	% Elemental carbon
Mobile sources		
Petrol powered vehicles	13	11
Diesels : Highway	19	49
: Ships, rail, etc.	7	18
: Aircraft and others	1	3
Fugitive sources		
Tyre and brake wear, paved road dust	21	7
Fugitive combustion	24	5
Stationary sources		
Fuel combustion	4	3
Industrial sources		
Point sources	11	4

Source: From Grey and Cass (1998).

having higher traffic volumes. Calculations of emission rates gave values of 30 ± 2 mg/kg of fuel burned for light vehicles and 1440 ± 160 mg for heavy-duty diesel vehicles.

3.6. Particle Deposition

There are many processes by which air pollution is transported to the surface, which can be gathered together into wet and dry deposition, with the former being processes of scavenging by cloud and rainwater. Dry deposition, which occurs by adherence or physical absorption of the pollutant to the surface, is most important for soiling. The term is somewhat misleading since humidity and surface moisture are important controlling mechanisms, including deposition from fog and mist. Water also has an important role in the removal of particles from surfaces.

Dry deposition is a term that includes a number of processes by which particles and gases transfer to surfaces by impaction, sedimentation and Brownian motion. Air is rapidly mixed by turbulent motions generated by the friction of the wind at the surface ensuring roughly uniform particle concentrations throughout this layer, except for a millimetre or so layer immediately adjacent to the surface within which air movements are retarded (the boundary layer). Particles deposit from this layer by a combination of gravitational settling, Brownian diffusion, interception and impaction. Brownian motion is the erratic movement observed in small particle suspensions resulting from the variations in the number and directions of impacts of air molecules on the surface of the particles. The smallest particles show the greatest response to molecular impacts, and the effects decrease with increasing particle size. This phenomenon causes the slow dispersion of particles in still air and increases collisions of particles with each other and with surfaces.

3.7. Deposition Velocities

The flux density of particles deposited on a surface depends on the concentration of the particles in the air and on the deposition velocity. Deposition velocity can be defined as the net velocity with which the particles move to the surface, i.e. the ratio of the flux density of particles depositing per unit time and area, and the number of particles per unit volume in the airborne state.

The size of the soot particles in an urban environment is determined by their sources, which are mainly combustion and automobile exhaust. In both cases, the main fraction (> 80%) of the particles is in the diameter range between 0.05 and 0.5 μm. In this size range, both the velocity under the influence of gravity and the inertia of the particles is sufficiently small that the particles reach the surface by diffusion due to Brownian motion, since sedimentation and impaction are unimportant as deposition mechanisms. The deposition depends on the gradient of the particle concentration in the vicinity of the surface, which varies with the thickness of the surface layer (which depends on the flow characteristics around the surface).

Deposition velocities have been determined by different authors (Milford and Davidson, 1985; Vawda *et al.*, 1989; Nicholson, 1988; Crump and Seinfeld, 1981); values differ by up to an order of magnitude, which may depend on the assumed flow conditions and

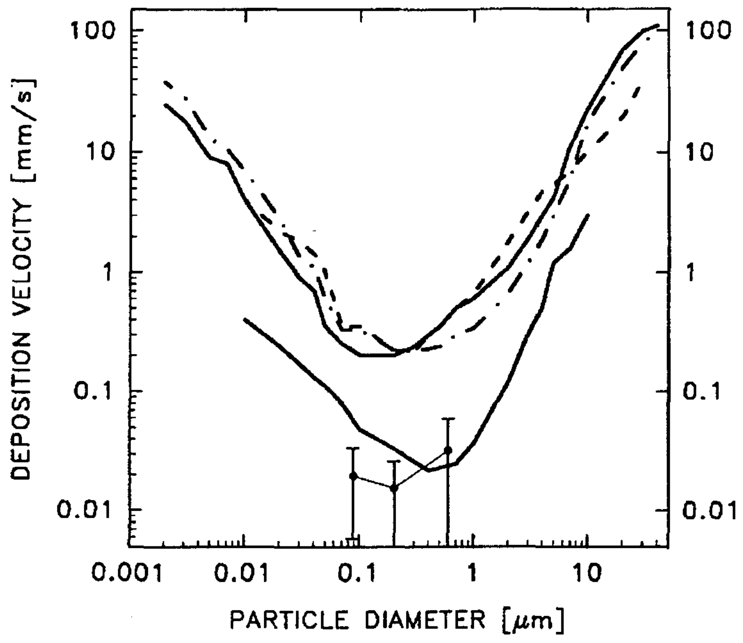

Fig. 3. Deposition velocities for particles of various sizes.

the laminar surface layer thus formed. As examples, two sets of curves obtained by theoretical considerations by different authors are presented in Fig. 3. The upper set of curves is obtained for a model of a very structured surface (grass), the lower for a fairly flat surface. The difference between the two is an order of magnitude for the size range between 0.05 and 0.5 μm particle diameter.

The upper set of curves is taken from Milford and Davidson (1985), the lower set of curves is taken from Hollander and Pohlmann (1991). The data points with the error bars were determined experimentally by Horvath *et al.* (1996) (see below) for deposition to building surfaces.

4. Soiling Models

Soiling is produced by deposition of particulate material onto a surface over a period of time. The rate at which soiling occurs depends on the deposition velocity together with the colour and chemistry of the particles. The nature (especially roughness) and orientation of the receptor surface remains important. All of these factors combine to produce a very site-specific set of deposition and removal processes (re-suspension, washout). A number of field studies have provided data describing the rate at which the soiling process occurs in a given situation. Some of these studies have attempted to clarify the nature of the particles retained on the deposition surface by subjecting the surface to physical and/or chemical analysis, particularly by electron microscopy. By their very nature, these field studies are capable only of describing the soiling process at the location and time at which the studies occurred; a deeper theoretical understanding is required if the results are to be generalised to other sites and other times. This is particularly important if the effect of predicted trends and scenarios for airborne particulate emissions and concentrations is to be evaluated in terms of the consequence for soiling. Two types of model have been produced — empirical models in which the soiling rate is deduced from examination of the relationships produced by a series of measurements (of dose/response over time) and theoretical/physical models derived from consideration of the underlying processes.

4.1. Field Studies

The earliest field studies were largely descriptive. Parker (1955) reported the occurrence of black specks on the newly painted surface of a building in an industrial area. The black specks were not only aesthetically unappealing, but also physically damaged the painted surface. Depending on the particle concentration, the building required repainting every two to three years. Spence and Haynie (1972) published data on the effects of particles on the painted exterior surfaces of homes in Steubenville and Uniontown, OH, Suitland and Rockville, MD, and Fairfax, VA. There was a direct correlation between the ambient concentration of particulate matter in the city and the number of years between repainting. The average repainting time for homes in Steubenville, where particulate matter concentrations averaged 235 $\mu g/m^3$, was approximately one year. In the less polluted city, Fairfax where the particulate matter concentrations only reached 60 $\mu g/m^3$ (arithmetic means), the time between repainting was four years.

The first attempt to produce a general dose-response relationship for particles was produced by Beloin and Haynie (1975) of the U.S. Environmental Protection Agency. They introduced the idea that soiling could be measured using the contrast in reflectance of a soiled surface to the reflectance of a bare substrate. Six different types of material (painted cedar siding, concrete block, brick, limestone, asphalt shingles, and window glass) were monitored over a two-year period at five sites with TSP concentrations ranging between 60 and 250 $\mu g/m^3$. The five locations included rural, urban, industrial and mixed-use areas. The effects of direction of exposure, use of preservative to prevent mildew on painted surfaces and sealant on concrete, brick and limestone were also tested. Rainfall, temperature and dewfall were not different between the sites at the 0.05 probability level. One site had higher relative humidity, which led to some problems with mildew formation. Analysis of variance of each of the controlled sources of variability (location, exposure time, exposure direction, paint preservative, surface film and colour) and the interactions between them, revealed that location and months of exposure were significant for all materials. The interaction between these sources of variance was significant for all materials except glass. Some effects of the other sources were seen and discussed. The correlation index (R^2) values for the totalled effects of location, time and the interaction between them were highest for unsheltered acrylic emulsion paint (0.972) and white asphalt shingles (0.903).

The results were expressed as regression functions of reflectance loss (soiling) directly proportional to the square root of the dose. These relationships took the form:

$$\begin{aligned}\Delta R &= A + B\sqrt{C_{TSP}t} \\ &= A + K\sqrt{t} \qquad (1)\end{aligned}$$

where ΔR = change in reflectance

C_{TSP} = concentration of total suspended particulate

A, B and K were constants obtained by best-fitting the data to the equation.

Haynie and Lemmons (1990) conducted a soiling study at an air monitoring site in a relatively rural environment in Research

Triangle Park, NC. The study was designed to determine how various environmental factors contribute to the rate of soiling of white painted surfaces. White painted surfaces are highly sensitive to soiling by dark particles and represent a large fraction of all man-made surfaces exposed to the environment. Hourly rainfall and wind speed data, weekly data from dichotomous sampler measurements and TSP concentrations were collected. Gloss and flat white paints were applied to hardboard house siding surfaces and exposed vertically and horizontally for 16 weeks, either shielded from or exposed to rainfall. Particle mass concentration, percentage of surfaces covered by fine and coarse mode fractions, average wind speed and rainfall amounts, and paint reflectance changes were measured at two, four, eight and 16 weeks. Scanning electron microscopy stubs, that had been flush-mounted on the hardboard house siding prior to painting, were also removed and replaced with unpainted stubs at these intervals. The unsheltered panels were initially more soiled by ambient pollutants than the sheltered panels; however, washing by rain reduced the effect. The vertically exposed panels soiled at a slower rate than the horizontally exposed panels. This was attributed to additional contribution to particle flux from gravity. The reflectivity was found to decrease faster on glossy paint than on the flat paint.

Based on the results of this study, the authors concluded that:

(1) coarse mode particles initially contribute more to soiling of both horizontal and vertical surfaces than fine mode particles;
(2) coarse mode particles, however, are more easily removed by rain than are fine mode particles;
(3) for sheltered surfaces, reflectance change is proportional to surface coverage by particles, and particle accumulation is consistent with the deposition theory;
(4) rain interacts with particles to contribute to soiling by dissolving or desegregating particles and leaving stains; and
(5) very long-term remedial actions are probably taken because of the accumulation of fine rather than coarse particles (Haynie and Lemmons, 1990).

Similar results were also reported by Creighton *et al.* (1990). They found that horizontal surfaces, under the test conditions, soiled faster than did vertical surfaces, and that large particles were primarily responsible for the soiling of horizontal surfaces not exposed to rainfall. Soiling was related to the accumulated mass of particles from both the fine and coarse fractions. Exposed horizontal panels stain because of dissolved chemical constituents in the deposited particles. The size distribution of deposited particles was bimodal, and the area of coverage by deposited particles was also bimodal with a minimum at approximately 5 μm.

In one of the first studies in the U.K., Mansfield and Hamilton exposed white wood tablets for 250 days in a road tunnel. These authors also placed the same type of white wood plates on the top of a roof in the London urban area over a period of 110 days. The results of both exposure experiments related the rate of soiling to the atmospheric levels of black smoke. During the various experiments performed, meteorological variables such as wind intensity, wind direction and rainfall were monitored in an attempt to relate the rate of soiling to meteorological conditions. Physical models, which took into account deposition processes, were developed to explain soiling processes; empirical models allowed for meteorological conditions by their best fit approach to real data (Hamilton and Mansfield 1992; Mansfield and Hamilton, 1989).

This early work was extended into two major research contracts sponsored by the European Commission. The first of these, undertaken with partners in Portugal, Austria and the U.K., examined the effect of airborne particulate matter on building surfaces (Contract Number: STEP-CT90-0097).

The programme was concerned with describing both the rate at which airborne particulate pollution is soiling buildings and the influence which acidic aerosols may have on stone deterioration. The nature of the particulate pollution was investigated in the course of the programme by collection of particulate matter using several different techniques. Theoretically derived emission inventories for elemental carbon and trace elements provided data to estimate soiling rates and apportion contributing sources to the collected particulate pollutants.

Filter samples using high volume samplers were collected from London, Vienna, Oporto and Coimbra. For comparative purposes, additional samples were collected at a suburban site near London and a rural site near Vienna. A portion of each filter was used to measure black carbon, organic carbon and carbonates, a second portion to analyse water soluble cations and anions and a third portion was extracted with acids and analysed for trace element content. Black smoke measurements were carried out.

Soiling and corrosion experiments were performed using a previously tested exposure protocol and materials provided by the Building Research Establishment in the U.K. Two different types of tablets were used for soiling measurements: white painted wood and calcareous Portland stone. One sample of each material was placed vertically in the exposure system facing the four cardinal directions, north, south, east and west, either in an uncovered position on the top of a mast where it was affected by wind and rainfall or under a roof, which protected the samples from rain but left them open to the wind. The main conclusions of this research programme were:

- Sheltered stone tablets showed a weight gain.
- Unsheltered stone tablets showed a weight loss and this loss showed a strong correlation with atmospheric SO_2 level.
- The input of sulphur and nitrogen via the aerosol form represented a small fraction of the total input.
- Soiling appeared to proceed in two stages; an initial stage which can be well represented by an exponential relationship and a later stage which can be well represented by a square root relationship.

The study was extended in Portugal by the Portuguese research team (Pio *et al.*, 1998), who concluded that sheltered surfaces had a continuous decrease in reflectance, which followed a square root equation on exposure time. Their data predicted a 30% decrease in reflectance would take between 5.5 and 8.8 years. They attributed 70% of the black carbon particles responsible for this soiling to vehicle emissions.

The second experimental study undertaken by Middlesex University and its co-workers was sponsored by the European Union (Contract: EV5V-CT94-0519) and ran from 1 July 1994 to 31 October 1996.

The project was established to examine the ways in which the rate of soiling of buildings from our cultural heritage can be directly related to the composition of depositing particles and their deposition velocity. The study was again undertaken in the three European cities — Oporto, Vienna and London, building on the previous collaborative research at the same locations. For comparative purposes, additional samples were again collected at a suburban site near London and a rural site near Vienna.

This project extended the examination of the nature and properties of particulate pollution likely to affect buildings in three ways. Analysis of organic and elemental carbon was undertaken to provide data on carbon levels sampled from the air by low volume filtration and to compare them to analyses of crust samples. TSP was monitored at two sites in central and north London. The distribution of some important PAHs in both air and crust was studied using gas chromatography/ mass spectrometry.

Monitoring of TSP and subsequent analysis of the particulate matter for total organic carbon, particulate elemental carbon, 16 PAH compounds and 23 *n*-alkanes revealed higher concentrations of all of these compounds at the central London location. Clear signatures associated with transport sources were identified in both atmospheric and crust samples. Weather factors were found to be important. Good inter-site relationships existed between the two sites for TSP, total organic carbon (TOC) and PEC. In Oporto too, multivariate statistical analysis lead to the conclusion that the predominant alkanes and PAHs were characteristic of urban dust and urban area emissions (especially diesel and fossil fuel combustion).

Particle characterisation by scanning electron microscopy (SEM) described the individual chemistry of particles deposited at St Paul's Cathedral, London. The SEM also revealed some very interesting examples of some of the structures associated with early development of black crusts. Different stages of crust development or structure were tentatively identified, including apparent growth stems, which protrude from the crust surface. The visual correspondence of these structures to those predicted by fractal modelling (next paragraph) for early simple disk aggregation provides great encouragement for further development in this area. SEM examination of different crusts from London's St Paul's cathedral revealed large numbers of particles of anthropogenic origin, probably emitted from oil and coal combustion sources, which accords well with other published research but may largely reflect earlier deposits.

As discussed above, it is generally accepted that, in modern cities, the unpleasant appearance of many stone surfaces of old buildings is mainly due to the deposition of soot particles. These particles cause blackening of the surface, and can also react with atmospheric gases, especially SO_2, which consequently produce sulphate and $CaSO_4$, deteriorating the stone. The manner in which the structure and porosity of particle agglomerates develop is known to affect the physical properties of materials and may also control the growth rate of the crusts formed (Massey, 1993). The U.K. Building Research Establishment examined the growth and structure of the agglomerates in more detail using a computer model based on a variation of the Diffusion Limited Aggregation algorithm. Computer generated pixels or pixels agglomerated into disks were deposited, one by one, onto a line to simulate the deposition of particles on to a planar surface in two dimensions. Fractal analysis, which is ideally suited to describe irregular surfaces such as those encountered in particulate deposition and the agglomerates formed, was used to characterise the structure (Watt *et al.*, 2000).

Conclusions from the fractal studies were that aggregation models provide a controlled way to examine the dynamics of particle growth. It was clear that disk models provide a more intuitive representation of agglomeration than pixel models. These simulations were used to make an estimate of the rate at which soiling might occur based on the model. Preliminary calculations were made of how soiling would build up over time based upon realistic values of atmospheric concentration. The calculations from the model gave a figure of about seven years for soiling to occur to a level that equated to a fairly dense covering of sub-micron particles approximately 0.5 μm thick over the surface of the material. Although this accords well with estimates from soiling rate models described above, it must be stressed that the fractal model under discussion is very preliminary and this result has not been fully substantiated. It has been shown that useful information concerning the internal structure of the agglomerate can be gained from measurements taken from a surface profile. This information can potentially be used to assess the strength of the agglomerate.

4.2. A Theoretical Framework

Following the initial field studies, which yielded empirical relationships between soiling rate and air quality, such as equation (1) above, the EPA 1983 "Workshop on Research Strategies to Study the Soiling of Buildings and Materials" highlighted the need for a theoretical model of soiling of surfaces by airborne particles. Haynie (1986) reported such a model, which provided an explanation of how ambient concentrations of TSP are related to the accumulation of particles on surfaces and ultimately the effect of soiling by changing reflectance. Soiling is assumed to be the contrast in reflectance of the particles on the substrate to the reflectance of the bare substrate given by:

$$R = R_0 (1 - X) + R_p X$$

where R = reflectance of soiled surface
R_0 = initial reflectance
R_p = reflectance of deposited particles
X = fraction of surface area covered by particles.

Assuming a deposition surface area A_0, of which an area A is covered ($X = A/A_0$), the mass deposition rate to the uncovered surface will be given by:

$$\frac{dm}{dt} = (A_0 - A)\, C\, V_d \tag{2}$$

where m = mass of particulate matter deposited, C = concentration of particulate matter in the atmosphere, and V_d = deposition velocity.

A simple relation between mass deposited and area covered results from considering the properties of n particles, each of radius r and density ρ:

$$m = 4/3\, \pi\, r^3\, \rho\, n \quad : \quad A = \pi\, r^2\, n$$

It follows that:

$$\frac{dA}{dt} = \frac{3}{4 r \rho} \frac{dm}{dt}$$

Substituting into equation (2) gives

$$\frac{dA}{dt} = (A_0 - A) \quad \text{where} \quad k = (3\,C\,V_d)/(4\,r\,\rho).$$

Under constant conditions, the rate of change in fraction of surface covered is directly proportional to the fraction of surface yet to be covered. Therefore, after integration:

$$A/A_0 = X = 1 - \exp\ (-kt)$$

where *k* is a constant, known as the soiling constant, and is a function of particle size distribution and dynamics and t is time.

It follows that reflectance will change according to:

$$R = Rp + (Ro - Rp)\ \exp\ (-kt).$$

In most situations, $R_p << R_0$, so the above equation reduces to:

$$R = R_0\ \exp\ (-kt) \qquad (3)$$

An alternative approach (Lanting, 1986) assumes the specific absorptivity of PEC is responsible for soiling, eliminating the assumptions about particle size. This model assumes that the exposed surface is covered at a uniform rate and that reflectance decreases with increased light absorption by deposited particles, which is determined by the thickness of the soiling layer. The theory is similar to that for X-ray attenuation and results in an exponential dependence as described by equation (3), but in this case

$$k = 2\alpha\,C\,V_d$$

where α is the specific absorptivity of PEC and the factor 2 is included to account for the fact that light passes through deposited particles twice on a smooth surface. Specific absorptivity is assumed to be $1 \times 10^4\ m^2\ kg^{-1}$. Attempts to model the soiling process, using the results from field studies, have normally employed equations (1) or (3).

Haynie (1986) examined the soiling of a gloss painted vertical surface and described his results as:

$$R = R.\ \exp\ (-0.0003\ [0.0363C_f + 0.29C_c]\ t)$$

where R and RO are reflectance and original reflectance, respectively; C_f and C_c, are fine and coarse mode particle concentrations in µg/m^3, respectively, and t is time in weeks of exposure.

The road tunnel experiments carried out in England by the Middlesex University team (Mansfield and Hamilton, 1989) were well described by the equation:

$$\Delta R = 100\ (1 - e^{-1.92t}), \qquad \text{(a)}$$

where t is time in years.

The level of black smoke in the tunnel was estimated as 246 µg/m^3.

These authors also related the rate of soiling with the atmospheric levels of black smoke using their results for white wood plate exposures on the top of a roof in the London urban area either using the empirical equation of Beloin and Haynie (1975), equations (c) and (d), or an exponential fit, equation (b):

$$\Delta R = 100\ (1 - e^{-0.044}\ C_{BS}\ t) \qquad \text{(b)}$$

$$\Delta R = 2.8\ (C_{TSP}\ t)^{1/2}, \quad \text{for exposed surfaces} \qquad \text{(c)}$$

$$\Delta R = 4.2\ (C_{TSP}\ t)^{1/2}, \quad \text{for sheltered surfaces} \qquad \text{(d)}$$

where C_{BS} is the concentration of black smoke in the atmosphere during the exposure period, in µg/m^3.

Comparison of equations (a) and (b) shows that, in these two sets of experiments, the soiling constant is not proportional to black smoke concentrations.

Recent experiments (Pio *et al.*, 1998) have used multiple regression techniques in an attempt to identify which air quality parameter (TSP or black smoke or PM_{10} concentration, humidity, rainfall etc.) has most effect on the soiling constant but no clear picture emerged. At this time, soiling rate can be described by either model but the soiling constant is site-specific.

5. Deposition Velocity

Camuffo and Bernardi (1993) demonstrate the importance of microclimatic factors on the deposition of particulate matter and resulting damage due to air pollution on the Trajan Column in Rome. They are able to show that Rome has two daily maxima of air pollution concentrations, and that these occur at times when the deposition regime at the column is very different. The authors examine the effects of temperature, humidity and wind conditions on deposition and show that the column frequently has different processes operating at different locations vertically and around the circumference. Such studies demonstrate the dangers of generalising deposition rates from average values and show that the latter only provide a first order approximation of what actually occurs.

Horvath *et al.* (1996) considered the need to devise a new experimental method for examining the deposition velocity for particles in the size range of atmospheric soot particles, which is in the order of fractions of millimetres per second. Direct determination of the deposition velocity of naturally occurring soot particles by weighing samples is impossible, since any mass increase by deposition is masked by other processes occurring simultaneously (such as gypsum growth). Deposition could be measured in an environment with an extremely high aerosol concentration or by using a method where the aerosol particles deposited on the surface can be determined independently from any other processes causing a mass increase or decrease of the sample. Since the mass of one single aerosol particle of a diameter of 0.1 μm is 5.23×10^{-16} g, the deposit formed in one hour in the above example represents 17 million particles on a surface of 25 cm^2 or 60 particles on a 100 μm by 100 μm field of view in a microscope. This is easily countable if the particles of this size can be made visible. Spherical latex particles, which contain a fluorescent substance, can be obtained in sizes between 0.025 and 3.0 μm as liquid suspensions and from 7 to 165 μm as powders. When using these particles for the deposition investigations, the fluorescent light emitted by the particles is used as a yes-no decision, i.e. seeing a luminous dot simply means that a particle is present at the surface which is inspected in the fluorescent light microscope. Thus even particles having diameters far below the detection limit of the microscope can easily be seen. Any other particles, which do not show fluorescence, are not seen. Preliminary laboratory results were presented in Fig. 3 above.

For experimental measurements outdoors at monuments, special surrogate surfaces were prepared consisting of 3 × 3 cm sheet metal plates coated with a mixture of cement and glue, in order to imitate the wall-structure of stone as closely as possible. They were magnetically affixed to the six sides of a 3 cm cube. This set-up allowed the investigation of the effect of different orientation of the surrogate surface with respect to the wind on the deposition velocity.

Four atomisers were used to generate the aerosol, consisting of fluorescent latex spheres of diameter 0.6 µm, which was introduced to a tube of approximately half a metre length. A fine wire grid attached at the end of the tube produced a uniform veil of aerosol. The velocity of the aerosol in the tube was about 10 cm per second. When leaving the tube, the particles almost immediately gain the velocity of the surrounding air.

The cube carrying the surrogate surfaces was exposed to the aerosol for a time of 2.5–4 hours. Afterwards the deposited particles on the surrogate surfaces were counted by means of a light microscope provided with an optical filter.

In contrast to other methods such as weighing or washing off the deposit, this procedure permits a direct and unequivocal identification of the examined 0.6 µm particles. The accuracy of the measurements is solely statistically determined when comparing particle deposition on different locations of the surface relative to each other. This fact allowed a reasonably precise determination of the deposition pattern on the cube sides. The deposition velocity is calculated from

$$v_d = v_f \frac{n_s}{n_f}, \quad v_t = \frac{V}{r_f^2 \pi \cdot T_m}$$

where n_s and n_f are the counted number of particles on the filter and on the surrogate surface, respectively, and v_f the face velocity to the filter with r_f as the filter radius, V is the volume of aerosol drawn through the filter, and T_m is the exposure time of the cube to the aerosol.

