The Effects of Air Pollution on Cultural Heritage

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Editors

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Cover illustration: The cover image shows cherubs damaged by both soiling and corrosion. They are on the outside of St Mary Woolnoth, a fine Hawksmoor Church in the City of London. Our thanks to The Revd Andrew Walker for his permission.

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Preface

Managing the risk to our heritage is, of course, an enormously diverse and complex task, reflecting as it does the tremendous variety of history, style, art and culture that is represented. We have many different types of monument, they are made of many different materials, they range in age over centuries and they are located in radically different environments. Air pollution is only one of the risks that threaten this heritage and may frequently not be the most pressing. In addition we have the added complication that weathering occurs naturally and indeed is often felt to contribute to a sense of age and serenity that is fundamental to the way that we value our ancient buildings.

The damage done by air pollution, however, is real, measurable and in many cases obvious. Our industrial development has left us with a legacy of faceless statues and blackened buildings that will take many years to repair and conserve, even when pollution levels are sufficiently reduced to make it sensible to do so. There are important questions to be asked. How much damage has been done and is being done? What is this costing us? How can we be practical in our conservation to prevent unnecessary loss while protecting context and artistic merit? How much value do people actually place on intangibles like the peace of a Gothic Cathedral and how can we account for these very real benefits and others like them (such as the desire to pass on our legacy to our children and grandchildren) in order to help us raise the money to carry out our repairs and maintenance?

The threat posed to cultural heritage, especially built heritage, by air pollution has been studied for many years and this book is designed to bring together a number of strands of that research to make it accessible to the people responsible for looking after our historic buildings, monuments and artefacts. It will help both these heritage managers to prioritise conservation action in response to this threat within the context of other risks and also environmental policy makers to evaluate the economic benefit of taking action to improve air quality.

We look at the way that buildings weather in the natural environment and then show how pollution adds an extra dimension of damage. We focus on two types of damage – corrosion and soiling – and also briefly review an emerging area of research, the role of air pollution in affecting bio-deterioration of buildings. To develop this discussion we need to present the results of a number of scientific studies. First of all we look at current, past and projected levels of the pollutants that cause the damage. The picture has changed dramatically over the years. Before the policy actions to reduce coal burning, pioneered by the Clean Air Act in the UK but now reflected throughout the developed world, the major corrosion was caused by sulphur dioxide (later know as acid rain) and the buildings were darkened by black smoke. We will show how this scene has changed and examine the new, multi-pollutant, urban environment with its lower domestic and industrial emissions but greatly increased traffic. Second, we look at the way that pollution actually attacks buildings and review the findings of a long series of experiments where typical materials have been exposed to a range of different natural and pollution situations across the world. Assessment of the rate at which they are corroded and soiled has allowed scientists to develop equations that predict the amount of damage that will result from a given amount of pollutant. These are known as "dose-response functions" and can be very powerful when we try to assess the harm that might come to a given building in a given environment. Such studies take many years and are therefore very expensive. It is therefore no surprise that dose-response functions are only available for a limited number of materials. We discuss ways to make use of these insights to evaluate pollution impact in any situation. This leads us to the idea that certain materials can be used as indicators for a more general situation and simple test kits produced to utilise them.

This is not just a book about science, however, it is also about geography and economics. Modern map making tools such as geographic information systems are ideal for showing how the risk is distributed spatially. We show how the science discussed above can be mapped – pollution maps are developed into corrosion and soiling maps by application of the dose response functions. One of the themes of this book is scale and maps can provide information at many different scales. This is illustrated in Fig. 1. The risk maps are another way that building managers and owners can access the scientific data. If the risk categories can be made accessible and relevant, then it is relatively simple to locate the particular building or monument on the map and have an estimate of the likely impact.