The deposition experiments in the open were performed in winter and spring at the town hall of Oporto, St. Paul's cathedral in London, and the University of Vienna. All measurements were carried out on the roof of these buildings. The range of measured deposition velocities was within one order of magnitude at each side of the cube. The ratio between the deposition velocities on the six sides stayed remarkably constant. A careful analysis of the deposit showed that the particles were distributed non-homogeneously on the surface. The deposition velocity showed a maximum at the upwind and downwind edges and a minimum somewhere in the middle of all laterally orientated surrogate surfaces (on the top, bottom, left and right sides of the cube). In most cases, the maximum was higher at the upwind edges. In order to study this effect, the cube with the six surrogate surfaces was positioned in the symmetrical axis of a wind tunnel. The deposition velocities were lower than the results from the field measurements and the differences between the deposition velocities of the six sides of the cube were lower because of the altered pressure gradients due to the presence of the walls of the wind tunnel. Nevertheless, the distinct deposition pattern (highest deposition at the edges and higher deposition on the front side compared to the back one) was reproduced in the deposition measurements performed in the wind tunnel. A complicated flow field around, and especially within a few millimetres of the sidewalls of the cube, is evident from these data. Therefore, care must be taken not to over-generalise the conclusions about deposition characteristics from this single example to those found in other experiments. Though a higher deposition was not always found on the upwind edge compared with that on the downwind edge, there was always a minimum in the middle of the surrogate surface. The reason for a higher deposition on the downwind edge is the existence of small variations in the alignment of the cube with respect to the airstream.

The rougher surfaces showed a higher deposition velocity, as could be expected. The lower deposition velocity on the back compared to the smoother surface is within the statistical error. On the other hand, since the back is in the wake of the cube, it may be the case that the surface structure plays only a minor role in the deposition process.

Particles with diameter between about 0.1 and 1 μm have the lowest deposition velocities, because all deposition mechanisms are least effective. For the 0.6 μm particles, the only possible deposition mechanism (assuming no electrophoretic or thermophoretic forces) is turbulent diffusion, even for the lower turbulence. The deposition rate experiments undertaken by Pesava *et al.* (1999) have demonstrated that, although there are important differences in conditions, existing literature values for deposition to rough surfaces accord very well with measured rates to surrogate building surfaces.

Using a cube for deposition experiments, one can determine deposition velocities in all main orientations with respect to the wind. Usually, however, an object or an ornament is attached to a plane surface, which can be the floor or the wall of a building. The presence of a plane surface like a wall alters the flow field by introducing a boundary layer adjacent to the wall.

To study this special case, a box of 3.0 cm width, 2.3 cm height, and 8.6 cm length was placed on the floor of the wind tunnel, with the cross-section of 3.0, 2.3 cm facing the wind. The height of the box was approximately equal to the boundary layer thickness at the measuring station. The front was tilted to the left at an angle of 1.5° to the channel axis. This set-up allows the investigation of an alignment effect on the deposition pattern, which was suspected to produce the higher deposition that sometimes occurred on the downwind edge of the cube.

The deposition velocities on the left side of the box are lower than on the right side at both the upwind and downwind edges. Due to the tilt, the left side experiences an adverse pressure gradient, which extends the separation region, compared to the right side. On the right side the edge effect is more pronounced, hence the deposition is higher, particularly at the downwind edge and the right edge of the front surface of the box.

The deposition velocity on all sides, except the top surface, decreases from top to bottom. This is the result of the boundary layer: the rate at which particles are transported to the surface diminishes with decreasing velocity relative to the location where the particle concentration of the free airstream is sampled.

Turbulence intensities in the boundary layer of the atmosphere are dependent on height, velocity component, and eddy scale (Hall and Emmott 1994). The lateral and vertical components of the large-scale turbulence intensity have the same effect as fluctuations in wind direction. Only the small scale eddies act in the same way as the velocity fluctuations in the wind tunnel. This is the reason that the deposition velocities in the experiments performed in the open were higher compared to the wind tunnel. Both the alignment effect and the higher turbulence intensity enhance the deposition. In addition, there are considerable microscale variations due to complexities in the flow field of bluff objects. Thus, one has to proceed with caution when deposition velocities from laboratory data are used to calculate particle deposition rates for real buildings in the open.

6. Indoor Soiling

Ligocki *et al.* (1993) studied potential soiling of works of art. Concentrations and chemical composition of suspended particles were measured in both the fine and coarse size modes inside and outside five museums in Southern California in both summer and winter. The seasonally averaged indoor/outdoor ratios for particle mass concentrations ranged from 0.16 to 0.96 for fine particles and from 0.06 to 0.53 for coarse particles, with lower values observed for buildings with sophisticated ventilation systems that include filters for particle removal. Museums with deliberate particle filtration systems showed indoor fine particle concentrations generally averaging less than 10 μg/m. One museum, a historic house in Los Angeles with no environmental control system showed indoor fine particle concentrations that averaged 60 $\mu g/m^3$. Fine particle concentrations at this site were almost identical to outdoor concentrations and therefore significant fractions of the dark-coloured fine elemental carbon and soil dust particles present in the outdoor environment may constitute a soiling hazard to displayed works of art. Analysis of indoor versus outdoor concentrations of major chemical species indicated that indoor sources of organics may exist at all sites, but that none of the other measured species appear to have major indoor sources at the museums studied. This finding is interesting since smoking and use coal or wood burners are forbidden, and these are the usual source of raised indoor particulate matter. All sites do appear to have detectable black carbon values indoors. This finding that fine particle chemistry inside a museum was similar to the results outside was also reported by DeBock *et al.* (1996) for the Correr Museum in Venice. They demonstrated differences in the coarse particles but reported great similarities in the fine particulate.

A simplified steady state material balance model (Nazaroff and Cass, 1991) was used to explore the relationship between indoor and outdoor fine particle components to attempt to reveal indoor source contributions. Given that similarly sized particles ought to have the same contribution from outside, since their dynamics will be similar, it was interesting to see that modelled outdoor contributions for elemental carbon were sometimes higher than for organic matter or sulphate, implying that filtration efficiency was lower for these particles. Average ratios for elemental carbon in the indoor fine fraction compared to outdoor values ranged from 0.2 to 0.5 for buildings with fine particle filter systems and it is therefore clear that there is a risk of indoor soiling wherever elemental carbon values are high outdoors, even if filtration is undertaken.

The Nazaroff and Cass (1991) model applied above was also used to examine possible control strategies at the historic house museum, Sepulveda House. According to model results, the soiling rate can be reduced by at least two orders of magnitude through practical application of methods that included reducing the building ventilation rate, increasing the effectiveness of particle filtration, reducing the particle deposition velocity onto surfaces of concern, placing objects within display cases or glass frames, managing a site to achieve lower outdoor aerosol concentrations, and eliminating indoor particle sources. Combining improved filtration with either a reduced ventilation rate for the entire building or low-air-exchange display cases would be likely to extend the time taken to achieve noticeable soiling from years to centuries at a site like Sepulveda House, which might be considered to be analogous to many European cultural buildings, being in relatively polluted environments and with little or no existing ventilation control.

7. Economics of Soiling

Several types of economic costs can be associated with material damage and soiling, which may include the reduction in service life of a material and additional required maintenance, including cleaning. There may be a decrease in utility, a need to substitute a more expensive material and additional costs of protecting susceptible artefacts.

The relative importance of these various losses will vary between materials and between locations. The cost of materials is only one component in assessment of the value of the building, and clearly the same materials will have different apparent values when a modern dwelling is being considered compared to when the damage is occurring on an ancient monument. There are a number of methods that have been used to estimate the magnitude of the effects of air pollution.

The first of these is known as the damage function method, which in the context of the effects of air pollution on materials, is most advanced in the consideration of corrosion, especially from SO_2, NO_x and O_3. This field has progressed to the point where sensible first order calculations of associated costs can be made, at least for modern materials. A recent evaluation of the current situation was undertaken by the workshop on Economic Evaluation of Air Pollution Abatement and Damage to Buildings including Cultural Heritage, which took place in Stockholm on 23–25 January 1996. The workshop was organised jointly by the International Co-operative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments (1CP Materials) and the Task Force on Economic Aspects of Abatement Strategies.

One of the conclusions adopted by the workshop was that a methodology for corrosion cost assessment of the built environment had been established. It is based on dose-response functions, damage functions, modelling of the most important environmental degradation factors, statistical building inventories to establish the stock-at-risk and an estimation of the costs. It has been developed and used in the Czech Republic, Germany, Norway, Sweden, the United Kingdom and the United States. Attempts have been made to extrapolate these results to the European level (ApSimon and Cowell, 1996).

The damage function approach requires a number of steps to be elucidated:

- A *dose-response function* relates the dose of pollution, measured in ambient concentration and/or deposition, to the rate of material corrosion. As far as corrosion is concerned, ICP Materials has developed dose-response functions for a number of pollutants and materials. Even taking corrosion effects in isolation, there are as yet no satisfactory dose-response functions for particulate matter and, as discussed above, the soiling models are not yet sufficiently advanced to produce reliable functions to relate reflectance change to atmospheric concentration.

- A *physical damage function* links the rate of material damage (i.e. only corrosion damage at this point; soiling damage could perhaps be broadly estimated) to the time of replacement or maintenance of the material. There are additional difficulties when assessing the soiling damage function since the requirement to clean a structure is not a direct function of damage alone but relates to a perception on the part of the local population or the building manager. Different levels of soiling will be tolerated in different locations and at different times.
- A *cost function* links changes in the time of replacement, cleaning or repainting to monetary cost.
- An *economic damage* function links cost to the dose of pollution by an amalgamation of the previous steps.

Once the economic damage functions have been established, cost calculations can be performed after identification of the stock-at-risk. There are a number of methods for drawing up building inventories, assessing the relative proportions of each different material and for evaluating the degree of damage based on lifetime assessments. The following categories can be distinguished — residential, industrial and other buildings; infrastructure; and cultural monuments. Stock-at-risk data can be collected at different levels of detail: (i) building types; (ii) construction materials; and (iii) repair/replacement materials. The identification of groups of buildings or parts of a building with statistically the same mixture of material (known as "identikits") is an important part of the methods developed. These identikits have to be adapted to local conditions when applied in different locations.

There are very large gaps in the stock-at-risk data as far as cultural heritage is concerned. The biggest difficulty in estimating damage to cultural monuments is related to the economic valuation. However, there are also problems in identifying the stock-at-risk and determining which buildings should be considered as cultural monuments. In

Italy, a national risk mapping exercise for cultural heritage is under way which singles out the risk from air pollution damage among a list of other factors.

The US EPA Air Quality Criteria Document (United States Environmental Protection Agency, 1996) reviews some of the literature that covers economic losses associated with soiling. The following section is based on this review, since much of the material covered refers to EPA reports that have not been seen in the original. The references are retained in the text. Haynie (1990) examined the potential effects of PM_{10} non-attainment on the costs of repainting exterior residential walls due to soiling in 123 counties in the United States. The analysis was based on a damage function methodology developed for an earlier risk assessment of soiling of painted exterior residential walls (Haynie, 1989). The database was updated with 1988 and 1989 data. The costs of soiling to exterior residential walls were estimated to be US$1 billion.

An experimentally determined soiling function for unsheltered, vertically exposed house paint was used to determine painting frequency (Haynie and Lemmons, 1990). An equation was set up to express paint life in integer years because the painting of exterior surfaces is usually controlled by season (weather). Different values for normal paint life without soiling and levels of unacceptable soiling could be used in the equation. If four was taken as the most likely average paint life for other than soiling reasons, then painting because of soiling would be likely to be done at one-, two-, or three-year intervals.

Soiling costs by county were calculated and ranked by decreasing amounts and the logarithm of costs plotted by rank. The plot consisted of three distinct straight lines with intersections at ranks 4 and 45. The calculated cost values provide a reasonable ranking of the soiling problem by county, but do not necessarily reflect actual painting cost associated with extreme concentrations of particles. Households exposed to extremes are not expected to respond with average behaviour. The authors concluded that repainting costs could be lowered if:

(1) Individuals can learn to live with higher particle pollution, accepting greater reductions in reflectance before painting;

(2) Painted surfaces were washed rather than repainted; and
(3) If materials or paint colours that do not tend to show dirt were used.

Extrapolating the middle distribution of costs to the top four ranked counties reduces their estimated costs considerably. For example, Maricopa County, AR, was calculated to rank first at US$70.2 million if all households painted each year as predicted, but was calculated to be only US$29.7 million based on the distribution extrapolation.

Based on these calculations and error analysis, the national soiling costs associated with repainting the exterior walls of houses probably were within the range of US$400 to US$800 million a year in 1990. This sector represents about 70% of the exterior paint market, so that extrapolating to all exterior paint surfaces gives a range of from US$570 to US$1140 million (Haynie and Lemmons, 1990).

Math Tech Inc. (1990) assessed the effects of acidic deposition on painted wood surfaces using individual maintenance behaviour data. The effects were a function of the repainting frequency of the houses as well as pollution levels.

The loss of amenity or direct financial losses can also be estimated econometrically in studies that do not use the physical damage approach to derive monetary economic damages. These approaches have been used to relate changes in air pollution directly with the economic value of avoidance or mitigation of damages. Such studies are prone to errors in accounting for all factors that affect cost other than air quality. In general, all approaches to estimating costs of air pollution effects on materials are limited by the difficulty in quantifying the human response to damage based upon the ability and the incentive to pay additional costs (Yocom and Grappone, 1976).

McClelland *et al.* (1991), conducted a field study valuing eastern visibility using the contingent valuation method. Given the problem of embedding between closely associated attributes, the survey instrument provided for separation of the visibility, soiling, and health components of the willingness-to-pay estimates. Households were found to be willing to pay US$2.70 per $\mu g/m^3$ change in particle pollution to avoid soiling effects.

8. Costs to Cultural Heritage Caused by Soiling

As described above, many past studies that have tried to relate air pollution damage to construction or cultural materials have often used the avoided maintenance cost approach to estimate the benefits of reduced emissions, i.e. they have calculated the savings implied from a reduction in maintenance costs due to reduced damage rates. However, maintenance costs are probably not the correct measure of the benefits derived by society from reduction of damage to cultural resources. An estimate of economic value is given by the public's willingness to pay (WTP) for reduced damages or, equivalently, their willingness to accept (WTA) these damages. WTP to prevent damage may be larger, smaller or equal to maintenance or mitigation costs. Original valuation studies are expensive but, in the case of cultural resources, calculation of maintenance costs may seriously underestimate the damages, since there are likely to be substantial non-use values. Valuation studies must also examine the effects of maintenance practices themselves, since they may not prevent injuries from occurring, with part of the value being irreversibly lost when the original material is altered or replaced.

Mourato, (1997) presented an overview of the existing literature on the economic valuation of cultural goods with a special focus on damages arising from air pollution. She found that cultural heritage valuation studies were scarce and limited in scope and content. With a few exceptions, they were mostly confined to finding a price for the goods in question, without properly describing the extent of the quality change that occurred, without any systematic attempt to test for validity or reliability of the estimates produced or to fully explore the nature of people's preferences towards cultural goods. Only three papers dealt specifically with the estimation of air pollution damage.

Navrud (1992) reported results from a contingent valuation study to assess the value of losses to visitors from corrosion of Nidaros Cathedral in Trondheim, Norway, from air pollution. A sample of 163 Norwegian and foreign visitors were asked to value two alternative options: a "restoration option" where all the cathedral's original parts were replaced, versus a "preservation option" where the remaining original parts were preserved through reduced air pollution. There was no statistically significant difference in the mean annual WTP for each option: 318 NOK (US$49) per person for the preservation option versus 278 NOK (1992 US$43) for the full restoration scenario. This is a fascinating result, in that it implies that, on average, those surveyed did not seem to derive any extra benefits from having the original, as opposed to a restored, building. However, 65% of respondents said that the original meant more to them than the restored church and this group had a significantly higher WTP for preservation than for restoration. Mourato concludes that the results from this study indicated that there was a significant WTP for preservation of the Nidaros cathedral from air pollution damage — although no extra benefit is attached to preserving original parts rather than replacing them. However, the authors did not report: (i) what payment vehicle was used (i.e. tax or donations); (ii) what the damages from air pollution were; (iii) what exactly did both preservation and restoration options imply in terms of future rates of decay; or (iv) any validity tests on the WTP estimates. Hence, the accuracy of their results cannot be established.

Grosclaude and Soguel (1994) estimated the social cost of damages from air pollution from traffic to historical buildings in Neuchatel (Switzerland). Two hundred residents were asked about their willingness to make a voluntary contribution to a fund to be established to maintain 16 historical limestone buildings. Respondents were shown pictures of the 16 buildings and asked to identify those in need of immediate conservation measures. An average of six buildings was selected. The elicitation procedure included an open-ended WTP question followed by a bidding game to determine the maximum WTP amount. Forty-three per cent of respondents declared a zero WTP — of those, 25% did not consider the damage to historical buildings to be a problem (the "indifferents" or "true zeros"), 19% could not afford the payment (the "non-solvents") while the remaining 56% were considered "false zeros" and hence classified as "free riders". The average observed annual WTP to repair damages to historical buildings was SFr. 172 (US$123) for the total sample and SFr. 192 (US$137 with the exclusion of "true zeros"; the average predicted WTP is SFr. 121 (US$86) for this latter group. On aggregate, the annual social cost of damage caused to historical buildings by road traffic air pollution is estimated to be SFr. 1.7 million (US$1.2 million) with a cost SFr. 283,000 per building (US$202,000).

Mourato pointed out that no indication was given of what the maintenance works would imply in terms of aesthetic improvements or future rates of corrosion, the link between damages to historic buildings and road traffic air pollution was extremely tenuous, an essentially arbitrary procedure was adopted to screen valid responses by differentiating between respondent's motivations and no mention was made to other cultural resources to which Neuchatel citizens might also attribute some value.

Morey *et al.* (1997) conducted a comprehensive stated preference valuation study of damage from acid deposition to marble monuments and historical buildings in Washington, DC. Considerable effort was put into specification the pollution damage scenarios: respondents were presented with descriptions, photos and a map of outdoor marble monuments in Washington DC; written descriptions of erosion and chemical alteration with supporting illustrations were given; digitally enhanced photos in a time line were used to suggest damage levels from air pollution now, in 75 and in 150 years time; the same procedure was used to depict the reduction in the rates of deterioration that would arise from specified preservation programmes. Four possible evolution patterns were considered: the current injury levels "baseline" and three alternative damage reduction programmes. The three latter options delayed the appearance of weathering effects in the time line: 25% later in Option A, 50% in option B and 100% in Option C. The proposed scenario involved hypothetical preservation programmes based on (imaginary) chemical coating procedures.

A random sample of 272 paid respondents was interviewed in two locations (Boston and Philadelphia), with the chosen procedure being group presentations followed by individual answering of a questionnaire. The chosen elicitation format was pair-wise choices with different combinations of two attributes: price (a one-time household payment) and preservation option, with nine and four different levels, respectively (including a zero priced baseline option). A follow-up payment card was included as a comparator. The payment mechanism was not specified.

Predicted mean household WTP (from "male" respondents — women were found to be willing to pay twice as much as men; instead of averaging out responses, the authors adopted the "conservative" approach of treating every respondent as male) was US$26 for a 25% shift in the injury time line (Option A), US$38 for a 50% shift (Option B) and US$56 for a 100% shift (Option C). Assuming that the WTP estimates were sufficiently representative of the populations from which the samples were taken (Boston and Philadelphia), mean aggregate estimates were calculated to be US$50, US$72 and US$105 million, respectively for preservation Options A, B and C.

Mourato considered this study to be the best available for estimating economic damages from air pollution on cultural resources. It was the first attempt to link the changes in the goods, as perceived by the consumer, to the source of the damage, as described in the scientific literature. The survey comprehensively described the goods to be valued and the proposed changes with an extensive use of visual aids. It recognised the fact that the relevant valuation issue is to achieve a decline in the rate of deterioration and not an unattainable goal of complete preservation.

The currently available literature is insufficient to provide overall estimates of the value of cultural resources in general, and of the damages caused by air pollution in particular, with any degree of reliability or precision. However, people do seem to place a value on cultural heritage and these early estimates indicate that this may amount to a considerable sum. A lot of work clearly remains to be done, with many more surveys needed. Any attempt to generalise from particular case studies needs to examine the possibilities for benefit transfer. Here there will be many difficulties, for example differences in materials and use make it difficult to generalise the way in which changes in air pollution damage will affect values as perceived by consumers. Further research will also need to examine how measured WTP can be transferred between societies. In the case of cultural heritage buildings, many of which are unique, this has additional problems (it is important not to seem to imply that Stonehenge is somehow more important than, say, the Acropolis). A direct and uncritical comparison of the Grosclaude and Soguel (1994) and Navrud (1992) studies seems to imply that an average of six buildings in Neuchatel has, for some reason, a considerably larger value to the local population than the Nidaros cathedral has to Norwegians. In relative terms, the former estimate corresponds to 0.32% of Switzerland's per capita income while the latter amounts to only 0.17% of Norway's per capita GNP. Navrud (1992) has demonstrated the difficulty of transferring health impact of air pollution values measured in one country for use in another.

Nevertheless, valuation studies are valuable because they remain the only way to account for benefits that may be unrelated to any specific use but simply arise from the knowledge that cultural assets exist (existence value) and will be available for the enjoyment of other people (altruistic motive) and future generations (bequest value) or for one's own possible future use (option value). These benefits are usually known as non-use values and are thought to be a significant proportion of total value in the case of cultural heritage.

In the case of damage due to soiling, where the dose response functions are not well elucidated as discussed above, valuation studies may be particularly effective. Soiling damage would seem to be particularly suitable for translation into descriptions of visible effects on cultural resources that are detectable to the untrained eye.

9. Conclusions

Soiling is an integrating process, which occurs over a number of years and there need to be ongoing studies to relate soiling to air quality and meteorology. Modelling is clearly important and we see scope for further theoretical approaches to develop a fundamental understanding of the empirical relationships developed in these studies.

The aim of achieving improved models describing the deposition and accumulation of pollutants under real conditions has been addressed by a number of innovative experimental studies. The fractal model work showed that realistic time-based soiling curves could be constructed using the model. These ideas can be readily developed, and as the fractal model becomes more complex with additional data from further interpretation of the experimental results on deposition rate, size distribution and adhesiveness of particles, soiling curves will be produced which will form the basis for prediction of effects of different air pollution and remediation strategies.

Analysis of the formation and structure of particle agglomerates may also assist in the treatment of the crusts regarding cleaning and protection of surfaces. Given that the strength of the agglomerate is determined by particle contacts, then selection of a cleaning regime that utilised the least effort to break these contacts can be specified. The fractal model is still a relatively simple one and its initial finding, that early cleaning may be the most efficient strategy for mono-sized particles, will need to be further investigated to include such factors as adhesion, stickiness and size distributions. These factors may have a significant effect on the number of grain contacts and the compactness of the agglomerate, which will have a corresponding influence on any recommended cleaning strategy.

Despite a large amount of qualitative evidence that air pollution can cause substantial harm to culturally important buildings and monuments, there remains little quantitative data to link pollutant exposure with material damage, and trends are inconclusive. Clearly, more quantitative evidence is required if control strategies are to be effective in reducing the impacts of particle soiling in urban areas.

It seems reasonable to suggest that economic costs associated with atmospheric pollution can be described and that households are willing to pay positive amounts to reduce material damage and soiling. However, perception of nuisance varies and, although blackening of buildings has been shown by surveys of public attitudes to traffic nuisance to be a factor that people resent (McCrae and Williams, 1994; Williams, and McCrae, 1995,) there have been no studies that examine these effects in relation to concentration, particle size and chemical composition. Indeed it would be difficult to imagine how this might be achieved and yet without such information it is very difficult and highly uncertain to quantify the relationship between ambient particle concentrations, soiling and associated economic cost.

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CHAPTER 11

CHANGES IN SOILING PATTERNS OVER TIME ON THE CATHEDRAL OF LEARNING

W. Tang, C.I. Davidson, S. Finger, V. Etyemezian,
M.F. Striegel and S.I. Sherwood

1. Introduction

Air pollution has been responsible for increasing the deterioration rate of structures made of limestone and marble. These calcareous stones are vulnerable to attack by several natural processes, including dissolution by rain, physical stresses such as freeze-thaw cycles, and microbial activity on the stone surface. Anthropogenic pollutant emissions may accelerate the natural erosion, resulting in pitting, cracking and discolouration (Sherwood *et al.*, 1990).

One major cause of anthropogenic degradation is the formation of gypsum. This is the product of the reaction between calcium carbonate and acidic forms of sulphur, such as sulphuric acid. Gypsum occupies a greater volume than calcium carbonate, causing the stone to crack when gypsum forms. Furthermore, gypsum is more soluble in rain water than calcium carbonate, and thus rain may wash off the gypsum deposits, leaving pits in the stone. Gypsum is also more porous than the original stone, and can serve as an effective surface for the deposition of particles such as soot carbon. This can lead to discolouration of the stone, which is well-documented for limestone buildings (Sherwood *et al.*, 1990).

In previous work (Etyemezian *et al.*, 2000; Davidson *et al.*, 2000), we hypothesised that soiling on a tall limestone building in Pittsburgh, Pennsylvania has been the result of two competing processes. The first is the deposition of pollutants on the stone, especially on sections of stone where gypsum has formed. The second process is washoff of soiled material by rain. Soiling patterns change when the relative rates of pollutant deposition and rain washoff vary over time.

In this paper, the changes in soiling patterns over time on the same limestone building have been studied based on archival photographs, analysis of soiling on architectural features, and computer modeling of horizontal rain flux. The results are used to support the hypothesis that soiling is determined mainly by the two competing processes.

2. Changes of Soiling Patterns

2.1. Background

The structure of interest is the Cathedral of Learning, a National Historic Landmark located in the densely populated Oakland area of Pittsburgh. This is a 42-storey Indiana limestone building on the University of Pittsburgh campus, constructed between 1926 and 1937. Two sides of the Cathedral have extensive soiling, particularly on the lower half of the building. Since the time of construction, soiling has been evident as a result of numerous air pollutant sources within a few kilometres of the building. These include steel manufacturing plants that employ coke ovens and blast furnaces, a coal-burning steam heating plant, motor vehicle traffic, coal-burning railroads and riverboats, and a large number of domestic coal combustion sources such as home furnaces.

The Cathedral of Learning has attributes which lend themselves to this type of study. The location of the Cathedral in an urban setting with detailed records of pollutant sources and concentrations allows the study of changes in soiling over time. Archival photographs of the building are available to permit comparisons between observed soiling and pollutant levels. The Cathedral is the tallest structure in the area, and thus prevailing wind and weather patterns will not be altered much due to surrounding structures, at least on the upper levels. There are certain architectural features repeated at many locations on the walls of the Cathedral, which can be used to quantify the amount of soiling at different elevations. The Cathedral has never been cleaned, except by natural rainfall. Finally, the Cathedral has historic and cultural value in its own right.

Since the time of construction of the Cathedral, Pittsburgh has experienced substantial changes in air pollution concentrations (Davidson, 1979). During the 1930s and 1940s, coal burning was responsible for the city's notorious smoke levels. In the late 1940s and throughout the 1950s, enforcement of smoke control ordinances reduced pollutant emissions. Stricter county ordinances in 1960 and 1970 as well as new federal regulations resulted in continued decreases in air pollution levels. Figure 1 presents annual average dustfall in or near the downtown area over an 85-year period. The continued decrease through recent decades is evident, especially the rapid

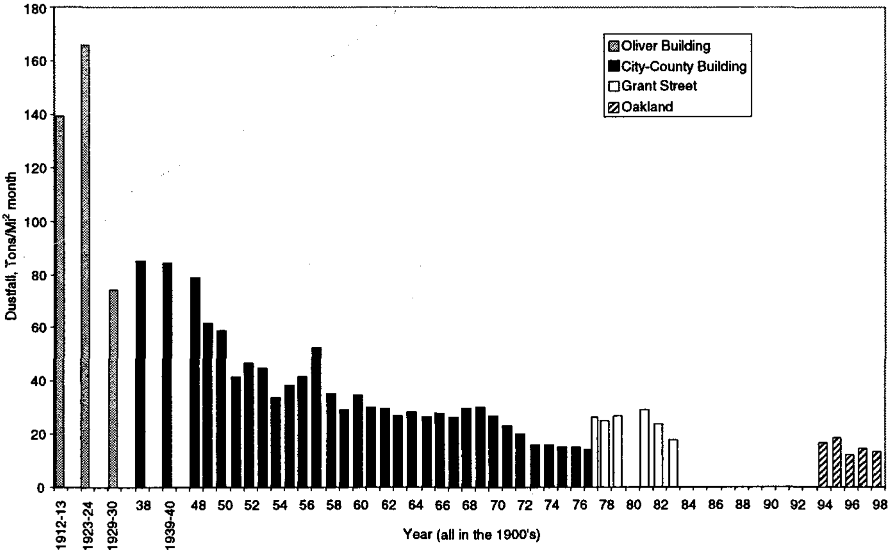


Fig. 1. Annual average dustfall at four different sites in or near downtown Pittsburgh. No data are available for 1980 or for 1984–1993. Data are taken from archival and recent records at the Air Quality Program of the Allegheny County Health Department.

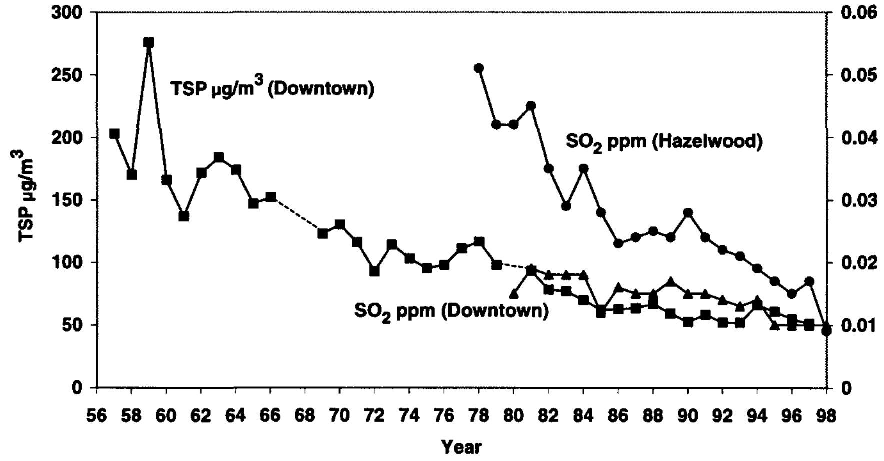


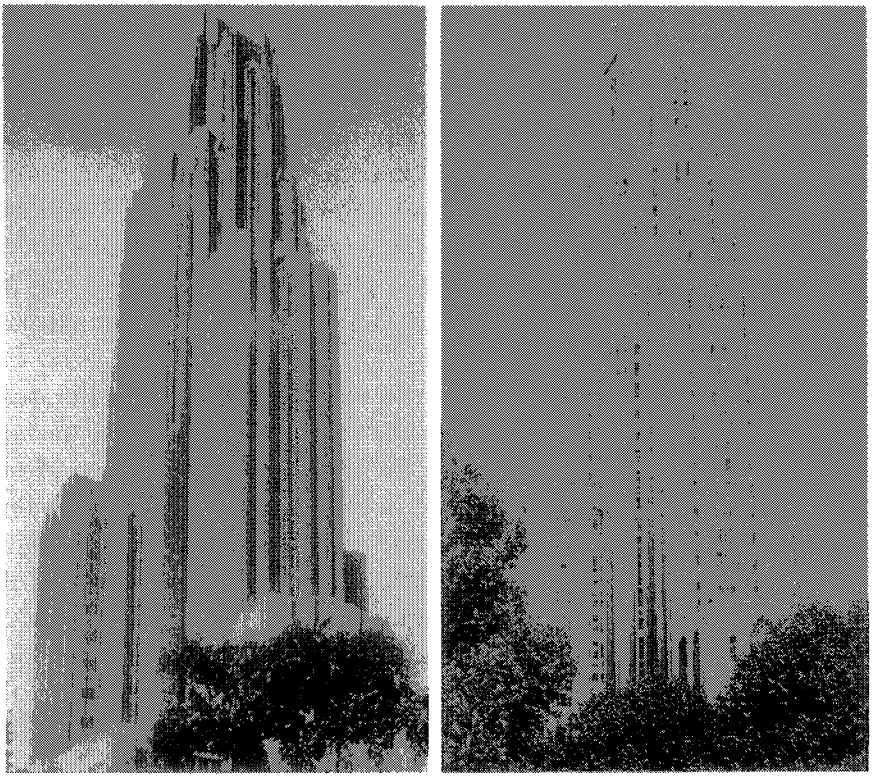
Fig. 2. Annual arithmetic average concentrations of total suspended particles (TSP) and sulphur dioxide (SO_2) in or near downtown Pittsburgh. The TSP measurements were made with high volume samplers at two downtown locations: the County Office Building (1957–1982) and Flag Plaza (1983–1997), as part of the National Air Sampling Network and the Air Quality Program of the Allegheny County Health Department. Reliable data are not available for 1967, 1968 and 1980. The SO_2 measurements were made with continuous monitors at Flag Plaza downtown (1980–1998) and in the Hazelwood section of the city (1978–1998). Reprinted with permission of the American Chemical Society (Davidson *et al.*, 2000).

decrease in dustfall during the late 1940s and early 1950s. Figure 2 shows airborne concentrations of total suspended particles (TSP) from 1957 to 1997 and airborne concentrations of sulphur dioxide from 1978 to 1998 measured in or near downtown Pittsburgh. General decreasing trends are again observed.

2.2. *Changes in Soiling Patterns Over Time Based on Archival Photographs*

We can study how variations in pollutant levels shown in Figs. 1 and 2 have affected soiling patterns on the Cathedral by examining photographs taken in previous years. For convenience, the faces of the Cathedral have been labelled with names of nearby streets. These are Bigelow Boulevard (southwest side of the building), Fifth Avenue (northwest side), Bellefield Avenue (northeast side), and Forbes Avenue (southeast side).

The first pair of photos in Fig. 3 shows the Bigelow Boulevard side of the building. The photo from 1937 shows heavy soiling from approximately the fourth floor to the roof, except for the very top floor. An interesting feature of the building is that between 1929 and 1931, stonework was installed from the fourth floor up to the top. After that, work was stopped due to financial problems. It was not until the mid-1930s that stones for the lowest four floors were added



1937 1995

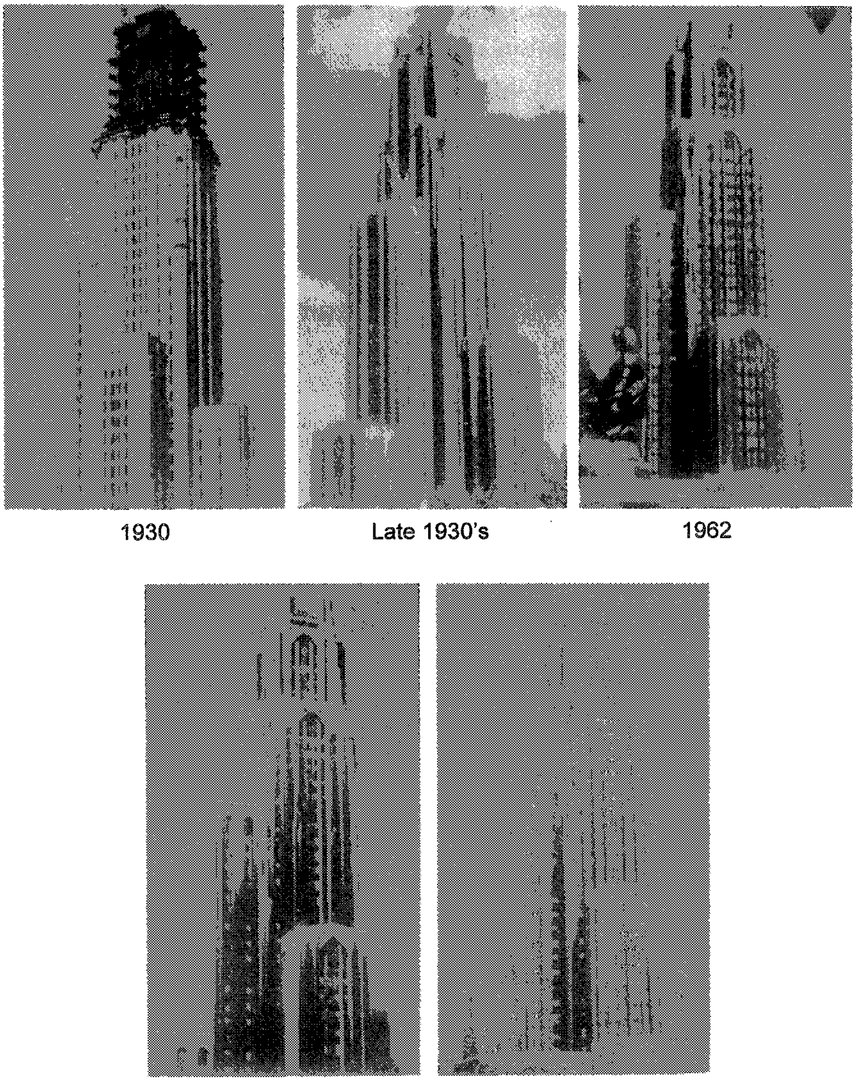
Fig. 3. The Bigelow façade of the Cathedral of Learning in 1937 and 1995. (Sources: 1937 — University Archives, University of Pittsburgh; 1995 — Justin Parkhurst.)

and the top floor was reconstructed (Brown, 1987). Because of this fact, white stones at the top of the Cathedral (visible in the 1937 photo on the right side) have been a reference point to distinguish soiled sections from white ones. Using this reference point suggests that a significant amount of soiling occurred during 1931 to 1937. This coincides with heavy smoke in the 1930s throughout the region. In contrast, the photograph from 1995 shows that the entire Bigelow face of the building is almost free of soiling. Since no cleaning or renovation has been done since the completion of construction, it is likely that the reduction in soiling has been influenced by natural processes over time.

The photographs of the Forbes façade from 1930 to 1995 in Fig. 4 are useful for observing changes in soiling patterns over several time intervals. The photo from 1930 shows that the surface was relatively white shortly after laying the exterior stonework began in 1929. By the late 1930s, however, the surface had become highly soiled. The soiling progressively decreases in the three later photographs. Generally, the decrease of soiling on this face is not as dramatic as that on the Bigelow Boulevard side. However, the later photos show that the top one-third of the building on the Forbes Avenue face has been virtually free of soiling since 1989.

In addition to observations of the whole building, smaller scale changes on individual sections provide insight into the rain washing process. The location marked with an arrow on the first two photographs points out where there have been notable changes in soiling. On the photo from the late 1930s, the region below the arrow shows a demarcation between soiled and white areas on the left side of the Forbes Avenue face. The white region appears as a "notch" in the soiling, which has become enlarged in the downward direction over time. The bottom of the notch reaches the fourth window from the top of the section. By 1962, the notch has reached the middle of the fifth window. The photo from 1989 shows that the notch now reaches between the fifth and sixth windows. By 1995, the notch extends to the sixth window.

These archival photographs suggest that the Cathedral of Learning has been washed by natural rainfall over time, which supports the hypothesis that soiling on building surfaces is the result of a competitive



1930 Late 1930's 1962

1989 1995

Fig. 4. Archival photographs of the Forbes Avenue (southeast-facing) side of the Cathedral of Learning on the University of Pittsburgh campus. Changes in soiling patterns, such as those in the region below the arrow in the first two photographs, are apparent by comparison with the later photos. [Sources: 1930 — University Archives, University of Pittsburgh; Late 1930s — Carnegie Library of Pittsburgh; 1962 — University Archives, University of Pittsburgh; 1989 — Ferguson Photographic Enterprises; 1995 — Justin Parkhurst. Reprinted with permission of the American Chemical Society (Davidson *et al.*, 2000).]

process between pollutant deposition and rain washoff. The overall trend of annual precipitation in Pittsburgh has been roughly constant over these decades (Etyemezian, *et al.*, 1998). However, airborne concentrations of SO_2 and particles have decreased steadily over the same time period (Davidson, 1979). Thus, those areas of the façade that were soiled in the late 1930s have become white in recent years because the rate of removal of soiled material by rain washing is greater than the rate of soiling by pollutant deposition and chemical reaction. The opposite was true in the 1930s when air pollutant concentrations were considerably greater than at present.

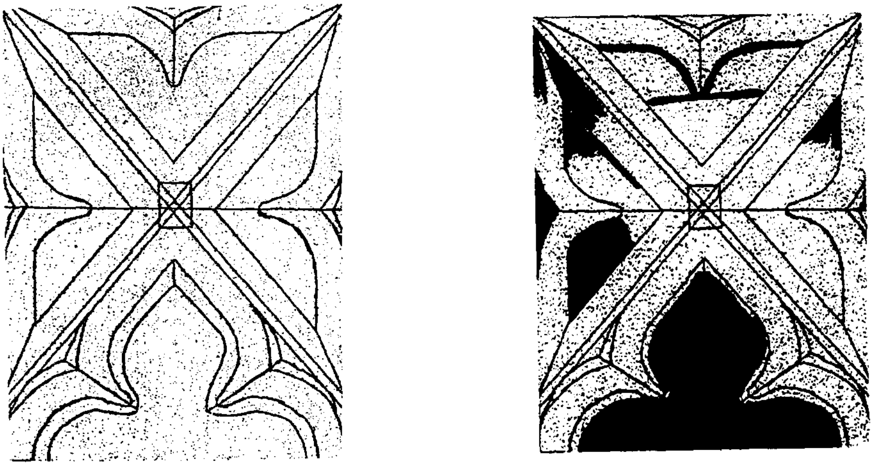
The rates of washoff of soiling have been different on the four faces of the Cathedral. During the early years when pollutant deposition was dominant, soiling was almost uniform on each face, as shown by numerous archival photographs from the 1930s. However, it is likely that the Bigelow face has received a greater rain flux than the Forbes face, as will be discussed below, so that the decrease of soiling on the Bigelow face is much more significant.

2.3. Analysis of Soiling on Architectural Features

To assess quantitatively the patterns of visible damage that have occurred on the Cathedral, the soiling patterns of repeated architectural features have been documented. One such repeated feature is a stone carving 0.56 m × 0.75 m in the shape of a large “X”, hereafter referred to as a “cross”. There are 226 crosses scattered on all four faces of the Cathedral at different elevations. The soiling patterns on each cross have been sketched and scanned into a computer, and the percentage of discoloured area has been determined (Gould *et al.*, 1993; Lutz *et al.*, 1994; Etyemezian *et al.*, 1995).

Figure 5 shows examples of four sketches with different percentages of soiled area. One sketch shows an ideal, unsoiled cross, while the other three sketches show soiled crosses on different floors on the Bigelow face of the building.

By examining data for all 226 crosses, we can find strong evidence for the hypothesis that pollutant deposition and rain washoff determine soiling patterns on the building. Most sharp edges of the carvings have been cleaned because they are exposed to raindrop impact and



0% soiled area

29.5% soiled area
37th floor

49.0% soiled area
23rd floor

72.7% soiled area
8th floor

Fig. 5. Soiling patterns on crosses carved into the stone, a repeated architectural feature on the Cathedral of Learning. The upper left sketch shows an ideal, "unsoiled" cross, used as a blank in the computations of percent soiled area. The other three sketches are examples of soiled crosses taken from different floors on the Bigelow face of the building.

downward dripping of rainwater. In contrast, the sheltered areas below the edges show more soiling. Even for the crosses with a small percentage of soiled area, the lower centre regions are black. The reason is that very little rainwater can flow over this area because it is sheltered by the edges. All crosses are at least 20% soiled, even in those areas where the flat sections of the wall are nearly entirely white.

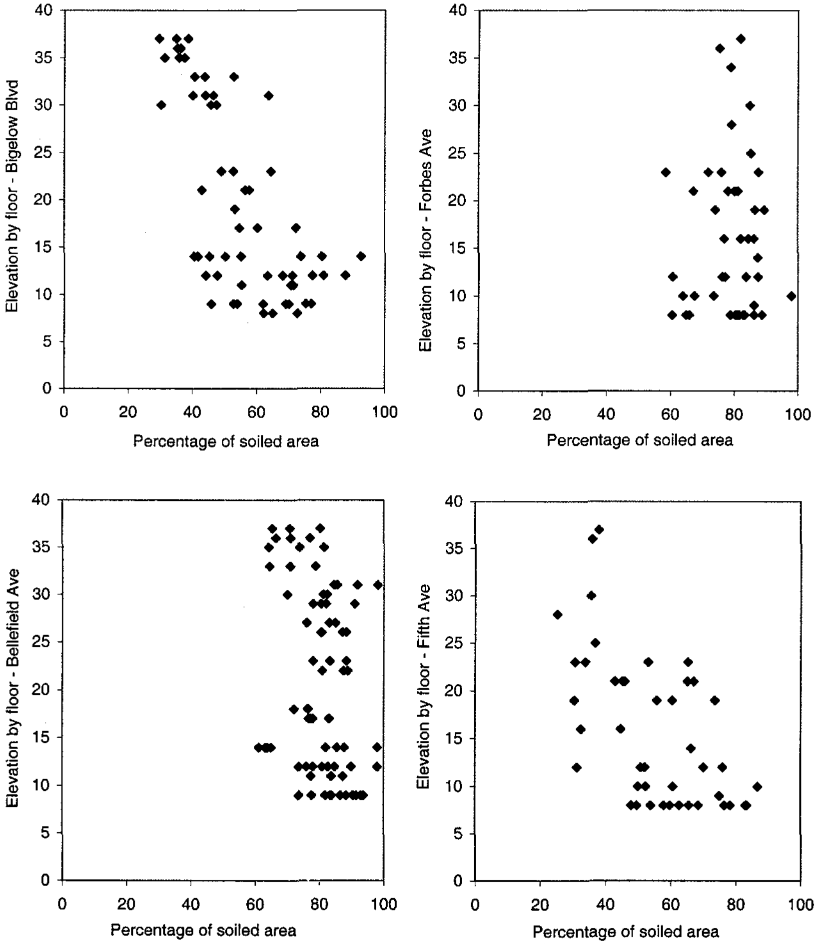


Fig. 6. Elevation versus percentage of soiled area for decorative crosses on the four faces of the Cathedral of Learning. [Reprinted with permission from the American Chemical Society (Davidson *et al.*, 2000).]

Data from the crosses are presented in Fig. 6 as plots of percentage of area soiled versus elevation. From this figure, a negative correlation between percent area soiled and elevation by floor is observed, especially for the Bigelow Boulevard and Fifth Avenue faces where more soiled areas have been washed off. However, in the 1930s, a vertically uniform soiling pattern had been present for each face of the Cathedral as suggested by Fig. 3 and other archival photographs. Furthermore, sampling of pollutants at the Cathedral has suggested that the distributions of airborne concentrations and deposition rates are roughly uniform with height at the building (Etyemezian *et al.*, 1998). This implies that differences in the amounts of soiled area as a function of height observed today are the result of differences in rain flux rather than differences in pollutant levels.

2.4. Comparison of Soiling Patterns with Modeling of Rain Impingement

To explore further the role of rain washoff, the delivery of rain to the walls has been approximated by modelling the Cathedral as a simple rectangular block. Each face has been divided into 15 sections (3 horizontal by 5 vertical sections), with each section having dimensions of 10 m × 32 m. The modelling results are presented in Fig. 7, based on the original data from Etyemezian *et al.* (2000). The highest values of rain flux are on the Fifth Avenue face while the lowest values are on the Forbes Avenue face; the Bigelow Boulevard and Bellefield Avenue faces have intermediate values. Despite differences in magnitude, patterns of rain delivery are similar for all four faces. The top sections of each face receive the greatest rain flux. Furthermore, the amount of rain delivered to the individual sections of a face increase with distance from the vertical centreline. In general, there is a reasonable, although not exact, correspondence between areas on the surface of the Cathedral that are white and sections of the rectangular block in the model that receive the most rain. Thus, the rain modelling results are consistent with both the observations of the crosses and with overall soiling patterns on the building.

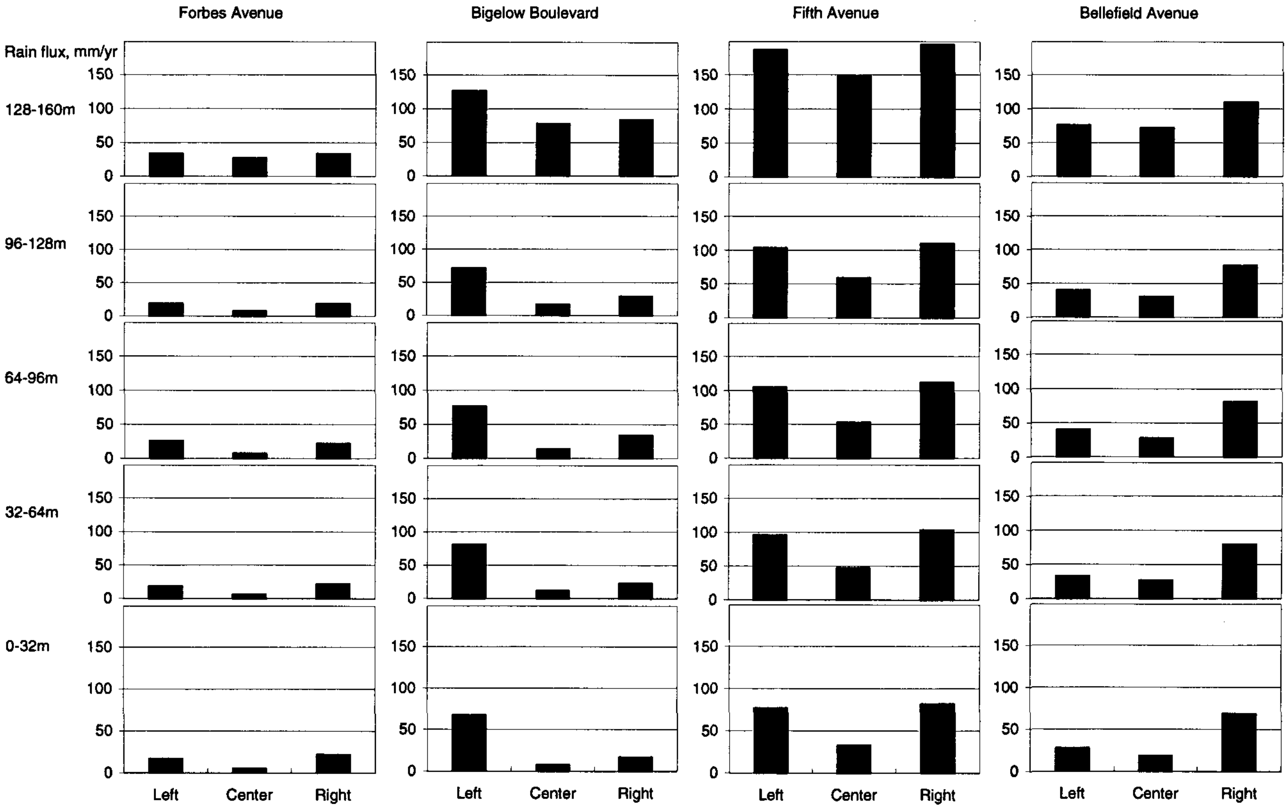


Fig. 7. Modelling results of rain fluxes on each face of the Cathedral of Learning. (Each face is divided into 3 × 5 = 15 sections with dimensions of 10 m × 32 m.)