The damage maps may be developed into cost maps, which illustrate some of the air quality policy implications, if there is good economic data on repair and maintenance costs and on the extent of the material potentially affected (the stock at risk). We discuss a number of studies that have examined these things. The cost estimates are relatively straightforward in area terms (e.g. per square metre of exposed limestone) but it is much more difficult to estimate how much heritage material is affected. We discuss pioneering estimates of what might be termed technical materials (i.e. materials used in houses, factories and infrastructure), which use generalisations about ratios of materials to develop "identikit" buildings whose numbers are then estimated from land use maps or population density. Unfortunately, while it is relatively safe to say that, within a

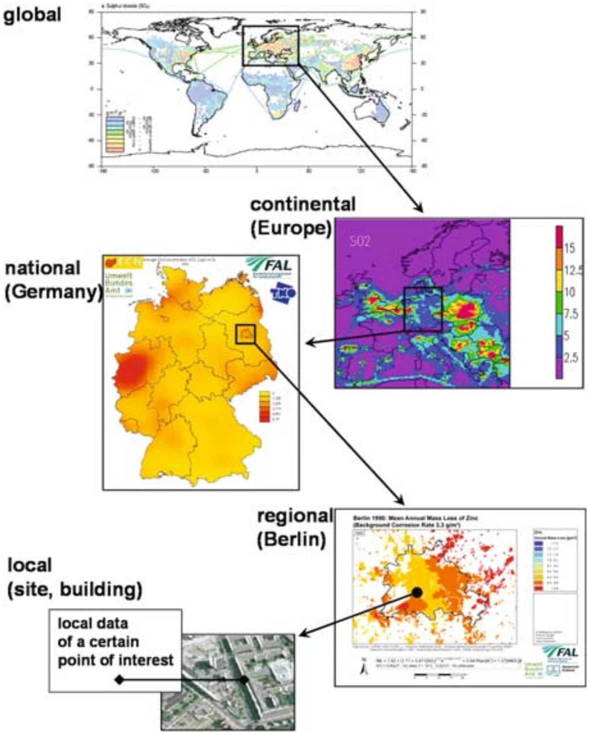

Fig. 1 Maps provide information at many different scales

limited area, most houses are of a certain type, it is certainly not possible to do this for heritage buildings. The latter are, by their nature, less frequent and may reflect a wholly different material makeup due to their importance at time of construction, and therefore use of special materials, or due to their having survived from an earlier period with different construction materials to those used later. We discuss newly emerging research that is starting to address stock at risk inventories for cultural heritage, sometimes including estimates of construction materials.

This is also a book about risk management and policy. We discuss ways that people's values may be brought into decision making. Risk management cannot rely solely on numbers, however much scientists and economists might like it to. Numbers come laden with value judgements anyway, of course, and we discuss the ways that both can inform each other. We show how conservation values such as "truth to original materials" or "reversibility of treatments" can be built into the costs calculations but, just as importantly, we show how it is possible to use peoples' willingness to pay to protect heritage and to develop more equitable business cases for fund raising. We discuss the way economic impact assessments are used in air quality policy making. The cost-benefit analysis in this field rely today largely on human health impact but other costs should also be accounted for, especially impacts on crops, ecosystems and materials. Heritage materials are important here too and people have pointed out that materials may be more sensitive than plants and animals since they have no healing capacity. The final part of our discussion unites all of our threads into an evaluation of what heritage owners and managers can do.

The book has been developed to permit access to the material at a number of different levels. A short overview is presented at the beginning of each chapter to summarise the discussion and place it in the context of the narrative laid out in this preface. Each chapter is a review of the studies undertaken to date within the topic to present the aims and objectives of the research and the main features of the methods used. Results are discussed in terms of the current state of the art and any consensus view that may be articulated. Implications and likely future scenarios are evaluated. These discussions are written for a general reader without assuming prior specialist knowledge and, where technical results are presented, they are fully explained. More specialist readers will find expanded technical detail in the specially created "sources of additional material" sections that close each chapter.

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Chapter 1
Environment, Pollution and Effects

Ron Hamilton and Helen Crabbe

1.1 Overview

This chapter will look at the main environmental influences and controls on damage to heritage, which occurs even in the absence of pollution, and also examine the main characteristics and sources of the most important air pollutants that exacerbate this damage or, in some cases, add new types of damage. The types of damage are briefly reviewed at the beginning of the chapter. It is also important to understand the environmental factors that not only influence weathering in the absence of pollution but also are key to the control of pollution damage, and so these are also briefly reviewed.