3. Conclusions

We hypothesise that soiling on calcareous stone buildings is the result of two competing processes: deposition of pollutants and washoff by rain. We have explored this hypothesis for the Cathedral of Learning, a 42-storey limestone building constructed in the 1920s and 1930s in Pittsburgh, Pennsylvania. Several approaches have been used in this effort.

Comparison of archival with recent photographs shows that the Cathedral developed extensive soiling shortly after the completion of construction, and the soiling has decreased over the past several decades. This is consistent with decreasing trends in airborne pollutant concentrations and deposition rates since smoke control began in Pittsburgh in the late 1940s. Rainfall was roughly constant over the 60-year history of the building, and thus it is likely that the process of decrease of soiling began when pollutant levels had fallen sufficiently.

We have studied architectural features on the Cathedral to assess quantitatively the washoff of soiling on the building. By examining crosses carved into the stone at over 200 locations on the building, we have found that those carvings with the highest percentages of soiled area occur at the lowest elevations on the building. This is true despite airborne concentration and deposition data, suggesting a roughly uniform distribution of pollutants with elevation at the building. The findings are consistent with the result of modelling raindrop impingement: the lower floors of the building surface receive a smaller rain flux than the higher floors. Overall, these results suggest that soiling on buildings in polluted areas is determined largely by both pollutant deposition and by delivery of rain to the building surface.

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CHAPTER 12

EXPOSURE OF BUILDINGS TO POLLUTANTS IN URBAN AREAS: A REVIEW OF THE CONTRIBUTIONS FROM DIFFERENT SOURCES

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1. Introduction

The high density of human activities in urban areas leads to a related high density of emitted air pollutants. As a result, urban areas tend to be amongst both the major sources of and sufferers from pollutants. Both pollutant sources and their effects are multifarious. Pollutants carried by the wind disperse to cover steadily increasing areas and those from different sources overlap and combine to generate the overall level of exposure that is experienced at particular sites.

From the point of view of the recipient, whether human or inanimate, the individual sources that form this total exposure may not be readily distinguishable. For example, a given level of exposure may come from a relatively small polluting source close at hand or a large source at a much greater distance. Similarly, the contribution of individual sources to the total cannot be readily distinguished at the point of reception unless they have markedly different characteristics.

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This distinction is of more than academic interest. There is a natural and practical desire to avoid the effects of air pollution where possible. From a local point of view there may be no effective possibility of avoiding large polluting sources at long distances, which may pervade the whole urban area. However, there are greater possibilities for avoiding and controlling local sources so that their effects can be diminished by planning and regulation. This has been long recognised and the collection of urban emission inventories and their use in modelling pollution levels in urban areas became common practice as soon as it was a practicable activity (see for example, Benarie, 1980). Similarly, it is normal for static polluting discharges from combustion plant and industrial processes to be regulated by way of both emission controls and minimum heights of discharge stacks. In more recent years, there has been an additional growing control over mobile emission sources (Schwela and Zali, 1999).

Apart from the desire for pollution control in a public sense, there is also a more individual element of interest, for example in the choice of preferred sites for buildings or of the characteristics of buildings designed to suit particular sites. A particular example is the choice of ventilation systems and the placement of ventilation inlets and exhausts in order to minimise internal contamination problems. Dealing with such matters raises queries about the nature of the exposure to pollutants on specific sites and how it may vary from one site to another, over the area of the site or with the passage of time. Similarly, it may be useful to know whether pollutants are mainly due to local sources or otherwise. A further question may be the degree to which pollution levels on a particular site can be predicted from data collected elsewhere within the urban area.

It is difficult to deal with problems of this sort without some understanding of the character of discharged pollutants from different sources, especially those at varying distances, and the way in which their dispersion contributes to the overall pollution levels at a particular site. This is, of course, the usual subject of numerical dispersion studies of urban pollution. However, such studies do not cover all urban areas and it is unusual to find them using small resolution or short time scales. The smallest unit of area likely to be found in such a study is a kilometre square and the shortest time scale about an hour. At these scales, vertical and lateral gradients in the pollutant concentration are likely to be small and many models do not, in any case, consider such matters. However, individual interests are often on significantly smaller scales than this. The site of a single building, for example, may occupy scales of only 100 m or less. Within these smaller scales, there can be quite large variations in pollution levels in space and time which are significant from this smaller scale point of view.

A major factor in the dispersion of pollutants in urban areas is the severe topography due to the large number of surface obstacles, mainly buildings but including a variety of other structures. The effect of the urban topography on wind effects is well known and much discussed (see for example, Cook, 1985 and 1990), but its effects on the dispersion of pollutants at short ranges within the "urban canopy" is less well understood. The requirements for simple short range dispersion models in urban areas have recently been reviewed by Hall *et al.* (1996b) who discuss these problems in more detail.

The relationship between pollution levels at these different scales is the subject of discussion in the present paper. It is dealt with in a generic way, rather than with reference to specific pollutants or pollution problems and illustrated with examples from dispersion studies, both at full and model scales, and with pollution monitoring data from urban areas. One of the most important features that distinguishes the character of different pollution sources is their distance from the point of interest, so that in the discussion that follows, the characteristics of pollution sources are mainly treated in terms of increasing distance.

2. Dispersion Over Different Scales in Urban Areas

2.1. *The Definition of Scales and Spatial Variability*

The term "scale" of air pollutants can apply to both space and time. Both are important for various reasons and they are connected by way of the mean windspeed, which sweeps pollutants over a specific area in a given time while dispersing them. In his thorough and very interesting monograph on "The Design of Air Quality Monitoring Networks", Munn (1981) covers a number of aspects of urban pollution that are relevant to the present discussion. In considering time and space variability, he defines some characteristic scales of spatial air pollution patterns, which in order of increasing size are:

Microscale (0–100 m)
Neighbourhood scale (100–2000 m)
Urban scale (5–50 km)
Regional scale (100–1000 km)
Continental, hemispheric and global scales.

The ranges are as defined by Munn and do not overlap. However, as the values are approximate this is not important. These are roughly the different scale orders that have been used here, as they correspond fairly well to the different types of dispersion patterns that occur. Only the first three scale orders are of direct interest as variables within the scale of urban areas. Pollution levels at the larger two scales would show no significant variation over the scale of an urban area and would class as contributors to the "background level" of pollutants in the area. Quite what should be classed as "background" levels of pollution is considered later in the paper.

In a similar way, Munn defined a number of characteristic time scales associated with pollutants:

Minute to minute variations
The daily (diurnal) cycle
Large scale weather fluctuations (3–5 days)
Weekly emission cycles
Annual emission and weather cycles.

It can be seen that these are associated either with natural meteorological cycles or with patterns of human activity. For the shorter ranges mainly of interest here, it is useful to subdivide the shortest time scale into two further divisions related to the stochastic (i.e. the unsteady) nature of dispersing pollutant plumes:

Times below which the fluctuating characteristics of dispersing plumes are apparent (typically seconds)

Times beyond which the time-averaged concentrations in dispersing plumes are stable (typically minutes).

The time scales associated with this subdivision are a little arbitrary as the time scales for stable time-averaged concentrations do not have finite limits and are also affected by large scale wind disturbances, of the sort readily generated by windflows around buildings in urban areas.

It was noted earlier that the spatial and time scales are related to some extent by the windspeed. Thus, taking typical UK windspeeds around the mean, say 3–5 m^{-1} per second, the microscale and shorter neighbourhood scales are associated with time scales of seconds, the longer neighbourhood scales and lower urban scales with time scales of minutes and the upper urban scales and regional scales with time scales of hours. The continental and larger scales correspond to time scales approaching days and beyond.

It is the combination of the multiplicity of discharged polluting sources from this range of distances in the generally upwind direction that produces (simply by the summing of instantaneous pollutant concentrations) the overall pollution level that is experienced at the point of interest. In principal, the contributions of these sources to the overall level are not distinguishable and one of the major reasons for dispersion modelling is as a means of making this distinction. However, there are differences in the character of the contribution from sources at different distances, both in their spatial and tem-poral characteristics, that help to identify them and their contribution to the total. The ensuing discussion attempts to characterise these differences and the ways in which they affect the combined pollution levels experienced at the point of interest.

2.2. Dispersion at Short (Microscale) Ranges

The definition of "short ranges" is a little arbitrary, but implies here sources which are mostly within direct line of site of the point of interest or where dispersing plume widths are relatively small compared with the scale of the surface obstacles. The practical range may be anywhere from 10 m to 1 km, and in exceptional cases further. Thus, this may embrace both the microscale and neighbourhood scales defined by Munn. For low level sources in urban areas, the limiting distances are usually of a few hundred metres and are thus closer to Munn's microscales.

The critical characteristics of dispersing plumes within this scale range are their high pollutant concentrations, small footprint, rapidly fluctuating intensities and (especially within urban areas) meandering qualities. The majority of polluting discharges are from "point" sources, that is their cross-section at discharge is small compared with the plume cross-section even at short distances. This applies, for example, to most combustion and process plant discharges, vehicle exhausts and many ventilation discharges. In these cases, undisturbed discharge plumes are highly concentrated; most of the pollutant material is contained within a subtended angle from the source of about 10°. Thus within the small area of the dispersing plume, there are high concentrations of pollutant, with little pollutant material elsewhere. Also, because of the stochastic (unsteady) nature of dispersion, there will be large variations of concentration within the plume itself. Figure 1 (taken from Hall and Kukadia, 1994) is a visualised dispersing plume which shows clearly the intermittent nature of the concentrations locally within the plume. Because of the stochastic properties of dispersing plumes, at distances within a few hundred metres, it is possible for small regions of undiluted source material to exist and this has been observed in field experiments by Jones (1983).

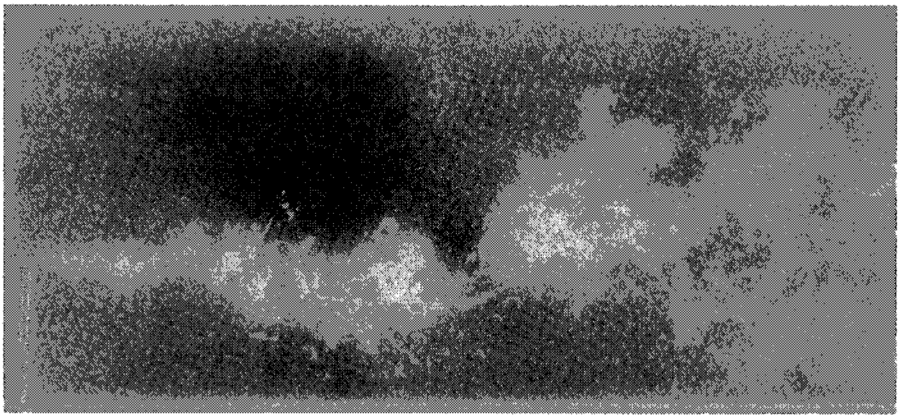


Fig. 1. Visualised dispersing plume showing variable pollutant content.

Besides the internal variability of pollutant concentration in the plume, the wind environment near the ground in urban areas usually shows a high degree of variability in speed and direction due to the aerodynamic disturbances from buildings and other large structures. This introduces an additional variability in the plume path, usually described as plume "meandering". Thus the overall characteristic of exposure to a dispersing pollutant at short ranges is usually of relatively infrequent, highly intermittent exposure over short periods (of the order of seconds) to relatively high pollutant concentrations. The importance of rapid fluctuations in pollutant levels in a number of applications has recently been discussed by Jones (1996).

In urban areas one strongly modifying factor to this description is the ability of buildings and other large structures to generate rapid dispersion of discharged pollutants over large areas in the aerodynamic wake regions behind their downstream faces. This generally results in a much larger area of exposure to the pollutants, though at lower concentrations than with the slender plume, and in a more persistent and time-continuous form.

Figure 2 shows an illustration (taken from Hall and Kukadia, 1994) of these two types of exposure to a dispersing plume at short ranges. It shows measurements made in the field by Helen Higson of the Environmental Technology Centre (UMIST), of a pollutant plume approaching and dispersing around a rectangular building in otherwise smooth terrain. The plots are of pollutant concentration against time and show two cases, in the undisturbed plume upwind of the building (Case a) and in the region of rapid dispersion in the wake region behind the building (Case b). On both plots, the mean concentration is shown as a broken line. The traces are typical of the two types of dispersion. That in the undisturbed plume shows large variations in concentration, with fluctuations well in excess of the mean, over periods of seconds, and a high degree of intermittency (i.e. there are significant periods when no pollutant is present in the plume). The concentration/time trace downwind of the building shows the continuous presence of pollutant with relatively low levels of fluctuation, so that levels of concentration remain close to the mean. If the plume were dispersing in an urban area, the concentration trace upwind of the building would show additional intermittency

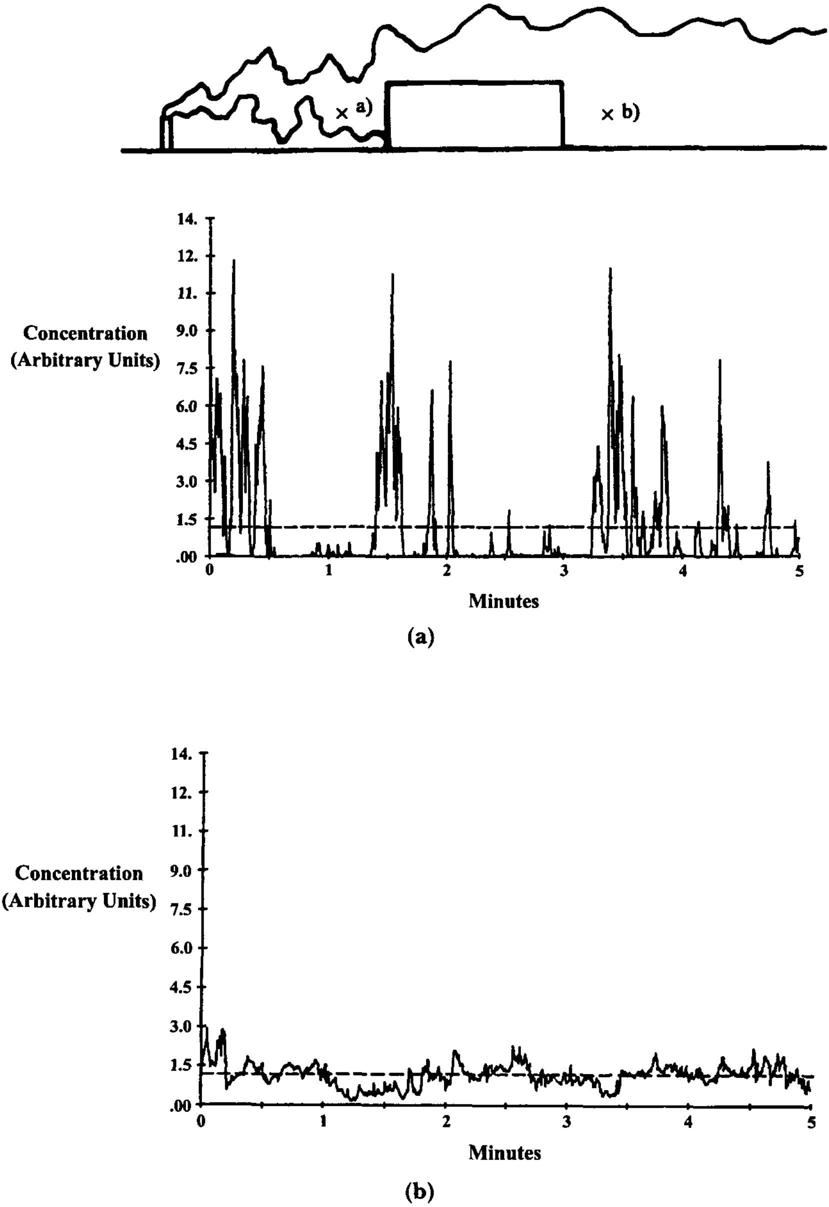


Fig. 2. Concentration/time measurements of the pollutant in a plume dispersing at short ranges near a rectangular building. (a) In the undisturbed plume just upwind of the building. (b) In the wake region in the lee of the building.

due to meandering of the plume and thus longer periods without the presence of any pollutant.

Exposure to pollutants at short ranges in urban areas is a combination of these two types of dispersion pattern, depending upon the siting of the discharge and the presence of buildings and other surface structures. The form of the exposure need not be one type or the other, it is also possible for both regimes to occur together, so that the exposure is the sum of the two traces (Fig. 2). Figure 3 shows a sketch of a situation in which this will occur, with a polluting discharge on the downwind side of a building. Here, over the longer term the discharge is dispersed in the building wake region, as in Fig. 2(b). However, since the point of discharge is also in the building wake region, in the shorter term there is an additional exposure to the highly concentrated meandering plume in the disturbed flow in the building wake, as in Fig. 2(a).

A practical example of this is shown in Fig. 4 (taken from Hall *et al.*, 1996a), which shows small scale wind tunnel measurements of concentration/time traces at the ground behind a building of similar shape to that of Fig. 2, for a pollutant source just behind the building at different heights ranging from ground level to 1.5 building heights. With the source on the ground, the mean wind carried the dispersing plume away from the point of measurement, so that only the longer

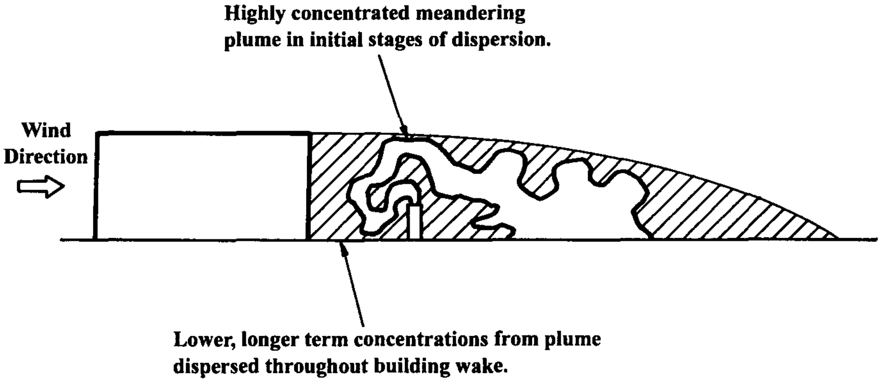


Fig. 3. Sketch of a situation in which the dispersion patterns of Fig. 2(a) and (b) can occur together.

term concentrations in the building wake, as in Fig. 2(b), were observed. However, for the next two pollutant source heights the discharge was within the wake region and the sampling station recorded both the longer term concentrations in the re-circulation regions

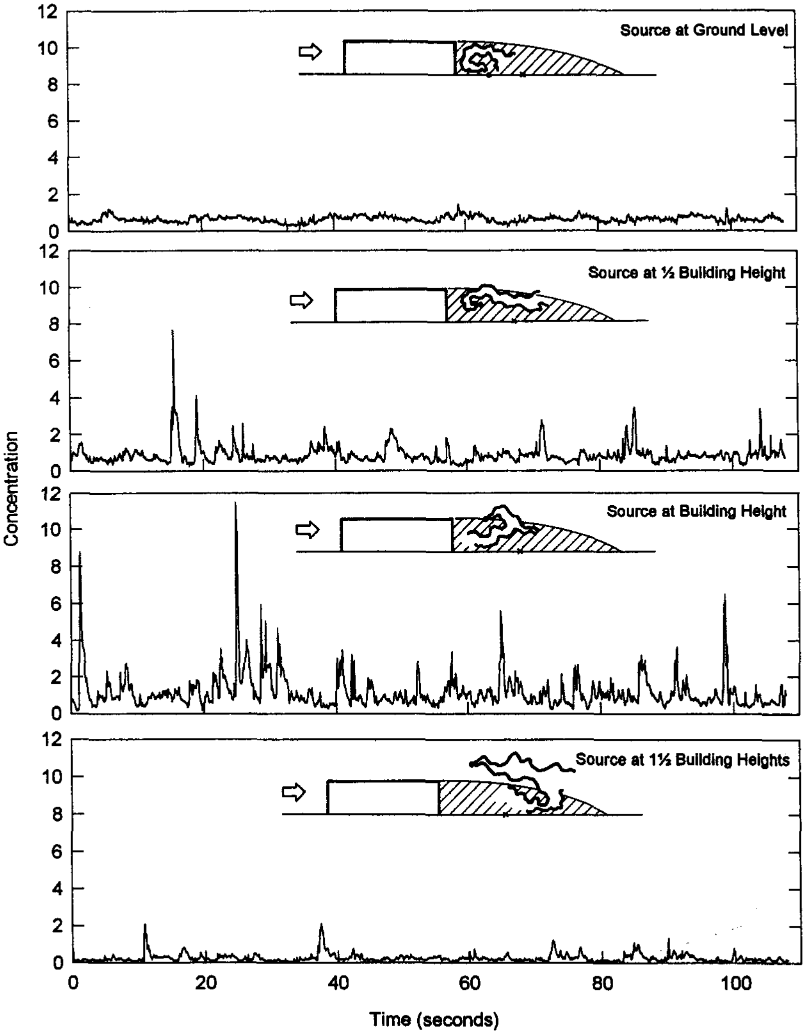


Fig. 4. Concentration/time traces at the ground in the lee of a building due to contaminant sources at different heights also in the lee of the building.

together with shorter term intermittent high concentrations from occasional exposure to the meandering plume. The final source height, at 1.5 building heights, discharged pollutant above the wake region, but part of the plume dispersed downwards and was entrained into the building wake further downwind. The sampling point was again then exposed to the two types of dispersion pattern, but concentrations were lower than before as only part of the dispersing plume was entrained into the wake. In urban areas, where the occupational density of buildings and other structures is high, dispersion patterns like those in Fig. 4 are likely to be the most frequently occurring at short ranges.

Polluting sources at short ranges generate high levels of spatial as well as temporal variability in urban areas. The disturbed windflows that are a feature of urban areas generate a spatial variability that is not only high but which is also sensitive to source position and to the meteorological parameters, especially wind direction. There can, for example, be very large variations in pollutant concentrations across the corners of a street intersection or between the windward and lee

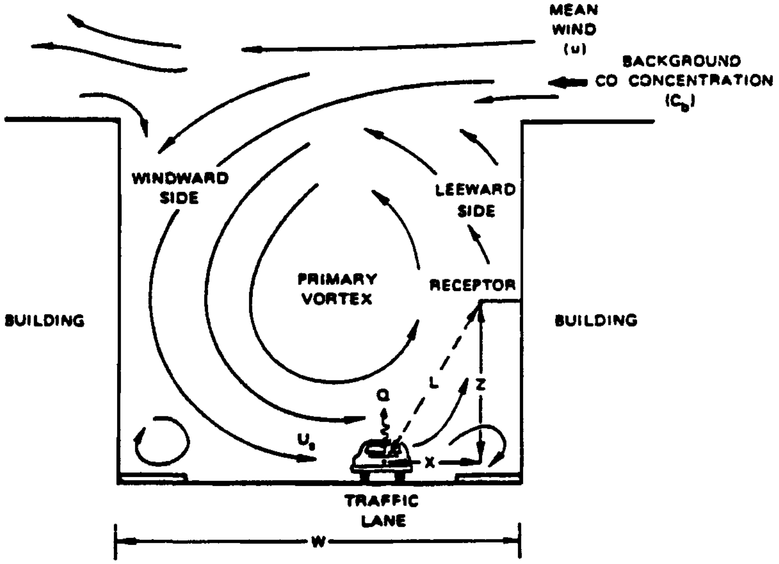


Fig. 5. Simplified flow pattern in a street canyon (from Dabbert *et al.*, 1973).

faces of a building. It is not proposed to discuss this complex subject in detail here, but a few examples of small scale plume behaviour at short distances are given which show the effects clearly enough. Figure 5, taken from Dabbert *et al.* (1973), shows a simplified representation of the flow pattern in the space between buildings in an urban area, frequently described as a "street canyon". Figure 6, from Oke (1987), shows some mildly misleading representative dispersion patterns in urban areas covering a variety of source positions and shows the complex plume paths that can occur. Diagrams like those in Figs. 5 and 6 usually imply a wind square on to the layout of buildings and streets and fail to take into account the additional complexities introduced by the more commonly occurring wind directions, which are skewed diagonally across the street array. Figure 7, from Hoydysh and Dabbert (1994), shows a more realistic example of the large variations in mean concentration that can occur at a street intersection for

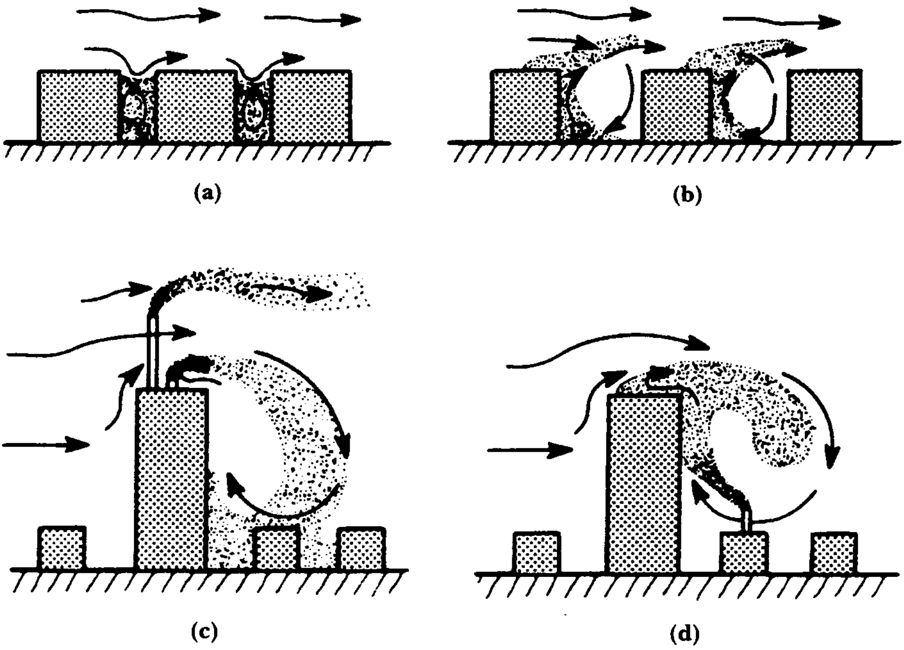


Fig. 6. Potential pollutant plume paths at short ranges from sources in urban areas. (from Oke, 1987).

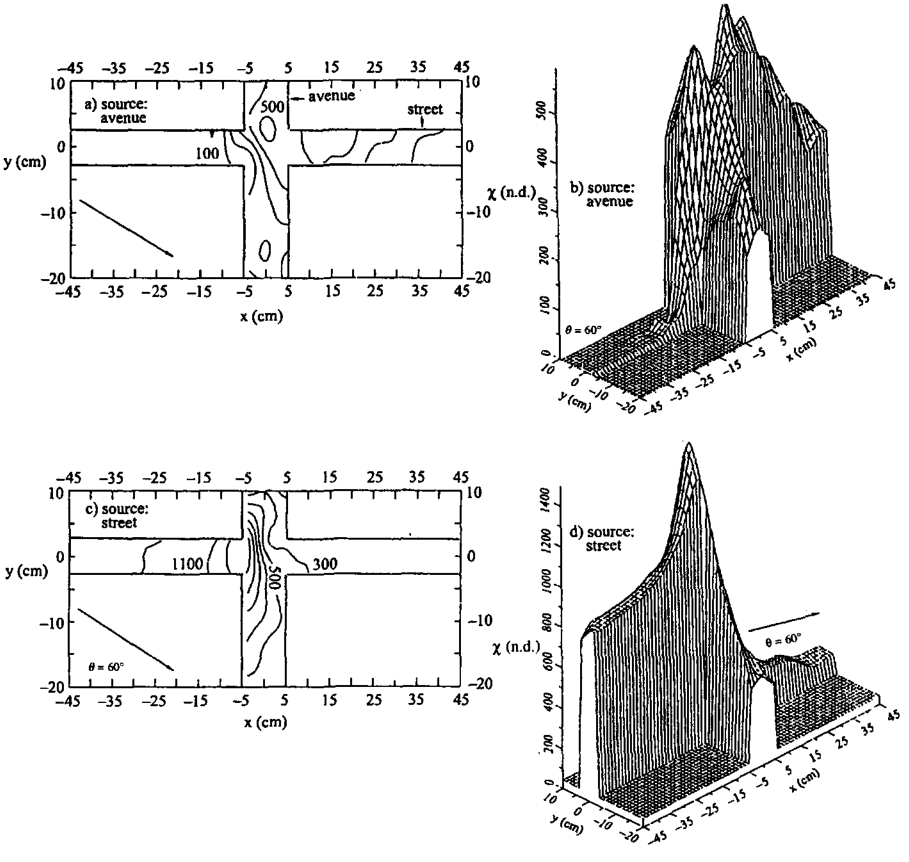


Fig. 7. Mean pollutant concentration patterns at a street junction with a skewed wind direction (from Hoydysh and Dabbert, 1994).

a fixed wind direction skewed across the street array (the measurements were made using a small scale wind tunnel model).

2.3. Dispersion at Neighbourhood Scales (100–2000 m)

Within the greater distances of neighbourhood scales, the high levels of spatial and temporal variability that mark out microscale dispersion patterns reduce. Though spatial and temporal variability in concentration remain, the associated time and distance scales increase. Apart from distance itself, the most important factor influencing this change remains the surface topography, mainly the buildings and other surface obstacles. At these greater ranges, however, it is the size, layout and packing density of the structures in urban areas that are the most important features, rather than the shapes of individual structures and their immediate surroundings, as is more the case with microscale dispersion patterns.

As a rule of thumb, once a source of pollutant is out of line-of-sight in an urban area, the effects of building wakes on dispersion become more important, so dispersion patterns become more stable and the short term variations in concentration should pass from a state like that of Fig. 2(a) to one more resembling that of Fig. 2(b). With increasing distance the diffusing effects of larger numbers of buildings come into play and the variability further reduces. There remain additional complex types of behaviour related to the surface topography. For example, the tendency of pollutants to be channelled along clear paths in the surface topography due to street patterns, which causes higher concentrations in this region.

The spread of pollutants at neighbourhood scales is not presently a well researched subject, though this is a rapidly growing interest (Hall *et al.*'s (1996b) review discusses most of the existing literature). It is difficult, therefore, to provide a clear description of pollutant dispersion at these distances. As noted above, it is the size, layout and packing density of the buildings that most affect the spread of pollutants. The most recent research suggests that, of the characteristics of the urban form affecting the spread of pollutants, it is the mean height and across-wind widths of the surface structures which has the greatest effect. The typical characteristic of the spread of pollutants at neighbourhood scale is a rapid vertical mixing over (and a little above) the heights of the surface structures in distances covering three to four rows of buildings in the direction of the wind. Beyond this distance, there is a slower rate of vertical spread to greater heights. Lateral spreading is fairly rapid over the individual building widths and further lateral spreading at greater distances depends upon the relationship between building widths and spacing.

It is within the neighbourhood scales and microscales that significant vertical gradients of pollutants can occur. This is a matter of practical interest, for example for human exposure and for the placement of ventilation intakes. As a broad generalisation, it might be considered that pollutant sources at or close to the ground would produce falling levels of pollutant concentration with increasing height, and that pollutant sources at or above the building heights would produce rising pollutant concentrations with increasing height. In urban areas, the dominant near-ground pollutant source is vehicular traffic. A recent emission inventory for the UK West Midlands area has suggested that vehicle emissions are now the major urban polluters (Anon, 1996); similar estimates have been made for Copenhagen and Milan (Vignatti *et al.*, 1996). The dominant pollutant sources at or above building height are mainly discharges from combustion plant and industrial process, for most of which activities there are regulatory requirements in the UK that discharges should be above their immediate surroundings. However, there are in addition a variety of other pollutant discharges at intermediate heights, for example ventilation exhausts (which are often associated with odour problems), standby generators and discharges from some types of gas-fired heating plant.

This broad generalisation for vertical gradients of contamination is of limited reliability. The plume paths sketched in Fig. 6 indicate that at the shorter scales there may be substantial short term local variations in the vertical pollutant gradient for sources at any height from changes in the dispersion patterns due to local aerodynamic effects. The longer term mean of the vertical gradient of pollutants can also vary. Figure 8 shows measurements of the vertical variation of pollutant from sources at the ground in a small scale simulation of an urban area in a wind tunnel, using arrays of cubes set in rows (from Hall *et al.* 1998). Measurements are shown for the surface obstacles occupying 16 and 69% of the ground surface area (the "Area Density"), typical values respectively for a suburban housing estate and the more densely packed central region of an urban area. The pollutant profiles are at distances covering one, three and about ten rows of the surface obstacles, which is a more important criterion than the absolute distance. For a typical urban area with buildings 10–20 m high, the equivalent range of distances was from 100 m to 2 km. The height of the obstacles is marked as a "building height" on the plots, below which the plot is shaded. For the greatest distance, both plots show quite

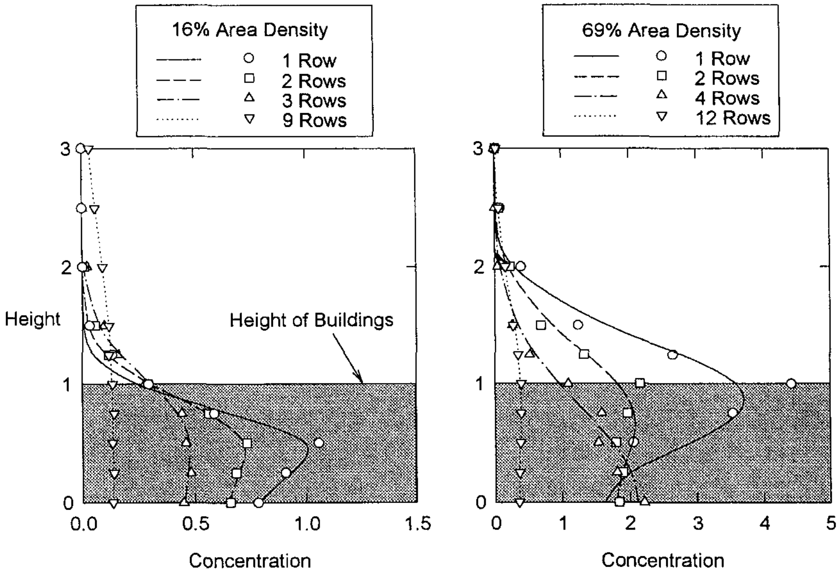


Fig. 8. Vertical profiles of pollutant concentration at different distances through simulated urban arrays with two different densities of building occupation (16% and 69%).

uniform gradients of pollutant to heights well above the obstacles. However, at the shorter distances of a few rows of the obstacles there are sharper gradients, both positive and negative. The measurements show positive gradients near the ground at the shortest distances (behind a single row of obstacles) for both area densities. However, with increasing distances covering additional rows of the obstacles, the gradients become more uniform at the lower area density but pass from positive to negative at the higher area density. In all the cases of distances up to a few rows, the gradient near the top of the obstacles was negative, so that there was a distinct reduction in the level of pollutant at the tops of the obstacles. The implication is that pollutant levels from nearby ground-based sources may well be significantly lower at roof level than lower down, but that below roof level, pollutant levels can vary in complex ways with no certainty as to the vertical gradient of pollutant. It can also be seen in Fig. 8 that, at a given distance from the source, pollutant concentrations are significantly greater for the higher density of obstacle packing than for the lower density.

There seem to be few field measurements of the vertical gradient of pollutants in urban areas. Figure 9 shows some early measurements by Georgii *et al.* (1967) of carbon monoxide (CO) on either side of a street. Since vehicular traffic is the major source of CO, the measurements are largely for a distributed, ground-based source. In this case, the gradient is of reducing concentration with increasing height, but it is interesting that measurements either side of the street are markedly different, the windward side having the lower values. Figure 10 (taken from QUARG, 1993) shows the results of a scan by a remote sensing device (a LIDAR) of the contours of nitrogen dioxide (NO_2) in a London street with dense traffic. The concentrations fall with increasing height above the ground, but show another maximum above building level. It was remarked in this context that the higher maximum might be due to further oxidation of nitrogen monoxide (NO) to NO_2 above the buildings, where more ozone was present. This argument seems a little tenuous for such short time and distance scales, but the higher maximum could equally well be due to

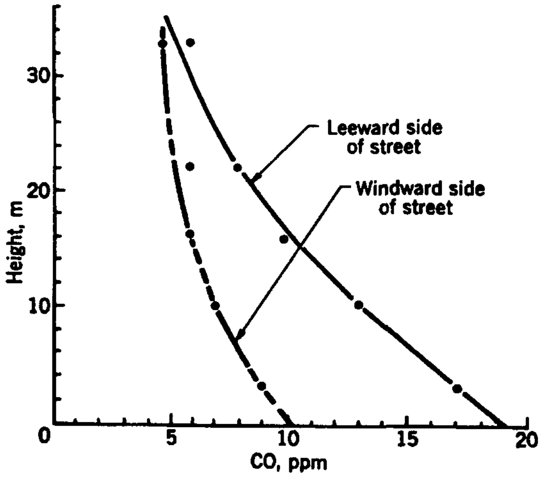


Fig. 9. Vertical profiles of CO concentration on the windward and leeward sides of a street (from Georgii *et al.*, 1967).

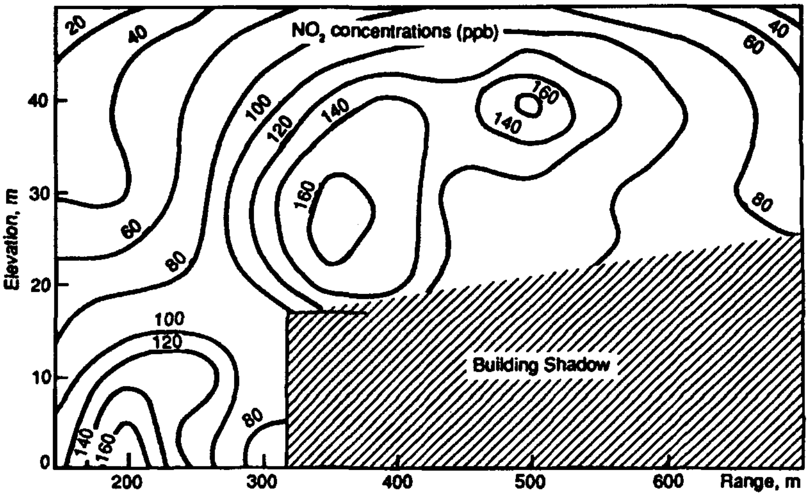


Fig. 10. Remotely sensed contours of NO_2 in a London street with dense traffic (from QUARG, 1993).

a high level discharge from a local combustion plant or some feature of the local dispersion pattern.

2.4. *Dispersion at Urban Scales (5–50 km)*

Pollutant sources at these distances and beyond, disperse to heights well above the heights of the surface structures and spread over relatively large widths. At 5 km distance, the bulk of the pollutant from a single source is contained within a height of about 250 m and a width of about 1 km. At 50 km distance, the respective heights and widths are about 600 m and 8 km. Pollutants are then starting to mix uniformly within the depth of the surface boundary layer. Also, the large numbers of pollutant sources likely to be contained in the upwind fetch at these scales, which contribute to the total pollution level at a point by addition, produce a more diffuse and slowly changing pollutant level. Thus there are negligible vertical and lateral concentration gradients over all but the very largest surface structures. This is also the regime for which pollutant residence times in the atmosphere are sufficient for chemical processes to occur, for example the oxidation of NO to NO_2, and the generation of photochemical smog.

Most urban modelling studies are carried out at these and greater scales, using mapped inventories of emission data from various pollutant sources and suitable meteorological data. Traditionally, these have been concerned with predicting pollutant levels over relatively long averaging periods, from a day to a year. However, with the recent recommendations of shorter term exposure limits for human exposure to sulphur and nitrogen oxides (EPAQS, 1995 and EEC, 1985) there is a growing interest in making shorter term predictions. Two examples of the results of modelling studies are shown here. The first, due to Ott (1977), in Fig. 11, is an example of the pollutant concentration pattern to be expected from vehicular traffic occupying a grid of streets. It shows the higher levels of pollutants at the junctions and the rapid fall-off of pollutant levels away from the road that appear to occur in practice. This can be compared with the measurements of pollutant concentration at a road junction shown in Fig. 7 from a small scale model experiment, which also show the high concentrations at the junction. The second is due to Timmis and Walker(1989), in

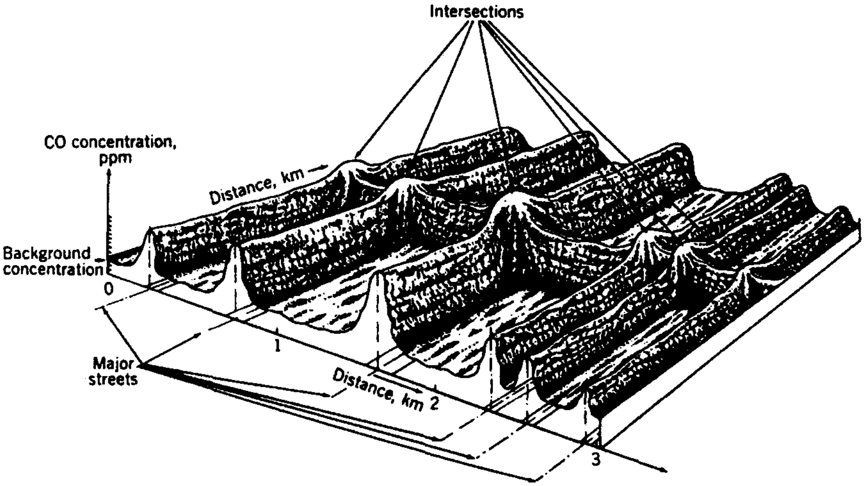


Fig. 11. Map of urban pollutant levels from vehicular traffic on a grid of streets (from Ott, 1977).

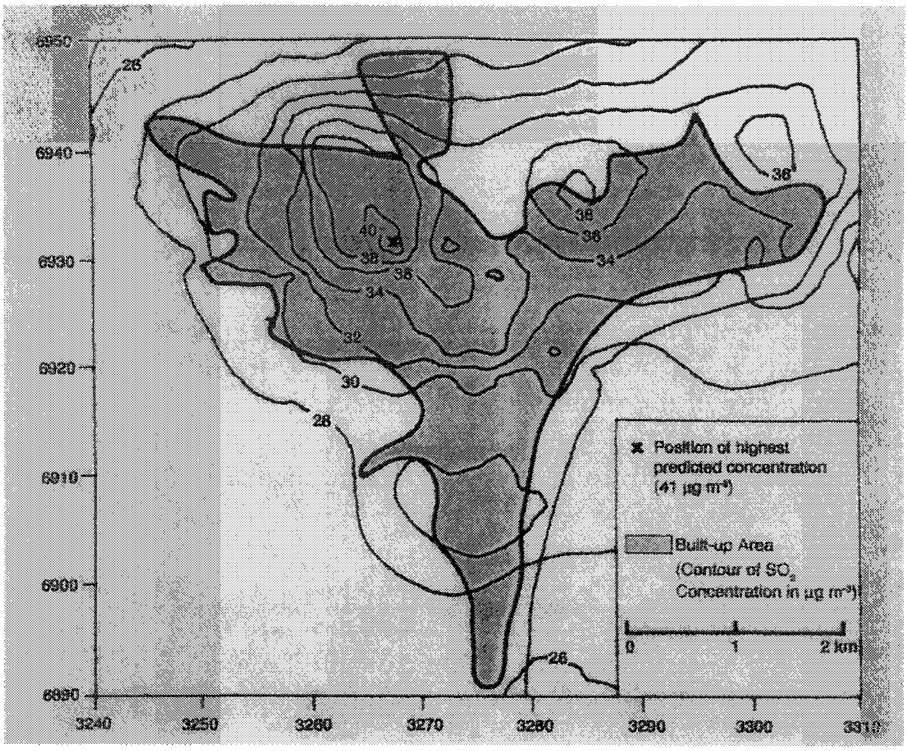


Fig. 12. Contour map of calculated winter mean SO_2 levels in Kirkaldy (from Timmis and Walker, 1989).

Fig. 12, and shows contours of calculated estimates of winter mean sulphur dioxide levels in Kirkaldy, Scotland.

2.5. Dispersion at Regional and Continental Scales (100 km +)

Pollutant sources at these distances uniformly pervade the surface boundary layer, and thus to heights usually well above those of the surface structures, and show only small variations over large areas and long times. At the same time, the pollutant level at a point is usually composed of the sum of the contributions from a very large number of individual sources. At the longer distances of these regimes, even diurnal variations in pollutant discharges are smoothed out and pollutant levels mainly vary with changes in the weather pattern or long term patterns of use. The "upwind" pollutants may have followed complex wind trajectories generated by the weather pattern. These are also the scales at which longer term atmospheric chemical processes occur, such as the further oxidation of nitrogen and sulphur oxides to nitrate and sulphate.

Pollutants at these distances thus constitute the true "background" concentration levels of urban areas in that they pervade the whole area at a uniform level which changes only slowly. They cannot be controlled or avoided within the scales of an urban area. Otts' diagram in Fig. 11 includes a base level of background pollutant concentration to which the local sources additionally contribute.

2.6. The Overall Pollutant Concentration Level Due to the Contribution of Sources at Varying Scales and "Background" Concentrations

It was remarked earlier in this paper that it is the sum of the pollutant concentrations from the multiplicity of pollutant sources at the whole range of upwind distances that produces the overall pollutant concentration level at a point of interest. From the descriptions of the temporal and spatial character of the pollutant levels from sources in the different distance regimes, it will be appreciated how the overall pollutant level is built up from components with a variety of characteristics. Figure 13 shows a hypothetical example of this, with the components from the different distance scales summing to produce the total pollutant level at some point in an urban area. The level of temporal fluctuation and its frequency increases as the scales of the pollutant source distances increase. Thus, the high frequency component of the overall pollutant level is due to the microscale and neighbourhood scale components and the stable long term base level of the pollutant concentration is due to the urban, regional and continental scale components. The spatial variability can be expected to follow the same sort of pattern, with the microscale and neighbourhood scales sources producing the greatest spatial variability and the urban, regional and continental scales, the lowest. It will also be appreciated that it is not readily possible to determine the precise contributions of pollutant sources at the different scales to

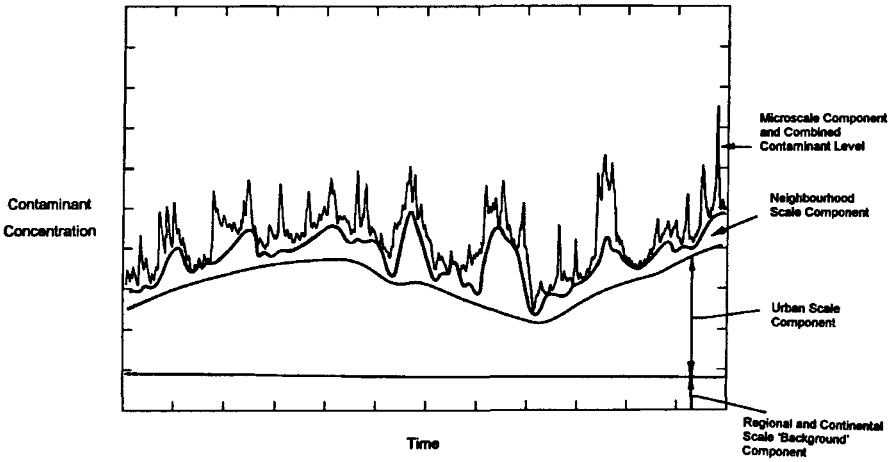


Fig. 13. Hypothetical example of the contributions of pollutants from different source regimes to the combined pollutant level at a point.

the total pollutant concentration level except, within limits, by their different frequencies of fluctuation.

The form of the overall pollutant concentration curve with time in an urban area will depend upon the relative contribution from the different distance regimes. For example, in the UK if there is an anti-cyclonic weather pattern with light easterly winds during a holiday period, then the long range contribution of pollutant sources from Europe will be high and the urban and smaller scale contributions will be low. Thus, the overall curve will show low relative levels of short term fluctuation and low spatial variation. Alternatively, if there are westerly winds carrying relatively uncontaminated air from the Atlantic during a busy working day, the long range contributions will be low but the urban and smaller scale contributions will be relatively high. Thus the overall curve will show a higher level of short term fluctuation over a relatively small "background" concentration.

The question of what should be considered as "background" pollution is not formally defined. It tends to be regarded as a nearly constant, all pervading level of the pollutant over the area which changes only slowly with time. As noted earlier, on this basis it is pollutants dispersing over regional and continental scales that may be regarded the true "background" level of pollutant. However, "background" is also used to describe the longer term average pollutant levels, irrespective of their source. This is a common procedure when, for example, dealing with the additional contribution of a new local source of pollutant. However, in this case it will be appreciated that there will be shorter term excursions in the pollutant level locally which are well above the "background". The definition of a "background" level thus depends to some extent on the purpose to which it is put. From the point of view of, say a single building, any pollutant level which is largely unvarying across the scale of the building might be regarded as a "background" level of pollutant. This would imply spatial scales of the order of a few hundred metres, though the associated temporal scales would be typically some tens of seconds. If, as an alternative, a "background" level was required that indicated the average level of exposure of a building ventilation system over its air exchange rate, a temporal scale of between ten minutes and an hour would be more appropriate, with the implied urban and regional spatial scales.