The danger to heritage from air pollution comes from two main sources – gases that increase the corrosivity of the atmosphere and black particles that dirty light-coloured surfaces. The main mechanism of the former occurs when acid chemicals are incorporated into rain, snow, fog or mist. Familiar as "acid rain", the "acid" comes from oxides of sulphur and nitrogen, largely products of domestic and industrial fuel burning and related to two strong acids: sulphuric acid and nitric acid. Sulphur dioxide (SO_2) and nitrogen oxides (NO_x) released from power stations and other sources form acids where the weather is wet, which fall to the Earth as precipitation and damage both heritage materials and human health. In dry areas, the acid chemicals may become incorporated into dust or smoke, which can deposit on buildings and also cause corrosion when later wetted. Atmospheric chemistry is, of course, far more complex than this and a variety of reactions occur that may form secondary pollutants that also attack materials. One further gas, ozone (O_3), has also been shown to be important. Ozone is a variety of oxygen with three oxygen atoms rather than two as in molecular oxygen. It is the major component of photochemical smog and this ground-level ozone is a product of reactions among the chemicals produced by burning coal, gasoline and other fuels as well as those found in solvents, paints, hairsprays, etc.

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Particulate matter is much more complicated because it is a mixture rather than a single substance – it includes dust, soot and other tiny bits of solid materials produced by many sources, including burning of diesel fuel by trucks and buses, incineration of garbage, construction, industrial processes and domestic use of fireplaces and woodstoves. Particulate pollution can cause increased corrosion by involvement in a number of chemical reactions and, often more importantly, it is the source of the black matter that makes buildings dirty.

This chapter looks in more detail at the sources of this pollution, its spatial distribution and trends in emissions over time. As we will see, the picture has changed dramatically over the last fifty years or so, at least in the developed world. The modern urban atmosphere is much less corrosive, in line with major falls in SO_2 brought about in particular by more stringent regulation, but problems remain. Soiling too has changed over time. We will examine the modern emissions pattern, and especially the role of traffic.

1.2 Damage to Cultural Heritage Materials

Managing the risk to our heritage is an enormously diverse and complex task, reflecting as it does a tremendous variety of history, style, art and culture. We have many different types of monuments, made of many different materials, ranging in age over centuries and located in radically different environments. Air pollution is only one of the risks that threaten this heritage and may frequently not be the most pressing. In addition there is the added complication that weathering occurs naturally and indeed is often felt to contribute to a sense of age and serenity that is fundamental to the way we value our ancient buildings. The damage done, however, is real, measurable and in many cases obvious. Historically, industrial development left a legacy of faceless statues and blackened buildings. This was originally seen as a relatively local problem (the damage was caused by emissions from local sources) but the wider scale of the problem was recognised following the acid rain studies in the 1970s.

Buildings weather in the natural environment, but pollution adds an extra dimension of damage (Brimblecombe, 2003; Saiz-Jimenez, 2004). Knowledge of basic damaging mechanisms of historic materials is indispensable for their appropriate and effective protection and safeguarding. In principle, historic materials are deteriorated by means of three mechanisms, which in many cases interact together, simultaneously or in a time sequence.

A very brief description of the different forms of deterioration associated with atmospheric pollution is given below.

Stone

- Surface erosion and loss of detail
- Soiling and blackening
- Biological colonisation
- Formation of “crust”

Metals
  - Surface corrosion
  - Development of a stable patina
  - Pitting and perforation
  - Deterioration/loss of coating (paint, galvanising, etc.)

Timber
  - Biological decay
  - Deterioration/loss of coating (paint)

Glass
  - Corrosion of medieval potash glass
  - Soiling of modern soda glass

Other materials
  - Concrete
  - Mortars
  - Brickwork

Structural
  - Cracking of walls
  - Water penetration

1.2.1 Physical Damage

Material deteriorates mainly mechanically due to the action of external forces (from loads, movements, impacts, human actions, etc.) or internal forces, (e.g. generated by forced deformations at uneven temperature and moisture changes). The time factor may be important for some materials, e.g. long-term overloading of timber. Further, erosion problems decreasing cross-sectional characteristics belong to this group. Physical damage typically results in a mechanical breakdown.

1.2.2 Chemical and Biological Damage

Material is chemically attacked by reactive compounds present in the surrounding environment or produced by biological agents. In the second case we can distinguish between assimilation and dissimilation damage. Where assimilation damage occurs, the material serves as a nutritional source for biological organisms that can, for example, decompose cellulose in organic materials. For dissimilation damage, products released from colonised organisms cause deterioration (biological colonisation can also be protective). Chemical damage can be initiated or accelerated by physical factors, e.g. temperature or light (or another form of radiation), usually termed thermal damage (which is well known for timber and marble) and photochemical damage. Fire damage has a role to play in this category, though in many cases the physical effects of the fire may be dominant. Chemical damage often results in solution and alteration.