3. Some Examples of Urban Pollutant Data

3.1. Pollution Monitoring Sites in the West Midlands Area

To provide an illustration of the characteristics of pollutant levels in urban areas, we have used data from the UK National Network sites in the West Midlands to investigate the degree to which pollution levels at a particular site are related to those at different sites within the same urban area. There are three sites normally operating in this large urban area, but for an additional period, recently, BRE carried out measurements of pollutant levels in the same area as part of a building ventilation study (Kukadia and Palmer, 1996 and Kukadia *et al.*, 1996). The ventilation study incorporated both external and internal measurements of various pollutants at a site in the centre of Birmingham. This has in effect provided an additional monitoring site as well as a comparison of indoor/outdoor pollutant levels. The main interest here is in the external measurements. The original report on this study (Hall *et al.*, 1996c) contains additional data to that shown here.

A map of the West Midlands area showing the National Network sites, the site of the building used for the ventilation study and of the meteorological site are shown in Fig. 14.

The buildings used in the ventilation study (site B in Fig. 14) were located in the central commercial district of Birmingham close to a

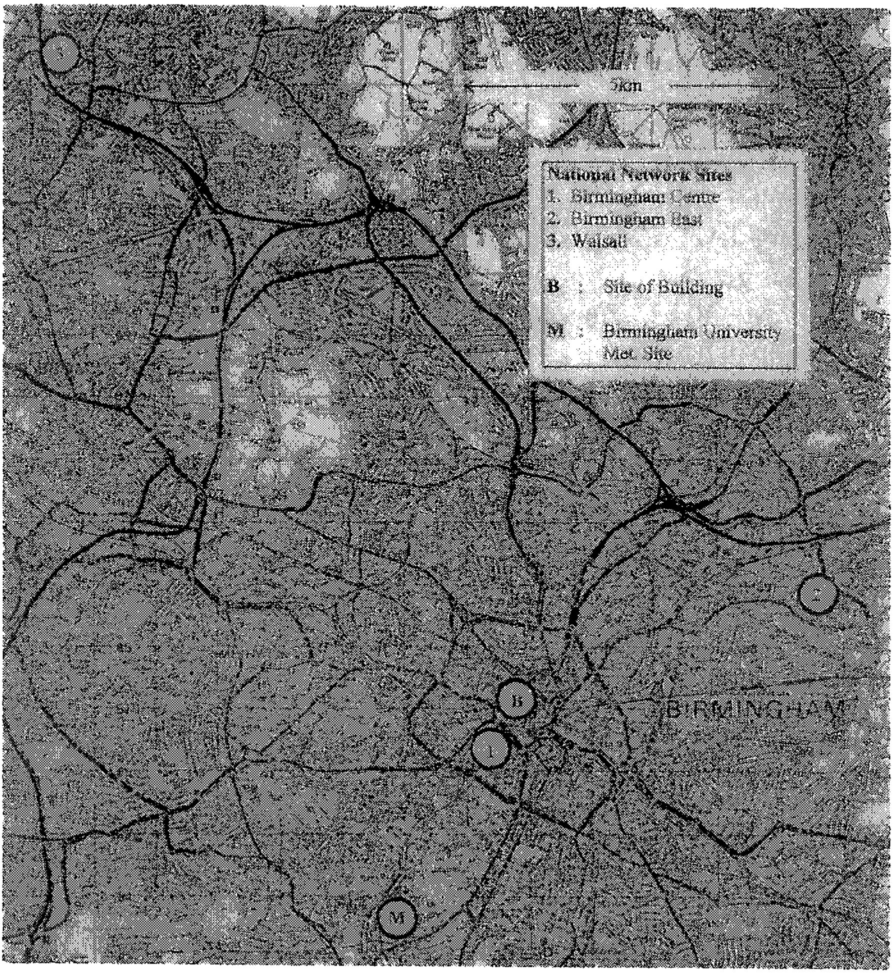
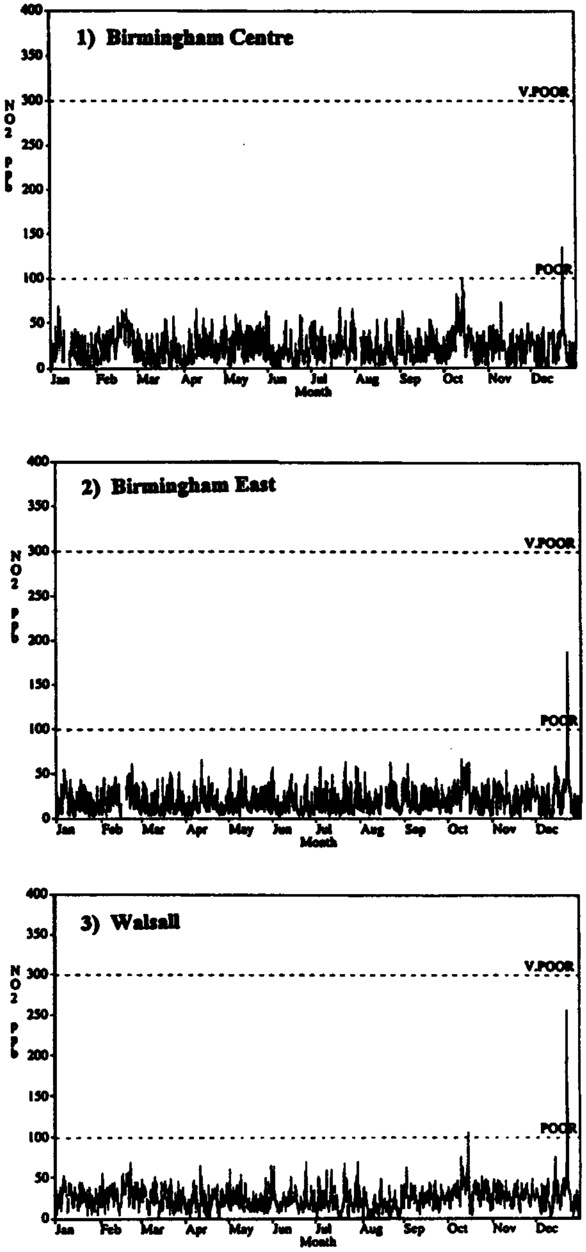


Fig. 14. Map of the West Midlands area showing the various monitoring sites.

busy eight-lane roadway (Great Charles Street). The external measurements were made outside the naturally ventilated building (referred to as the CB Building) about 3 m above the footway at the side of this main road. Of the three network sites (sites 1, 2 and 3 in Fig. 14), the closest to this building is the Birmingham Central site which is about 560 m to the south-west. This site is located in a pedestrianised area (Centenary Square) 100 m from a main road and 10 m from a small carpark. The other two network sites are located further away from the city centre. The Birmingham East site is about 5 km ENE of the building and is sited within the playground of a junior/infant school in a residential area. Finally the third site, at Walsall, about 13.5 km to the north of the city centre, is also a school site in a residential area, but is 200 m west of the M6 motorway (carrying 70,000 vehicles per day) and 500 m north of a smelting plant.

Pollutants monitored at the ventilation study site included sulphur dioxide (SO_2), NO, NO_2 and CO, these are also monitored at the two Birmingham network sites. The Walsall site only monitors NO and NO_2, so we have mainly looked at NO_2 as a common pollutant between the sites. Examples of the latest annual data (taken from AEA, 1995) are reproduced in Fig. 15 for hourly measurements of NO_2 at the three sites. The annual mean levels are broadly similar at 46 ppb (Birmingham Central), 38 ppb (Birmingham East) and 61 ppb (Walsall). However, inspection of the plots in Fig. 15 shows that though there are some observable peaks in common (like that towards the end of December), the shorter term fluctuations show only limited similarities between the sites even on this basis of hourly averages.

Data at the CB Building were available for the period 14–21 February 1996 and so this period was chosen for more detailed study. For the ventilation study, the data were recorded with an averaging time of 5-minutes, however only 15-minute averages were available for the network sites and so 15-minute averages were calculated from the CB Building data. Data for shorter averaging times than 5 minutes is difficult to find; most pollution monitoring instruments need to average over a few minutes to smooth instrument noise from the signal at low levels of concentration. However, there were significant differences between even the 5- and 15-minute averaging times noted


1) Birmingham Centre

2) Birmingham East

3) Walsall

Fig. 15. Annual, hourly mean, measurements of NO_2 for the three National Network Sites in the West Midlands.

above. Figure 16 shows this difference for one example, for SO_2 measurements on 14th February, together with data for a 60-minute averaging time; this latter averaging time matches the hourly mean annual data shown in Fig. 15. The data shows significant additional fluctuations with reducing averaging times, especially for 5-minute averaging time compared with 15. Shorter averaging times than 5 minutes would show much greater fluctuations.

Hourly wind speeds and directions were obtained from Birmingham University as part of the ventilation study. The University is located about 4 km south-west of the city centre, as shown on the map in Fig. 14.

The weather in Birmingham during the week of measurements began with a mobile anti-cyclone crossing the country on the Wednesday and Thursday (14th and 15th of February), resulting in fairly low windspeeds (1–5 m s^{-1}) from the north-west over Birmingham.

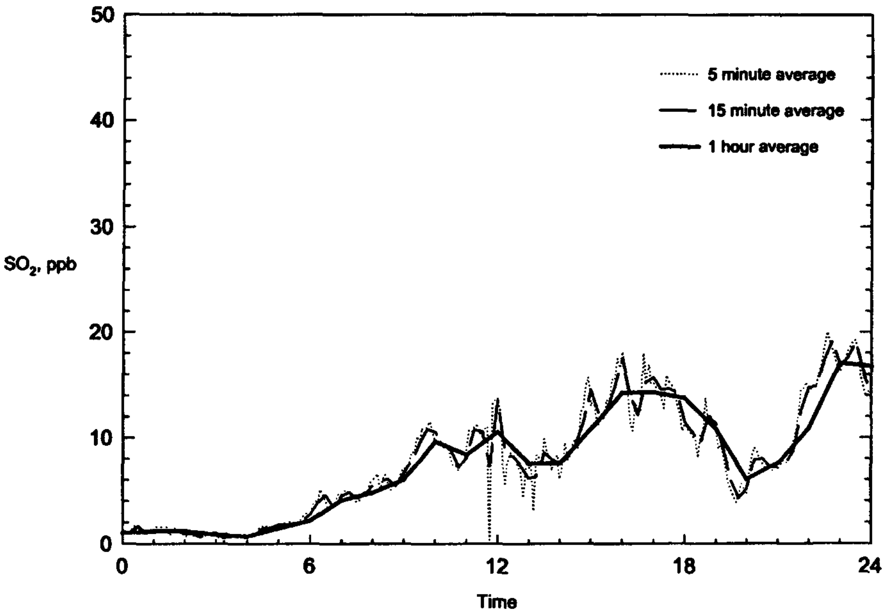
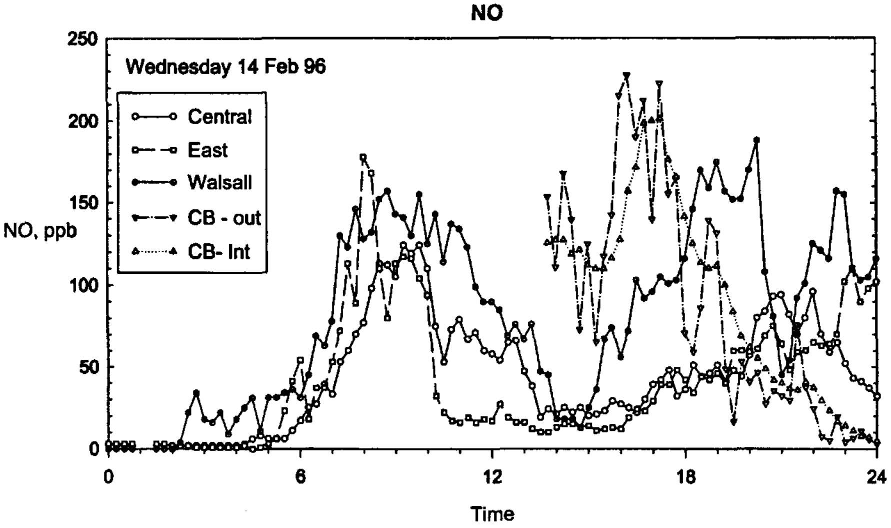


Fig. 16. Effect of 5-, 15- and 60-minute averaging times on concentration fluctuations (SO_2, 14th February).

This period was followed by a return to a changeable west/north-west flow across the country with windspeeds increasing during the second half of Thursday (15th) and during Friday (16th) to 10–14 m per second from the west. There was some intermittent rainfall during Thursday evening and early Friday morning but temperatures were mild. During Saturday (17th), the wind backed towards the south by the end of the day, with windspeeds falling to between 7 and 9 m per second. It was cloudy throughout the day with some rainfall during the evening. On Sunday (18th), a vigorous depression tracked south-eastwards from Scotland to North Germany bringing a very strong northerly airflow across the country. Windspeeds in Birmingham remained around 9 m per second throughout Sunday, Monday and Tuesday (18th, 19th and 20th), apart from a slight lull late on Sunday. The wind direction gradually veered from south-west early on Sunday to north by Monday morning and remained between north and north-west during Monday and Tuesday (19th and 20th). There were frequent rain and snow showers throughout the latter half of the study period (Saturday 17th to Tuesday 20th) and temperatures were low.

Figure 17 shows examples of NO and NO_2 measurements at all the sites for a single day, Wednesday 14th February. Measurements inside the building, when available, are also shown as the solid symbols on the plots. All pollutant levels were relatively low, none approached any limit or guideline value. The mean windspeed for 14th February ranged between 3 and 5 m per second up to about midday, after which it fell steadily to about 1 m per second at around midnight. The wind direction remained consistently in the arc 300°–330°. Thus, the Walsall and Birmingham Central/CB Building sites were nominally aligned with the wind direction, while the Birmingham Central/CB Building sites and the Birmingham east site were nominally aligned across the wind. To a first approximation at these windspeeds, in the 15-minute averaging time of the sampler, the accumulated pollutants from upwind distances of about 1–3 km are swept past it. Similarly, the lateral dispersion of pollutants over these distances results in pollutants over a band of about 200–500 m across the wind (at this greater distance) being averaged across the sampler. Thus, the sampler is averaging pollutant levels over a wedge-shaped area upwind of around



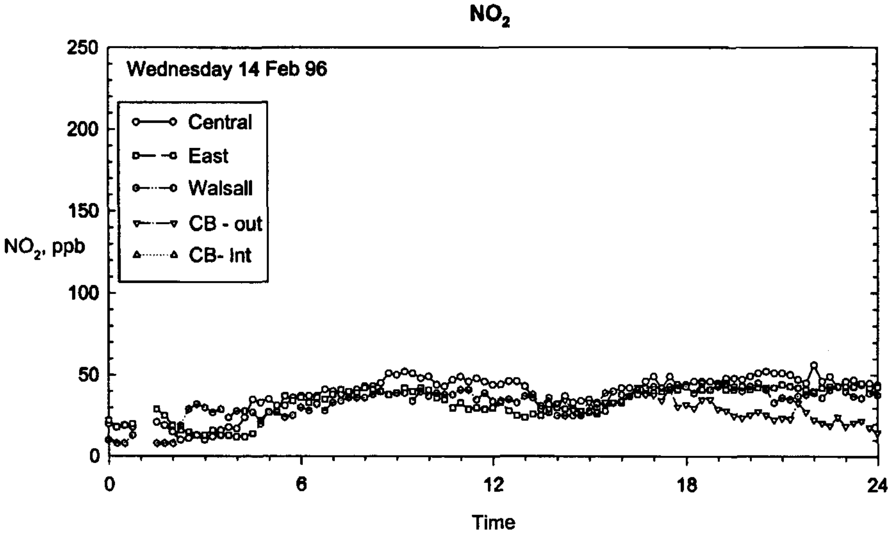


Fig. 17. Measurements of NO and NO_2 for a single day, Wednesday 14th February (15-minute means).

0.25–1 km^2. These distances correspond to the approximate boundary between neighbourhood and urban scales as defined by Munn.

The NO_2 concentrations showed relatively low levels of fluctuation and some similarity in trends between the sites. The NO concentrations showed quite marked variations during the course of the day and high levels of fluctuation even with 15-minute averaging times. Also, on a visual basis, none of the NO concentrations at the sites appeared to show much correlation between one another apart from the broad morning and evening peaks. This applied even to the Birmingham Central and CB Building sites, which were only about 500 m apart. Here, levels of NO_2 were generally higher at the Birmingham Central site, while levels of NO were lower.

The question of what might constitute a "background" level of pollutants for these sites is clearly not a fixed matter. The implication of the term "background" is of some lower limit below which levels do not usually fall, though other definitions have been used for different purposes. In practice, this can only be expressed on some statistical basis which will depend upon the application. For example, a "background" pollutant level for the West Midlands area, encompassing all the sites, might be defined as the common level of pollutant that occurs at all sites, that is the lowest common denominator of the data. In Fig. 17, a lowest common denominator "background" level is effectively the lowest data point at a given time from any site on the plot. All the sites contribute to this minimum at some point. For NO_2, where the level of fluctuation is relatively low, the "background" on this definition usually comprises a significant proportion of the overall concentration at any site. For NO, however, where the level of fluctuation is high, the Birmingham East site produced the lowest concentrations most frequently but not consistently. It will also be appreciated that when there are large fluctuations in pollutant level, such a definition would depend upon the data averaging time chosen. As this increases, the "background" level on this definition would tend towards the long term mean.

Thus for individual sites, it is difficult to define a "background" except on the basis of some pollutant level exceeded at a specific frequency, such as a 10%ile, for some particular averaging time.

3.2. Correlations of Pollutant Levels Between the Sites

In order to quantify the degree to which pollution levels at each site might be related to each other during the week 14–21 February, values of the correlation coefficient (r^2) were calculated between data from pairs of sites for each day and for each pollutant.

This was first investigated with the Birmingham Central and CB Building sites. Since these were the closest, it was thought that they ought to show the highest correlations. Initially, 15-minute averages were used and each 24-hour period was considered as a whole. Correlation coefficients between the data at the two closest sites, Birmingham Central and the CB Building, were calculated and the values obtained are given in Table 1. It can be seen that, with the exception of the last two days of the period, there is little correlation between pollution levels at these two sites. It was thought possible that the correlation might be greater for longer averaging times, since this would have the effect of smoothing out the high frequency fluctuations that are probably due to more local sources and emphasising the common elements in the two data sets. Two longer averaging periods were investigated, 30 minutes and 1 hour. The correlation coefficients obtained are also given in Table 1. In general, as would be expected, the correlations increased with increasing averaging time, but there are also some instances where the converse occurred. The changes in values of r^2 are mostly small and there is still only a limited degree of correlation between the two sites. Two cases, one showing higher values of r^2 (increasing with averaging time) and one lower (decreasing with averaging time), are shown plotted respectively in Figs. 18 and 19. It is of interest that even with such short spacings between sites, the correlations between the measurements can frequently be negligible.

The same approach was used to investigate the relationship between the Birmingham Central and Birmingham East Sites, which have a much greater spacing. We examined the correlation between data at the sites for occasions when the wind was largely blowing from the centre towards the east and compared these results with occasions when the wind was perpendicular to this, across the line of the sites. In the former case, there may be evidence of pollution from sources

Table 1. Correlations between Birmingham Central and CB Building for different averaging times.

Date	CO			NO			NO_2			SO_2		
	15 min	30 min	1 hour	15 min	30 min	1 hour	15 min	30 min	1 hour	15 min	30 min	1 hour
Wed (14.2.96)	0.13	0.14	0.17	0.36	0.34	0.40	0.10	0.11	0.14	0.07	0.08	0.12
Thurs (15.2.96)	0.01	0.004	0.01	0.12	0.12	0.10	0.01	0.005	4×10^5	0.11	0.13	0.18
Fri (16.2.96)	0.11	0.22	0.29	0.15	0.22	0.27	0.42	0.51	0.64	0.07	0.09	0.12
Sat (17.2.96)	0.001	0.001	0.002	0.001	0.002	0.01	0.10	0.10	0.09	0.05	0.06	0.08
Sun (18.2.96)	0.16	0.21	0.29	0.12	0.23	0.37	0.67	0.69	0.61	0.06	0.07	0.08
Mon (19.2.96)	0.002	0.003	0.004	0.02	0.02	0.03	0.03	0.03	0.03	0.04	0.04	0.05
Tues (20.2.96)	0.52	0.58	0.68	0.47	0.59	0.72	0.58	0.59	0.58	0.13	0.17	0.20
Wed (21.2.96)	0.35	0.52	0.72	0.50	0.57	0.62	0.23	0.29	0.39	0.56	0.52	0.79

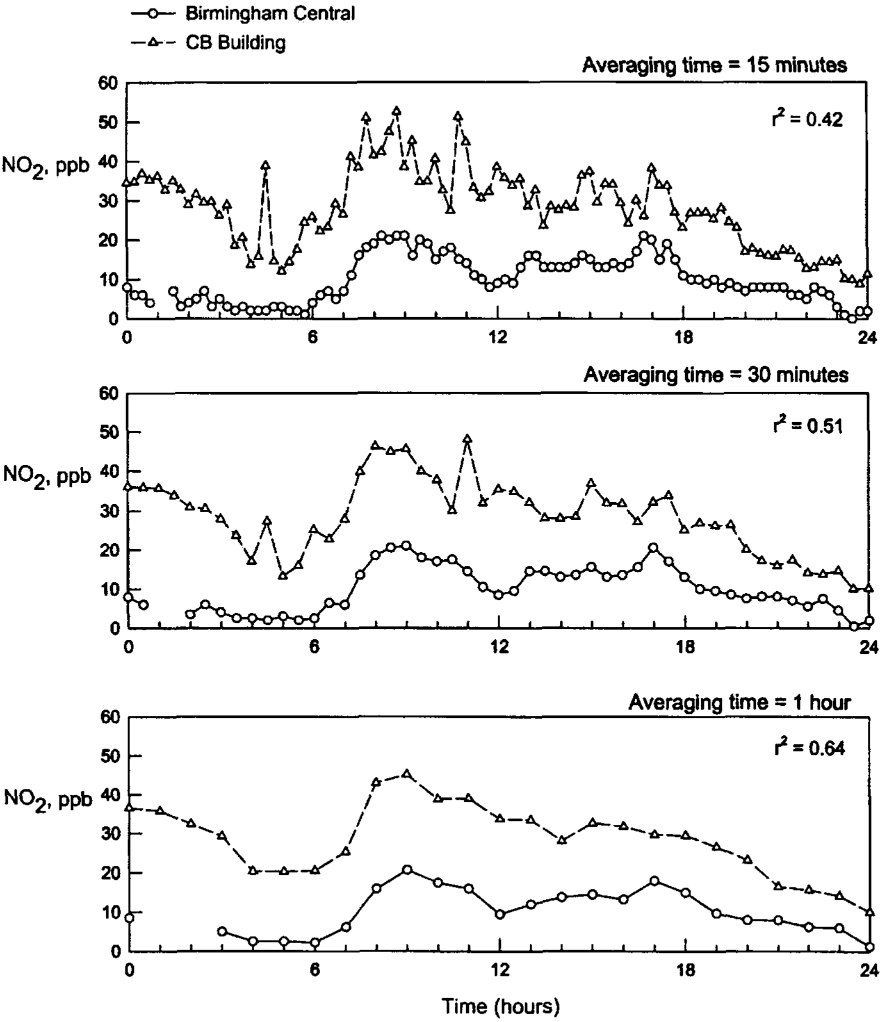


Fig. 18. Correlations between NO_2 concentrations at the Birmingham Central and CB Building sites for different averaging times (data for a period with high correlation, 16th February).

close to the central sites travelling to the eastern site, and so higher correlations may be obtained by allowing for this travel time. Conversely, in the latter case there may be larger correlations since the contributions in the two areas from more distant sources might be more similar as the area over which these pollutants originate is almost the same.

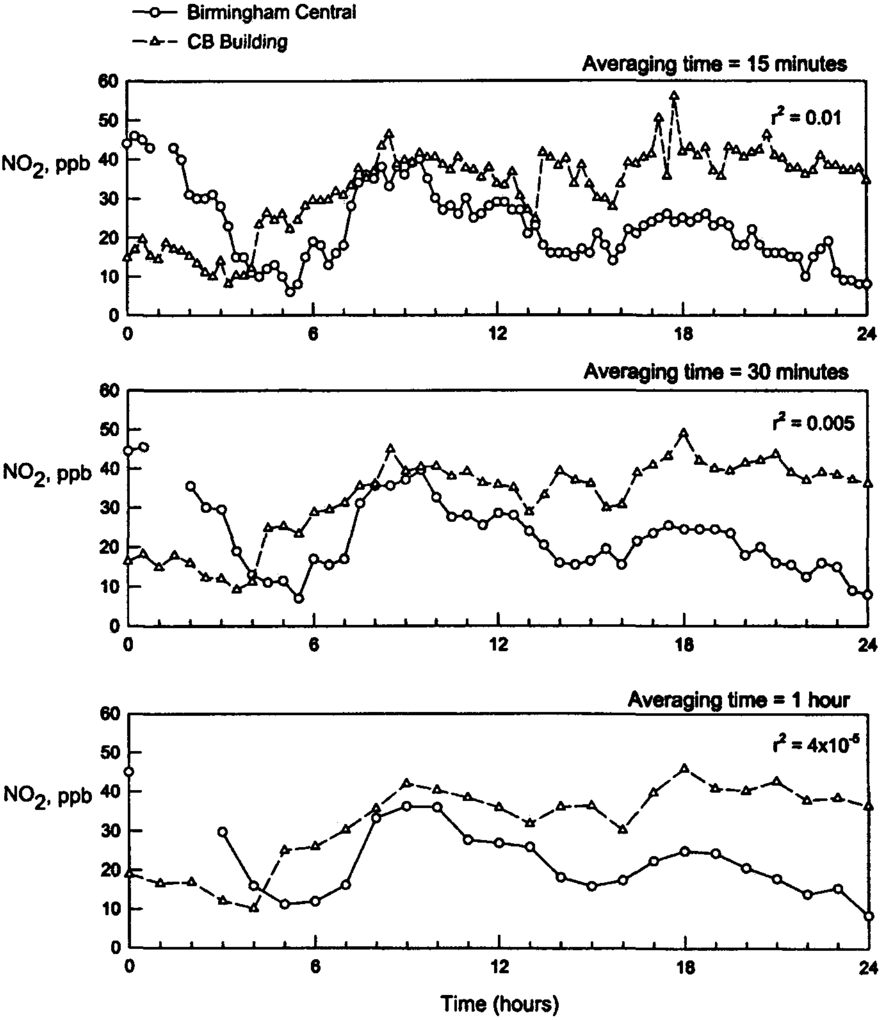
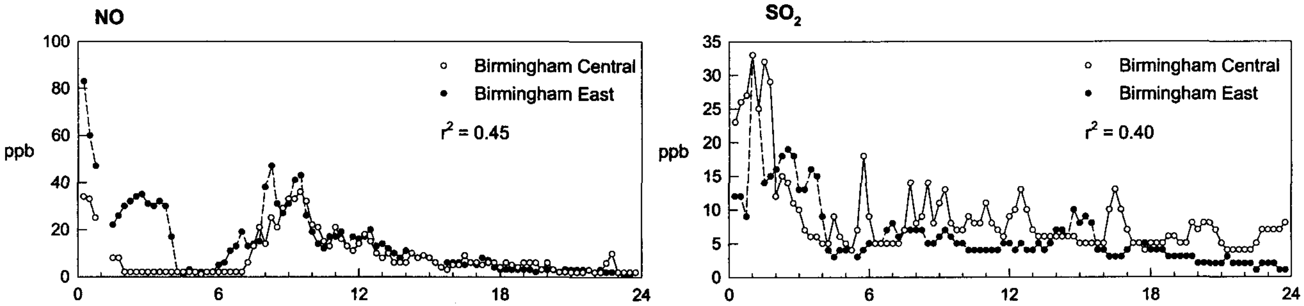


Fig. 19. Correlations between NO_2 concentrations at the Birmingham Central and CB Building sites for different averaging times (data for a period with low correlation, 15th February).

Two days were identified with wind directions largely from the centre to the east sites (i.e. south-westerlies) — Thursday 15th and Friday 16th. These were compared with three days when the wind was mostly from the north-west and thus blowing across a line between the

(A) No travel time between sites



(B) Allowing for travel time between sites

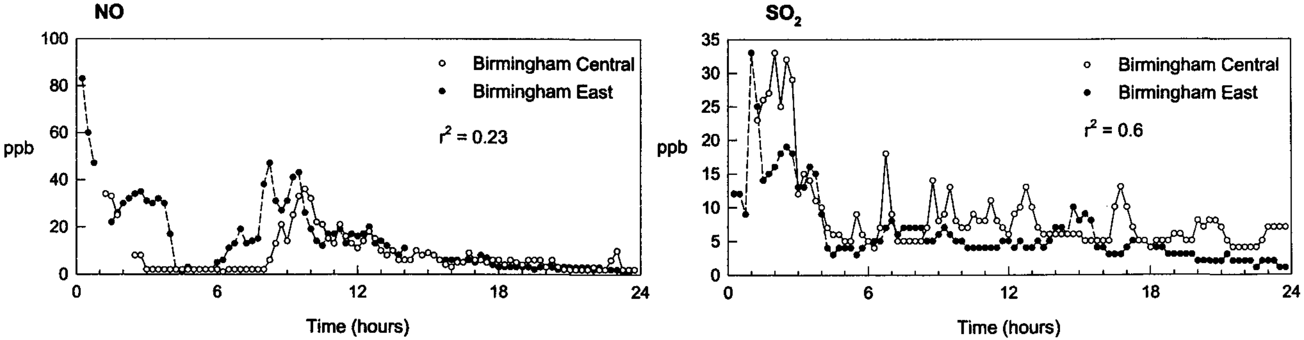


Fig. 20. Correlations for NO and SO$_2$ concentrations between the Birmingham Central and East sites with an aligned wind (15th February).

central and the eastern sites — Wednesday 14th, Monday 19th and Tuesday 20th. Examples of the time series and the correlation plots for NO and SO_2 are given for Thursday 15th in the upper plots in Fig. 20, when the wind was aligned between the sites. It can be seen that there is some broad consistency between concentrations at the two sites, resulting in a relatively high correlation.

One further type of correlation was briefly investigated, which was to account for the approximate travel times between the Birmingham Central and East sites. The same periods as before were used for this. Average windspeeds were calculated and the time of travel between the central sites and the east site evaluated, the data for the central sites were then time-shifted by this amount and the correlation coefficients re-calculated. It should be noted that, because 15-minute averages were used, this time shift could only be carried out to the nearest 15 minutes. The lower plots in Fig. 20 illustrate the effect of this time shift. The values of r^2 are given in Table 2. It is evident that overall, the time-shifting has little effect on the relationship between the data in the two regions.

The results of all of these calculations for the Central and East sites and for the Central and CB Building sites are given in Fig. 21. The correlations between each of the central sites with the east site as well as those between the two central sites are given for each of four

Table 2. Correlations between Birmingham Central and Birmingham East sites for occasions when wind blowing from central to east (correlations for data as measured and allowing for travel time between sites).

Pollutant	Day/Date	Data as measured	Including time delay
CO	Thursday (15/2/96)	0.09	0.13
	Friday (16/2/96)	0.13	0.02
SO_2	Thursday (15/2/96)	0.4	0.6
	Friday (16/2/96)	0.001	0.008
NO	Thursday (15/2/96)	0.45	0.23
	Friday (16/2/96)	0.46	0.58
NO_2	Thursday (15/2/96)	0.4	0.3
	Friday (16/2/96)	0.8	0.7

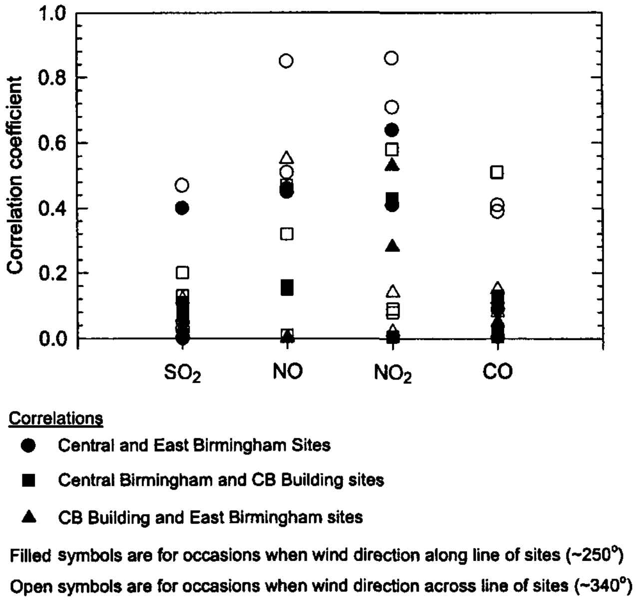


Fig. 21. Overall correlation coefficients between Birmingham Central, CB Building and Birmingham East sites for all pollutants.

pollutants. There is also a division between wind directions broadly aligned between and across the line of the sites. There is little consistency between the results and the correlation coefficients vary considerably. It can be seen that, overall, the higher correlations tended to be when the wind was across the line of the sites.

4. Discussion

It will be appreciated from both the initial discussion and from the example data analysed above that the prediction of pollutant concentrations at specific sites in urban areas is not a perfectly straightforward matter. However, the way in which different sources, especially at varying distances, contribute to the overall levels at a particular site, and the causes of variability in these levels can be understood. The sample data analysed here comprised only a snapshot of pollution characteristics over a short period. However, this is sufficient to show that wide variations in shorter term pollution levels over even quite short distances in urban areas can be expected as a matter of course. Data from monitoring sites is valuable as an indicator of trends in pollution levels and as an indicator of longer term pollution levels over a wider area, but its ability to predict local variations, both spatially and temporally at other places is limited. Most monitoring equipment has a relatively slow response, of the order of minutes and thus fails to record the quite substantial fluctuations that can occur over shorter time scales. Similarly the use of dispersion modelling to predict the pollution characteristics over large areas is mainly confined to relatively coarse grids, usually of kilometre or greater scale, and to longer term averages (one hour is the minimum period and much longer time averages are more common). Information on these small scale variations is presently quite limited. There is a need for pollution monitoring investigations in urban areas which look at both very short term variations in pollution levels and the spatial variation over short distances.

From the point of view of the needs of a specific site, it is clear that data from monitoring sites even relatively close by can only be certain indicators of broad-based, long term pollution levels and that more detailed data, especially if shorter term variations are of interest, would require site-specific investigations.

5. Conclusions

(1) The paper has outlined the way in which pollutant sources, especially from varying distances, contribute to different features of the total concentration at a point. Both spatial and temporal variations of pollutant concentration can be large and generally increase with reducing averaging time and spatial scale.

(2) An investigation of a sample of data from four sites in the West Midlands confirms these characteristics, with significant levels of temporal fluctuation and spatial variation over relatively short distances. Correlations of data between different sites frequently show negligible correlation, even over short distances or relatively long averaging times.

6. Summary

The paper describes the characteristics of different types of pollutant sources in the way that they are experienced in a fixed locality in an urban area. The locality in this sense can also be a building or part of a building (a ventilation inlet for example). The most important parameter is the distance of the polluting source and therefore the characteristic features of sources at different distances are discussed. The relationship between "local" sources and "background" levels of pollutants, their contributions to the total local pollution levels and the vertical and lateral gradient of pollution are considered. The discussion is illustrated by examples from measurements of dispersing plumes and of urban pollution levels experienced during a specific investigation in a large urban area.

Pollution levels can show large fluctuations, which increase with reducing time scales, and significant spatial variation over short distances. Measured pollution levels on four sites in a large urban area, the West Midlands, showed these characteristics for averaging times down to one minute and spatial separations of 500 m. Data correlations between the sites were generally poor.

Acknowledgements

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CHAPTER 13

THE WHOLE BUILDING AND PATTERNS OF DEGRADATION

R. Inkpen

1. Introduction

Degradation of natural building stone occurs at particular locations on different types of buildings that may have undergone different conservation treatments. The buildings may be simple monuments such as standing stones or complex configurations such as Norman cathedrals. In either case, the processes of stone decay cannot be divorced from the built form nor from the socio-economic framework that established and maintains that building. Most studies of stone degradation and suggestions for conservation measures, however, operate as if building stone degradation can be abstracted from the context of its formation. Laboratory-based and small-scale studies have outlined a range of degradation mechanisms for different stone types. From these studies, indices of degradation have been constructed, the effectiveness of different stone types and conservation treatments assessed and dominant agents of decay identified. The underlying assumption has been that degradation processes identified at the small-scale operate in the same manner at the large-scale. Similarly, the environmental system and its variation within which weathering occurs are assumed to be a mirror-image of the conditions constructed and controlled in the laboratory. The building scale is seen as a simple extrapolation of process/form relationships and their associated environmental parameters identified from small-scale studies. Initially, this chapter explores the role and limitations of small-scale studies for identifying and quantifying the processes and relationships causing stone degradation at the scale of the whole building.

Based partly on small scale studies, many workers have used information on process/form relationships to construct classification systems for degradation on buildings. From such systems, the spatial variability of forms thought to be associated with different weathering agents can be identified and mapped across the building (for example in Inkpen *et al.*, 2000; Inkpen *et al.*, 2001). Likewise, the spatial variability of environmental parameters, such as moisture content or chemical composition can be sampled and mapped over a surface. Combining the two spatial distributions a correlation can be established between different weathering agents and forms. Implicitly, such combinations suggest causal relationships between environment, agents and weathering forms. Some of these systems can also be predictive, highlighting where certain types of weathering agents are likely to be dominant on new buildings. Although some of these systems begin to tackle the complexity of relationships causing weathering at the scale of the building, they all tend to look at the forms produced rather than the context of production. Discussion of the limitations of these classification schemes forms the next section of the chapter.

Context is both multi-dimensional and spatially and temporally variable. It can include the general weathering environment which lie beyond the scope of the building itself as well as the composition of building elements. At the large-scale, the nature of weathering environment sets the constraints on the type of weathering agents present and the scope of their actions and so indirectly the range of weathering rates and forms. At the scale of the building itself, weathering context can be studied using the concept of the catchment area as a fundamental unit on the building. This unit is of use in exploring the socio-economic factors that impinge upon the weathering behaviour of the building. Decisions on the financing of construction and repair work as well as what conservation treatments to employ and when, for example, will all influence how weathering agents interact with the stone. Socio-economic factors are not, however, limited to those explicitly concerned with maintainence of the building. There are also wider issues which impinge upon current and future weathering behaviour over which architects, masons and monument authorities have no control. Issues such as sustainability, environmental policy and global climatic change will impact upon the building. As with the larger environment, these large-scale trends form the framework within which conservation is undertaken and set constraints upon the scope of activities and responses available for maintaining the building fabric.

2. Small-Scale Studies of Stone Degradation

Large-scale international and national surveys of stone degradation such as the NATO/CCMS project in Europe and the National Materials Exposure Programme (NMEP) in the United Kingdom have used only small-scale samples to collect data (Butlin *et al.*, 1993; Yates and Butlin, 1996). In both studies, small 50 × 50 × 8 mm tablets of different stone types, Portland Limestone, Monks Park Limestone and White Mansfield in the case of the NMEP, were used to assess weathering. Tablets were exposed at each site, either to rainfall or sheltered from it, and weighed every six months. Other data, such as chemical composition, were collected from specific tablets, but the weight change index was the main measure used in data analysis. Weight change of tablets from each location was averaged to represent the weight change for that site for a particular time period. Data from each site were plotted against indices of the nature of the general weathering environment — such as sulphur dioxide levels and rainfall, averaged or integrated over the same time period. From these data, weathering curves (usually based on linear regression) which express the relationship between the environmental variation and weathering of stone were derived. Using such a relationship, the potential implications of policy decisions that could alter environmental variables (such as pollution levels) could be assessed. For a given decrease in sulphur dioxide, for example, the regression equation predicted how much weathering loss should be reduced by. Such an analysis fitted in with the general move towards the concept of critical load assessment as a policy tool within the European Union (Bull, 1993; Bull, 1995; Cowell and ApSimon, 1995). Studies using runoff slabs to derive chemical mass balance equations for stone loss (Livingston, 1986; Reddy, 1988; Moses, 1996) have likewise tried to link general environmental variables and their variations to changes in stone loss over a given time period.

Laboratory-based studies concerned with single or, at most simple combinations of, weathering agents (Goudie, 1974 and 1999; Robinson and Williams, 1982; Smith and McGreevy, 1983) have tended to concentrate on illustrating the power of process or processes to cause degradation. The quasi-standard test for durability of limestone building stones in the UK, the sodium sulphate crystallisation test (Ross and Butlin, 1989; also prEN 12370), for example, uses a saturated salt solution and a heating and cooling cycle to induce "unnatural" weathering cycles. Weight loss of standard cubes (40 × 40 × 40 mm) under this regime are then used to assess the general durability of the stone to weathering relative to a standard set of limestone cubes. The test was originally designed to simulate frost weathering rather than general durability, but even within these terms the samples are exposed to rates of temperature change and a supply of salt that are unrealistic to say the least. Use of the test results as an indicator of durability is based upon the assumption that weathering behaviour in the building bears a direct relationship to the behaviour of the stone in the test.

More complex weathering simulations that try to model reality in greater detail by either matching salt supply to that found in reality or by combining more variables of appropriate magnitudes (Goudie, 1974; Smith *et al.*, 1987; Smith and McGreevy, 1988) are still limited in the direct relationship of these results to the weathering of stone on a real building. As laboratory-based simulations, they represent simplifications of the real world. The variables controlled are those thought by theoretical analysis, other laboratory studies and field observations to be those important for weathering. The weathering system is, however, defined by the worker and so only those variables identified, probably those capable of measurement, and which are capable of simulation at some of their properties will be analysed. This can severely restrict the type of weathering system simulated. Salt supply, for example, can vary in both the mode of delivery, its spatial and temporal characteristics, in composition and in quantity (McGreevy, 1982). Altering any of these, either singularly or in combination, could alter the amount of degradation induced in experimental samples. Variables that are difficult to measure or model may be excluded from study as will those not identified or considered inappropriate, such as the second to second variability of sulphur dioxide levels. Likewise, the experimental sample is analysed in isolation from its position on the building. Position could dramatically influence the types of weathering agents affecting the stone and specific micro-environment within which the stone weathers. Similarly, position can be an indication of the past weathering history of the surface. Past weathering will mean that, unlike most experimental work, the stone which weathers will already by altered and not a pristine, fresh stone sample. Past weathering will alter the physical and chemical characteristics of the stone surface at least as well as resulting in the storage of weathering products in the stone, the so-called memory effect (Smith *et al.*, 1988; Cooke, 1989; Inkpen, 1991).

The above discussion highlights the limitations of small-scale field trials and laboratory-based studies in explaining weathering at the scale of the real building and even real building surface. This is not to imply, however, that such studies do not serve a useful role. Controlled examination of specific weathering agents and associated mechanisms under limited, simulated conditions help to identify the potential power of agents and combinations of agents of particular characteristics to cause degradation. From such an analysis, a deeper understanding of the role of specific mechanisms or group of mechanisms in causing decay can be gained. It cannot, however, be assumed that the results of such studies can then be translated directly without further consideration and thought to explain patterns and forms of degradation observed in the real environment on building surfaces and over a building as a whole. Such studies can, however, point to particular forms of weathering that may be associated with particular processes or combination of processes. This can then be used to devise classification systems based on assumed processes of formation as well as suggesting which other environmental parameters to measure the variation of.

3. Classification of Building Degradation

Classification systems usually try to link a process or agent or combinations of processes and agents to particular types of weathering features. Links may be established from laboratory studies or from the common association of particular features with the presence of specific weathering agents. Sometimes, however, this tends to result in correlation being equated with causation. The presence of high concentrations of salts and a particular set of weathering forms, for example, may be taken to indicate degradation by salt weathering mechanisms. Such a conclusion may only identify one weathering agent whilst there are many other contingent factors such as the state of the stone, the continued supply of salt, the removal of weathered products and the position of the stone block or weathering feature that are also important determinants of weathering.

One of the simplest classification systems by Camuffo *et al.* (1982) divides weathered surfaces on the basis of colour. White surfaces are those that are rainwashed and are areas of surface loss. Black surfaces are areas of deposition where black crusts, such as sulphation crusts, form. Grey areas are areas of dust deposition rather than transitional zones between black and white areas. Location is central to this classification system as the degree of exposure has an important bearing on whether a surface is rainwashed or not. Other classification systems have concentrated on identifying and mapping a selected range of features. Robinson and Williams (1996), for example, identified and mapped areas of active and inactive cavernous weathering on sandstone blocks on churches of different ages in West Sussex. From these data, they suggested that a great deal of cavernous weathering occurred during the 18th and 19th century. This would suggest that this form of weathering is associated with pollution from industrial and urban activity which began in this time period. Antill and Viles (1998) used a classification system based on colour — a visual surface disruption to classify over 700 individual stone blocks in an external wall of Worcester College, Oxford. The maps produced were constructed by sketching the wall and then colouring each block individually according to its class. The patchy and distinct patterns of specific decay forms could then be related to the location of the patches on the wall and their relationship to other decay forms. Inkpen *et al.* (2001) carried out a similar study, but integrated the data into a geographical information system (GIS). In the latter study, the use of a pre-defined unit of classification, the stone block, was largely avoided by using the GIS maps of stone blocks as the base map upon which decay forms were mapped. This meant that the observer was not restricted to either percentage covers per block, nor to allocating a block solely to one decay class.

Zezza (1996) identified and mapped different types of weathering on four buildings in the Mediterranean: Cadiz Cathedral, Spain, Bari Cathedral, the Church of Sta. Marija Ta., Cwerra, Malta and the Sanctuary of Demeter Eleusis, Greece. Zezza used a methodology identified as Integrated Computerized Analysis (ICA) for Weathering to relate different types of information about weathering in a common framework. This method combines identification and mapping of building lithology with information on the distribution of weathering forms and other indices of alteration such as ultrasonic identification of sub-surface weathering forms.

Although the above integrated systems are in the early stages of development, the potential for deriving useful information for both understanding weathering behaviour and developing appropriate conservation strategies cannot be underestimated. Central to these schemes, however, is developing an appropriate classification system for weathering features. Fitzner (1990) developed a system based on a hierarchy of feature classification (Fitzner *et al.*, 1992; Fitzner *et al.*, 1996). The classification system has four groups of weathering forms at the highest level in the hierarchy: loss of stone material, deposits, stone material detachment and fissures/deformation. Within each of these groupings, there are further sub-divisions into 29 weathering forms with finer divisions down to individual weathering features. Further differentiation is possible by adding an intensity parameter to each individual feature. The relative success of these systems for aiding conservation work is in the early stage of evaluation.

The Building Research Establishment (BRE) in the UK uses the durability index in combination with a knowledge of the structure of a building to define damage zones (BERG, 1989). For each area of the building, the mix of factors that produce its weathering environment are reduced to a potential damage indicator. The classification is then used to identify which durability class would be appropriate for particular zones. Approaches such as these tend to ignore the problem of equating damage with a laboratory-derived measure of durability. The damage potential of any zone is the result of a combination of factors which vary both spatially and temporally. The same damage potential may be present on different parts of the building, but result from the combination of different sets of factors. The durability index is a general index, whilst weathering environments will be specific combinations of different factors.

Despite a range of classification systems for weathering forms, there is a tendency to imply a simple causal relationship between process and form. This may result from the focus on specific areas of damage on a single surface or façade. The BRE damage index and the damage index derived from Fitzner's work point to spatially, and presumably temporally, distinct zones of degradation. Zonation of forms may be explained by reference to solely process or agent differences. Consideration of the position or rather context within which forms occur on the building may be useful in identifying potential damage zones and also in providing a full explanation of such forms.

Context, like durability, is an elusive, but vital term in stone weathering. At the large scale, context can include factors such as the pollution environment which determine the types and quantities of pollutants available for reaction with the stone. A simple first approximation, pollution environment could be divided into urban and rural (Cooke, 1989). This division assumes that predominantly local pollution sources contribute to the creation of the pollution environment. Urban, residential and industrial areas with large local producers of sulphur dioxide are the areas with aggressive pollution environments. Rural areas have lower densities of low use and, it is assumed, less polluters, and so have lower levels. Recent trends, in Western Europe at least, suggest that this simple division of the environment and weathering rates may have be valid in the recent past (Attewell and Taylor, 1988; Kupper and Pissart, 1976; Cooke *et al.*, 1995), but there is a narrowing and, in some areas, parity in pollutant levels (Inkpen, 1989). Despite this, a difference in weathering between urban and rural locations persists (Honeybourne and Price, 1977; Jaynes, 1985; Jaynes and Cooke, 1987; Inkpen, 1989).

Although the larger scale context may set the limits to the types of interactions possible, characterisation of it does not fix the absolute nature and values of pollutants that react with the stone on different parts of the building. As the scale changes, so does the context and hence the factors that become influential in limiting and defining stone degradation. The building itself is not a passive element, it creates its own context rather than simply reflecting the larger scale environmental conditions. In this manner, it is analogous to the relationship between an organism and the environment in evolution. A simple view would be that the organism responds to the environment as it changes (Levins and Lewontin, 1985). The organism, however, only obtains information about the environment mediated by its senses. This means that environmental fluctuations may be reduced or enhanced in magnitude by the senses, and the organism responds accordingly. Similarly, the organism will create its own environment to alter its context. Fur and feathers, for example, could be seen as mechanisms by which the organism reduces the impact of the general environmental conditions by the creation of a particular, beneficial micro-environment. The building can be viewed in the same manner. Fluctuations in variables such as sulphur dioxide can be measured over small temporal and spatial scales, but the effect of these scales of change on the weathering of stone is unclear. These changes are mediated throughout the surface of the stone, which may have differential responses to different scales of change and to different types of pollutants. There is little in the literature to suggest that appropriate scales of change have been determined for the response of a building or even a single surface.