1.2.3 Soiling

Soiling is a general phenomenon which decreases the serviceability of historic structures and elements. Defects may be purely aesthetic but more serious failures can occur, e.g. reduction of pipe profiles, bridging of electrical circuits by mycelium, creation of a dark crust causing increased surface heating and elevated temperature stresses. The historic material frequently acts only as a carrier of the undesired layer which might initiate or accelerate the degradation types mentioned above. Soiling can be caused by alterations, deposition and biological colonisation.

1.3 Environmental Factors

It is important to stress that materials degrade even in unpolluted environments. Natural weathering effects are usually added to by pollution and, as we shall see later, this lack of a pollution threshold below which there are no discernable effects has important implications for the establishment of "tolerable" levels of damage and therefore of air quality. Important individual components of weathering are given here:

1.3.1 Radiation

Cultural heritage objects are almost permanently exposed to the action of radiation – whether cosmic, solar or Earth radiation. Physically we distinguish between particulate (nuclear) or electromagnetic radiation (divided according to different wavelengths into radio waves, heat radiation, infrared radiation, light, ultraviolet radiation, x-ray and gamma radiation). Specifically, objects directly exposed to solar radiation exhibit damage and failure due to heat and UV radiation or light. Here the ionic radiation, which is stronger from the point of view of energy, may cause chemical changes in materials (e.g. netting or cleavage of polymers) on one hand, whilst on the other hand the non-ionic radiation exhibits mostly thermal effects.

1.3.2 Temperature

Temperature is one of the influential climatic factors with consequences for cultural heritage damage. Temperature cycles can occur over a very broad band, which is dependent on the geographical position and the time of year.

In some Central Europe and North American locations, temperature falls into a range from about –25°C to about +30°C. All building materials are sensitive to temperature, and they change their volume in relation to its fluxes. This dilatation is positive (expansion) with temperature increase and negative (shrinkage) with temperature decrease in the majority of building materials. Temperature effects, particularly the temperature gradient, are usually underestimated in practice, even though they are known and published.

Temperature also affects the rate of chemical reactions as well as the time that surfaces remain wet. These factors have implications for the corrosion rates of metals. This is discussed in more detail in Chapter 3.

Temperatures affect emissions of atmospheric pollutants through driving the need for heating and cooling of living space for comfort. This impacts energy use and thus fuel consumption. During cold winter periods, fuel is burnt for space heating, whilst in summer cooling by fans and air conditioning drive energy needs. Increases in extremes in cold and hot periods outside of the normal temperature range as a consequence of climate change will only serve to exacerbate this effect.

1.3.3 Water

Water can affect historic materials and structures in all of its phases and, when acting together with temperature or other factors, can cause deterioration to or even completely destroy a monument. Water acts in its solid phase as ice or snow, and in the fluid phase it attacks as rain, condensation, water trapped in depressions or voids and as underground water which can flow and carry corrosive substances or compounds. The possible erosion of soil under foundations represents another very dangerous phenomenon. In the gaseous state, the water increases the relative humidity of the air and creates conditions for the increase of moisture content of materials as well as providing conditions that encourage biological growths. Wet processes should be avoided or at least substantially reduced to the minimum necessary extent during restoration works.

Among the greater threats to building materials in historic structures are *cyclical changes of moisture content* in materials, namely in the case of a material containing soluble salts (crystallization and hydration pressures generated at reversible changes of phases or crystal phases of salts) or clay materials (swelling of clay). In many cases, a relatively high but stable content of moisture in the building is less harmful than a fluctuating lower moisture content. In some cases, drying of permanently humid materials may be very dangerous (e.g. disintegration of marlstone due to a quick loss of freely bound water).

1.3.4 Air and Air Pollutants

The atmosphere is a thin layer of gas around the Earth. Atmospheric pollutants may be defined as those substances present in the atmosphere that can have adverse effects on health or the environment. The magnitude of the effect is normally closely related to the type and concentration of pollutants to which the systems (humans, ecosystems, buildings, etc.) are exposed. This exposure is a consequence of the location and characteristics of the emitting sources and the prevailing weather conditions.