There is evidence to suggest that the impact of environmental changes is also mediated through an environment of the buildings own making. The structure of the building itself results in the creation of numerous micro-environments that either enhance or reduce both the magnitude and frequency of environmental conditions as measured away from the building. These smaller scale micro-environments are the context within which weathering takes place, and again study of the appropriate scale on which to monitor these micro-environments is relatively poorly developed. Creation of these micro-environments is not, however, a random process. Any building was designed for a purpose and that dictates the general structure and layout of the building. Conservation of the building adds another layer of design. Combining these human inputs into the physical system results in a structure with unintentional, but designed micro-environments within which weathering occurs. This means that it should be possible to identify and map different types of micro-environments on a building and, to a certain extent, predict the conditions in each.

Identification of micro-environments does not mean that distinct units of study have been identified. Micro-environments may merge and interact with each other across a building surface. Analysis of weathering would be aided if it could focus on a distinct, functional unit of study. Defining sections of the building as a catchment area could be of help in establishing such a framework. Catchments have become a fundamental unit for analysis in hydrology (Chorley, 1969) and the particular characteristics of the concept make them particularly relevant for studying buildings, i.e. ease of demarcation, nested, ordered and interconnected nature of catchments, the topological and geometric integrity of the catchment, the catchment as the basic erosional and depositional unit in the landscape and as the basic unit of input/output analysis. A building catchment represents the area contributing to a runoff outlet or set of outlets, which may be linear or point features, e.g. a drainage channel or a number of drainage points across an area. Definition of the catchment area and characterisation of it using a few simple parameters indicates how water and material is transported about and between catchment systems. In particular, such descriptions could help to clarify the hierarchical and interconnected nature of the drainage system and the location and effectiveness of storage and removal networks across the building. Inputs and outputs are now tied to a defined, functional unit and any surface studied can be positioned within the context of this unit.

Building catchments, unlike their "natural" counterparts, have not developed in response to tectonic and erosional processes, rather they may have been designed with that specific purpose in mind. Within each catchment, there will be elements that can be regarded as either unconnected micro-catchments or flow barriers depending on the scale of study. These are usually isolated features which tend to deflect or concentrate water flow within the catchment. Their presence can, therefore, be important in determining patterns over material movement within the catchment and so influence the context of any surface under study. Seemingly similar surface in terms of properties such as slope, material and conservation histories may differ significantly in terms of their connectivity to other areas of the building, and hence in the material flows likely to influence their weathering behaviour. This framework also provides a conveniently scale-independent basis for incorporating and interpreting how the human dimension is likely to impact upon stone degradation.

The importance of context can be illustrated by the current environmental concern with climatic change. Various scenarios of climatic change have been suggested and are continually being refined and recalculated (Intergovernmental Panel on Climatic Change; Impact of Climatic Change on UK). Within the UK, data implies that there will be a general rise in temperature and rainfall, but that this change will be highly variable spatially. It is also likely that extremes of weather will increase in frequency as climatic change occurs over the next 50 or so years. Modelling of climatic change using General Circulation Models tends to model atmospheric movement and change on the scale of large cells of a resolution (e.g. 20 × 20 km) that makes prediction of conditions for particular locations difficult. If only general trends for the UK are considered, then three key contextual factors can be highlighted; i) a rise in carbon dioxide levels, ii) an increase in temperature (between 1.5°C and 4.5°C over 50 years) and rainfall amount and variability with global rainfall increasing by between 3% and 15%, and iii) a rise in sea level of between 20 and 50 cm over 50 years.

Local details of the impact of climatic change are sketchy. The global models used to predict large-scale climatic change usually use grid cells of a resolution greater than 20 × 20 km. Change below this scale is not modelled and the accuracy of prediction for a few cells of this size is relatively low. For the UK as a whole, only broad potential regional trends in climate are possible to predict. For Southern Britain, for example, climatic change is likely to result in increased winter precipitation and lower summer precipitation. Additionally, increased storminess of weather patterns coupled with prolonged summer heat will probably produce a more Mediterranean-style climatic regime. In these circumstances, assessment of current degradation processes and conservation practices in existing Mediterranean areas would help to predict the likely response of buildings to this type of change in climate. At a more local scale, it is virtaully impossible to predict the exact impact of climatic change at the scale of a single urban area, let alone a single building. Only general trends can be put forward and limits set to the potential range of scenarios for any local area. This may not be a major problem in determining the impact of such climatic changes on buildings for two reasons. Firstly, the magnitude of the changes outlined is not as significant as some urban to rural changes in environmental conditions that a number of historic monuments have already experienced over their life as urbanisation has progressed. Under these changing conditions, it is only when such climatic changes have been coupled with pollutants that severe damage appears to have resulted. Secondly, as well as the urban location of most monuments ameriolating the impact of climate change, the response of building materials will not be immediate nor necessarily dramatic. The level of temperature that is likely, 2–3°C, is of a similar or less magnitude than current differences in temperature resulting from aspect around the same building.

The rise in carbon dioxide will contribute to the "greenhouse" effect, but will only minimally alter rainfall acidity (Trudgill and Inkpen, 1993). Potentially of greater significance is the change in climate and sea level. The impact of a changing climate on a particular site will be a function of the precise combination of changes, e.g. rise in temperature, increase in rainfall or rise in temperature and decrease in rainfall, and the nature of the building under consideration. Buildings with short service lives (30–50 years) may be relatively unaffected by such changes. For such materials already in service, their expected service lives are too short for economically feasible alterations to the fabric to be important. For materials with short expected service lives yet to be used, a knowledge of climatic change can be incorporated into their design or specification.

In relation to both types of building materials, there are a limited number of possible alterations climatic change will induce. The first possibility is that the mix of weathering agents and the intensity of process operation will change as climate changes. Within geomorphology, the work of Peltier (1950) and climatic geomorphology in general is of relevance as he outlined the dominant forms of weathering associated with different climate zones. A transition from, say, a temperate to a more Mediterranean climate will be associated with a change in the suite of weathering processes. A second possibility as suggested by Brimblecombe (1997) is that a gradual change in environmental conditions can result in a change in the rates of operation of different weathering processes and so in a change in the dominant set of weathering processes. For both of these alternatives, any change in climate will produce changes in both the range of conditions experienced as well as the cycles of climatic variables, such as freeze-thaw activity, which will influence the rate and nature of degradation. A third possibility is that the change in conditions will alter the relationship between variables in the weathering system. In this case, the whole structure of the system will be re-defined by a change in climate. In this alternative, there is no gradual transition. Change is abrupt and dramatic with weathering forms previously adjusted to environmental conditions weathering rapidly as the relationships that define the weathering system alter. A final alternative is that the change in climate may not alter the dominant set of weathering processes, but may alter the extremes experienced by the building. In this case, the development of forms associated wtih extreme events will increase. These forms are likely to become more common and persistent as the operation of weathering processes during "normal" periods will not be sufficient to remove them from the building.

The impact of climate change does not depend solely on changes in climatic variables however. Any impact will be mediated by the building environment itself. An increase in external air temperature, for example, could result in a decrease in the amount of heating required in some buildings. This will alter the thermal gradient through the building materials and so reduce their thermal stress. Decreasing the steepness of the thermal gradient can also influence particle deposition onto the building surface by altering the flow of air close to the surface and so altering the settling velocities of particles. Likewise, an increase in the frequency of extreme conditions can increase the number of times high heating temperatures are required. Thus, although overall heating requirements may be decreased, the frequency of episodes of high thermal stress in building materials may increase. A similar complex-mediated sequence of alternatives can also be put forward for changes in rainfall amount. A decrease in the amount of rainfall can result in increased periods of sulphation for limestone surfaces. Increases in the frequency of extreme events, however, will result in the generation of runoff of higher velocity and potentially greater erosivity. The paths of such flows will still, however, be dependent upon the configuration of catchments on any individual building. Each building will also have a unique history of conservation work and building practices and decisions. This will mean that each building will have a unique set of weathering forms associated with its past environmental conditions and past building practices. Context is therefore, important not only for determining the mix of changes associated with climatic change in any area, but also for determining the mediation of these changes at the scale of the individual building.

4. The Building as the Physical Representation of Socio-Economic and Cultural Factors

A building stone is not merely a physical part of the building. Its weathered state and treatment also represents the underlying socio-economic and cultural currents of the society the building is within. What is an acceptable level of degradation, who decides this and what should be done are all questions that require a human agent to make a decision. Any decision will involve an individual or group of individuals in some particular historical and social setting (Inkpen, 1999). Decisions cannot, therefore, be divorced from the circumstances or context of the questions posed. In this sense, any building stone by its presence and subsequent weathering and treatment history represents the socio-economic and cultural values of society over time.

The importance of social and cultural values for what appears to be a purely physical phenomenon can be illustrated by looking at how durability and durability criteria have been used in stone degradation. Durability itself is recognised as a complex, vague and ambiguous term (Turkington, 1996). The BRE (1984) view of durability is based on the physical characteristics of the stone, resulting from a combination of the internal structure of the stone and the nature of the cementing material. The most recent digest from the BRE (1997) whilst still viewing the rate and form of weathering as being a function of the internal characteristics of the stone explicitly recognises the complex nature of durability and its dependence upon the location in which the material is placed and the relationships between the material and the rest of the building environment.

> *"Durability only needs to be assessed if stone intended for longer life or harsher exposures ... or severe environments. Because such assessment must take account both of the stone's position in the building and the weathering to which it will be exposed, a single durability test cannot be of universal application"* (BRE Digest 420, 1997; p. 3).

The digest regards the normal service life of a building of 60 years as too short a time for stone durability to be an issue, as seen in the particular cases cited above. This illustrates the impact of defining durability relative to economic concerns rather than as a purely physically determined entity.

Porosity and, in particular, microporosity have, however, continually been put forward as the key characteristic in controlling durability (Knöfel, 1991), despite studies showing that stones with similar structural and mineralogical properties exhibiting differing weathering behaviours. Garden (1980) views durability not as a fixed property of the stone, but as an outcome of the interaction of material and environment, including the in-service expectations. Nireki (1980) similarly, viewed performance over time as a vital element in durability. Performance implies that the stone is continually being assessed in relation to the fulfilment of some designed function. On this basis, the expected performance forms the criteria for assessing durability and not an absolute property of the stone. Duffy and O'Brien (1996) again highlight the importance of expected future performance for defining durability. They, however, point out that performance itself is different for different interest groups, such as architects and engineers. They settle on evaluating stone durability as:

> " *... should be concerned with assessing how resistant a stone is to changes of its physical, mechanical and aesthetic properties over time*" (Duffy and O'Brien, 1996; p. 254).

Central to their interpretation is the view that the surface environment is the important determinant of durability. They view the surface environment by determining the supply of weathering agents and the range of weathering processes. Using this definition, they view durability not as an absolute measure, but as being dependent upon the surface environment upon which the stone is exposed.

Despite the increasing complexity of the views of durability outlined above, there is still a tendency to view it as a physical phenomenon only (Cramer, 1994; Drever, 1994). The terms used, such as "performance" and "aesthetic", imply an important input from socio-economic and cultural concerns into the definition of durability. A central question which none of the above authors explicitly address, but which will implicitly be incorporated into the agendas of each interest group is, why is a concept such as durability required in the first place? Durability is defined by the architects, testing agencies and legislators in relation to a product, be it stone or any other building material. The drive to define durability via some standardised and repeatable measure is part of the view of building material as a commodity. In the case of natural building stone, a highly variable natural material is being characterised by a set of measurable parameters defined as important within a scientific and technological framework. It is the behaviour of these parameters in controlled conditions that become the descriptors of the material and the means of representing the material to other parties interested in purchasing stone. In this manner, the socio-economic framework is constraining the type of parameters considered to be valid for characterising building materials.

Putting a value onto stone also defines the temporal dimension of durability. Expectations of durability vary with the type of construction for which the stone is used, an issue recognised by Lewry and Crewdson (1994). They divide durability testing in four types: benchmark tests, reference or comparative tests, environmental or stress tests and site testing. Within this framework, they suggest that the construction product directive in the European Union (1989) and BRE digest (1994 and 1995) will promote the harmonisation of standards. As part of this scheme, they view the development of design standards that simulate the response of materials in every environment as central. They suggest that accelerated testing in this framework becomes significant as it provides data on the most important factors and mechanisms causing degradation. From these tests, models and damage functions for the end use environment can be constructed. The context of a building and the material within it is replaced by a set of experimentally derived damage functions developed and assessed over a time scale significantly less than the lifetime of the material. The imperative of standardisation within a market and the confidence in a product influence the time scale over which durability is determined. In this case, the time scale of assessment is reduced and formalised as a damage function applicable to a given material in a given environment.

In what could loosely be described as cultural monuments, value lies in the continuance of original material or its replacement by identical material. Durability in this context has a long time frame with material expected to survive over hundreds of years. The value of the stone lies not only in itself, but in the context into which it is placed. Stone used for conservation work has value imparted to it by the cultural significance of the monument and also takes on expectations associated with such a context. Within a modern building, stone may be used as a facing material. In this situation, durability is defined by the expected life-time of the building for its current use by its current occupants, a shorter time frame. The value of the stone is defined by its context as one element in a "disposable" building. This not only determines the manner in which the stone is used, as a thin skin (4–5 mm) designed for decorative purposes, but also the type of properties that affect its durability. Valuation of stone in each context uses different time frames and highlights different stone/environment relationships as important in determining the definition of durability.

The design of the building and conservation of the building fabric are immediately obvious human elements important for the degradation of stone. As with the physical environment, however, there are larger scale socio-economic factors that will impinge upon these human factors and affect both the types of conservation treatments applied and the evaluation of degradation itself. Current concerns over sustainability provide another useful illustration of the wider socio-economic context and its potential impact upon stone degradation. Sustainability itself is a multi-layered and complex term (Redclift, 1987; Redclift, 1991; Simmons, 1990) which has meant that it has been open to a range of interpretations ranging from maintaining current practices, the *status quo* view, to radical social and economic re-structuring as the means to achieve sustainability. Redclift (1987 and 1991) notes that sustainabiltiy can be interpreted in varied and often contradictory ways by different interest groups. Different definitions of the term become accepted in different locations partly as a result of the power relationships between these interest groups giving sustainability a political dimension. The Brundtland Commission (1987) highlights the importance of the political dimension for defining and acting to ensure sustainable development which is seen as:

> *"A process in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are all in harmony, and enhance both current and future potential to meet human needs and aspirations"* (Brundtland Commission, 1987; p. 46).

Often, however, sustainable development has been legitimated as a purely economic entity. Pearce *et al.* (1991), for example, interprets sustainable development as non-declining human welfare over time defined in terms of standard of living and in retaining a stock of capital assets. As with durability, economic value is used to re-define the concept and in so doing the concept becomes open to manipulation via the market. Within the quarrying industry, for example, there is evidence of an explicit acceptance of the economic definition of sustainable and hence on the need to define the environment and environmental impacts in similar terms.

> *"Better environmental performance requires better profitability, not less. There is a need to slow down the rate at which environmental demands are being made upon us, to enable us to adjust to all these changes."* (Jackson, 1994; p. 33).

Using an economic value for measuring all impacts and remedial measures means that sustainable practices are often assessed using only this criteria. Attaching a monetary value to the impact of a set of practices therefore becomes a vital element in assessing the sustainability of any conservation or building practice.

How these diverse views of sustainability are mediated by those involved in conservation will determine the impact of such diffuse social concepts on stone degradation. An interpretation of sustainability could be mediated via legislation in, for example, the need for an environmental impact assessment of conservation practices undertaken. This may involve determination, in monetary terms, of the ecological costs of undertaking a particular practice for local or regional scale ecological systems. Such an analysis, however, highlights another problem with sustainability. Sustainable practices at the scale of the building may involve costs that are unsustainable at a different scale and in different locations. Use of replacement stone from original quarry areas may limit the environmental cost, however, defined in a historic monument, but the transportation of that material and its removal will involve environmental costs at two scales. The area from where the stone is quarried will suffer environmental alteration as the stone is removed as well as local environmental problems from the traffic involved in transporting the stone. At the scale of the region and globally the removal and transportation of the stone will produce atmsopheric pollution both from the quarry functions and from the power required for the quarry to operate. Sustainability is, therefore, potentially open to different interpretations at different scales.

Likewise, sustainability also needs to be viewed as a temporary complex concept. As economic growth rates change and as society itself changes, then the valuation assigned to different types of buildings will change. Their worth as items of cultural heritage will alter and their status as objects worthy of continued conservation alter. This perception may change over time if the degradation caused by pollutants or other factors increases to a point where the costs of conservation outweigh the benefits of sustaining the monument.

It should also be remembered that the buildings themselves are not isolated individual entities. Brimblecombe (1997) noted that cultural heritage should be viewed as embedded, as architectural assembles rather than just as objects. In this manner, an analogy could be drawn with ecosystems and species preservation. Viewed in this manner, any single building would need to be valued in the context of both its local "ecosystem", city or cultural tradition, as well as valued for its contribution to the cultural diversity of an area. In this way, similar arguments to those employed, concerning conservation of biodiversity for future generations, can be made in relation to cultural diversity of a historic building stock. This adds a long-term dimension to the temporal considerations of sustainability in relation to cultural heritage.

The potential requirement for assessing the life cycle impact of the processes and techniques used is another area where legislated definitions of sustainability will impinge upon building degradation. A policy such as replacement of degraded stone with equivalent stone may have to consider the environmental impacts of quarrying of the replacement stone, the methods used to insert the replacement and remove the old stone and its disposal. In other words, the whole production and consumption system for any product will need to be evaluated in terms of its environmental impact and its sustainability compared to alternative conservation strategies. This means that not only does the physical environment become an important explicit determinant of defining an effective treatment, but the impact of that treatment as defined by its sustainability becomes a factor requiring consideration. Once you extend this form of analysis to conservation strategies and techniques, such as lime washing or epoxy resin emplacement, a range of issues concerning appropriate space and time scales of impact become clear.

Historic Scotland's policy in relation to the preservation of carved stone (Maxwell, 1996), for example, can be examined in the light of a board definition of sustainability. The percepts set out governing relevant action to protect stones (Table 1); can be re-interpreted as statements concerning the relative importance of sustainability issues. The percepts outlined can be taken as a general statement of

Table 1. Historic Scotland's percepts governing relevant action to protect stones.

- Retain stone *in situ* wherever possible particularly if it believed they have not been removed from their original locations.
- Where stones were retained *in situ* and protective enclosures were needed, each protective enclosure should be purpose-designed to create the correct environment for the stone with due regard for its surrounding conditions and location.
- Stones that needed to be removed should be kept locally.
- Where stones had to be removed consideration should be given to their relocation within an existing local structure. The long-term stability and public access to such a building should also be taken into account.
- Movement of stone to remote locations such as museums should be considered only a last resort.
- Consideration should be given to replacing stone with casts where movement of the original was essential.

Based on Maxwell, 1996, p. 936.

preferred options in conservation treatment as suggested by D'Avino (1996), where the preservation of the original material is seen as integral and fundamental to the conservation of the form. In this view, the material is the "soul" of the form and should only be removed or altered as the last resort to maintain the built form. Built into this view is a particular view of the material as a repository of cultural information and by implication conservation is both a *"critical-historical judgement" and "scientific-technical knowledge"*. Leaving the original material wherever possible implies a policy of non-intervention with the degradation system. Such a policy can be interpreted as one of long-term sustainability of the current relationships within the system. Maintaining the material may, however, imply altering the current relationships between the stone and its local environmental conditions (constant or altered) as suggested by the use of protective enclosures. Such enclosures would have associated with them an environmental cost, both in terms of their production and in terms of their impact upon the environment once in place. Comparing the different types of impact using a common measure or formula is difficult if not impossible, and each factor such as visual impact, alteration of runoff characteristics will be measured and assessed differently by different people.

Where intervention is necessary based on the "scientific-technical" side of the equation, it is usually only on the basis of a consideration of the small surface studied. The type of treatment employed will be a function of the general conservation policies of the appropriate management and the available treatments known to the consultant and management. Each treatment can also be considered in terms of its sustainability at different scales. Limewashing, for example, appears to be a relatively environmentally harmless treatment. (The following is not meant to imply that limewash is a hazardous treatment, it is only an illustration of the factors that need to be considered when making a full analysis of the impact of using limewash. A similar argument could be put forward, for example, when using new, quarried stone for restoration work.) The application of a limewash to a surface involves the use of no hazardous chemicals and is not viewed as hazardous to the stone itself. At the local level of the building surface this maybe the case, but to get the limewash a whole set of production processes need to occur. These would need to be considered in a full life cycle analysis and they may not have such a benign environmental impact. Likewise, applying the limewash is not the end point for the limewash within the environment. Over a period of time the lime is removed from the surface and transported initially within the building catchment of which the surface is a part and then out of the building system altogether. The interaction of the lime with the rest of the catchment and the potential interactions of the lime with the extralocal environment would need to be considered in a full life cycle analysis. Similarly, the frequency and magnitude of repeated treatments could influence the magnitude and frequency of effects associated with lime production and lime waste in the environment.

An important consideration is the economic aspect of conservation of whole buildings. For management of resources at the level of the building, it is important to know which materials are most sensitive to degradation. Using this knowledge, appropriate scheduling of repairs and conservation work in line with resources can be drawn up. This requires a good inventory of both the types of material in a building and their location. A combination of these factors can be used to plan where requirements for conservation may outstrip available resources in the future.

The individual building also needs to be considered in the wider context of economic priorities of funders, such as central government, as well as the planning context which may constrain both the flow of resources and the type of work undertaken. Despite the prevalence of cost-benefit analysis in this context as a means of comparative evaluation of competing demands, it is recognised that the valuation of cultural heritage is difficult (Lowenthal, 1994). In particular, the importance of the purpose of the valuation for its outcome is a key point for the valuation of cultural heritage. Mohr and Schmidt (1997) argue that the introduction of the concept of non-use valuation may be an appropriate means of valuing cultural heritage. Non-use valuation has been used in relation to natural resources and can be built into a complex set of different types of non-use. Non-use valuation assumes that when confronted with a change in the use or characteristics of an object, a person can be compensated for these changes. The individual decline in well-being experienced can be translated into an acceptable range of alternatives with monetary value for that individual. In economic terms, there is an assumption of substitutability in the valuation of cultural heritage, i.e. individuals are willing to make trade-offs (Mohr and Schmidt, 1997; p. 337). This requires that the non-use value of cultural heritage usually be related to some measurable, market-valued goods or services. As cultural heritage is viewed as a social good, its valuation requires a consideration of trade-offs at the social level in competition with other social goods. The valuation of self-selected sets of individual experts carries equal weight with that of any other individual in society, although the potential of different individuals to influence the valuation of heritage for others may differ.

Valuation of cultural heritage may be made by techniques such as contingent valuation. This method uses different hypothetical situations, such as the current state of decay of a building and its characteristics after conservation, and by various means, drawn into providing a monetary valuation. The monetary valuation provided is concerned their with willingness to pay for or accept different types and states of repair of a building. The valuations can be in pure monetary terms of willingness to forgo some other resource. Despite problems with the operationalisation of the technique, it does provide a comparative means of determining the "general" value placed on cultural heritage and their conservation in different contexts.

Importantly, economic valuation cannot be divorced from the context provided by sustainability mentioned above. Viewing culturally important buildings as part of a wider "architectural ecosystem" means that valuation cannot be made for one building in isolation. Maintaining the diversity of this architectural ecosystem may not only be important for maintaining the economics of tourism to the urban area. Snickars (1997) also suggested that the general attractiveness of an urban area will be affected by the amount of maintained cultural heritage it contains. If a high quality cultural buildings or set of building are allowed to degrade beyond a certain threshold, this can spark a reaction in the type of resident attracted to the area. Once began the exodus and image of the urban area is difficult to reconstruct and a cumulative economic impact upon the whole urban area is felt. This illustration highlights the need to value buildings not only in terms of their components, but also in terms of their relationship to their milieux.

5. Conclusion

Studies of degradation have tended to concentrate on extrapolating small-scale field and laboratory studies of process/form relationships to the scale of the whole building. Extrapolation in this fashion assumes that the different spatial and temporal scales of processes and forms associated with the building as a whole unit have no impact upon the operation of agents and processes of degradation. Whilst these small-scale studies do help in developing a detailed understanding of the mechanisms of degradation, they do not help in understanding why degradation occurs with a particular magnitude, frequency and form at particular locations on a building. Mapping patterns of degradation is an important element in recognising that order and pattern are present at the scale of the building itself. Such patterns cannot, however, be simply reduced to explanation by reference to the presence of particular weathering agents. The question of "why there and now"? still remains. Contextualising stone degradation by consideration of the wider environment and how its influence is mediated to a particular surface is essential to understanding how and why degradation occurs. Using a catchment framework within which to analyse and contextualise, such degradation provides a physical, functional unit for simple systems analysis.

From the above examples of durability and sustainability, however, it is clear that the role of socio-economic factors in stone degradation should not be undervalued or regarded as a mere extension of the physical environment of the stone. Focusing on a specific problem of degradation tends to limit consideration of appropriate and effective treatments and policies to those of effects identifiable and measurable only on the surface of stone itself. Using a catchment framework for contextualising the surface widens the scope of potential effects, including a larger portion of the physical environment. Recognition of the socio-economic basis of conservation work and the general trends which influence this also means that the appropriateness treatments need to be viewed within a wider and more socially and culturally sensitive context. As with the physical environment, however, general trends are translated to the stone in a variety of ways, and manner of this mediation will dramatically influence how concepts such as sustainability are used in any particular project on any particular building. Importantly, analysis and understanding cannot be solely focused on the scale of the surface. Such a scale of study limits the spatial and temporal horizons of analysis and therefore of explanation and understanding of stone degradation.

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