Gaseous pollutants in the air, mainly oxides of sulphur and nitrogen, have similar effects as the natural atmospheric gases but the effect can be more severe. Gaseous pollution disperses in a shape of a cloud which contains aerosol, salts, acids and alkalis soluble in water. The solid phase particles create an important component of the air pollution, e.g. sand, dust, soot.

Normal gases present in the air (oxygen, ozone and carbon dioxide) react with some materials and may cause their degradation. In recent years the ozone concentration has increased in some locations due to unfavourable factors caused by human impact, and this trend should be stopped if possible. But in many urban areas ozone concentrations are reduced by reactions between the ozone and nitrogen oxide.

1.3.5 Wind

Wind primarily causes loading and mechanical damage of structures; nevertheless, it can also increase or decrease the chemical action of water and gases on cultural heritage objects. The flow around monuments substantially influences the deposition of pollutants, biological colonisation, cycles of drying and wetting, as well as mechanical wear of the attacked surfaces. Wind transports water, salts, dust and gases to the object or building but can also conduct them away in certain conditions.

1.3.6 Meteorological and Climatological Factors

The main constituents of the atmosphere are nitrogen (N_2 – 78%) and oxygen (O_2 – 21%). Three-quarters of the atmosphere's mass is within 15 km of the Earth's surface. Because this thickness is so small compared to the diameter of the Earth (12,742 km) it has often been compared to the skin on an apple. This region of the atmosphere is called the troposphere.

The region between 15 km and 50 km above the Earth's surface is known as the stratosphere. This is the region which contains the ozone layer, which protects the Earth and human health from the sun's ultraviolet radiation. Ninety per cent of all atmospheric ozone is contained within this region. There are very limited mechanisms for air mass movements between the stratosphere and the troposphere but it is possible for some gases that do not experience chemical reactions in the troposphere to disperse into the stratosphere. There is a major concern that chlorine and bromine compounds can find their way into the stratosphere by this route. Chlorofluorocarbons (CFCs or freons) and bromofluorocarbons (halons) are the main sources of chlorine and bromine, and they are used in aerosol propellants, refrigerator coolants and air conditioning units. These compounds react chemically with ozone and lead to a reduction in ozone concentration – leading to what is often referred to as the hole in the ozone layer. Supersonic aircraft fly in the lower levels of the stratosphere and their emissions are thought to be involved in chemical reactions which contribute to stratospheric ozone completion.

Within the troposphere, most air mass movements occur at low altitudes, up to about 2 km. This is known as the mixing layer of the atmosphere. Basically, the Earth's surface is normally warmer than the atmosphere above it, with the result that air is warmer, and consequently less dense, at the earth's surface than at altitude and so turbulence sets in. The degree of turbulence within the mixing layer is a function of temperature, wind speed and surface roughness. Pollutants emitted into this turbulent atmosphere are dispersed and diluted.

It is possible for exceptional circumstances to occur whereby the air at ground level becomes cooler than the air above it. This is known as a temperature inversion. If this happens, and at the same time wind speeds are very low, air mass movements are reduced or even stopped and under these conditions any pollution emitted into the atmosphere will be trapped there. If emissions continue, concentrations will continue to increase. These conditions are known as smog.

Under normal conditions, pollutants emitted to the atmosphere experience dispersion and dilution. The extent of the dispersion depends on the prevailing meteorological factors. The concentrations of the pollutants in the ambient atmosphere is determined by this dispersion, and also by the characteristics of the emitting source(s) – location, height above the ground, speed and temperature of the emissions. The extent of dispersion and dilution within an urban street canyon is very different from that which exists in open countryside. Also, chemical reactions within the atmosphere can change the composition and chemical form of the pollution. These effects can be brought together into a mathematical model (a dispersion model) which allows prediction of pollution concentration, given an input of pollutant emissions and meteorological conditions.

The spatial extent of the dispersion and dilution means that the effects of the emissions may be experienced at local, regional, national or global scales. And equally, the effects experienced at a specific location may be the result of local emissions or emissions a significant distance away from the source. This applies to the full range of adverse effects associated with pollution: from stratospheric ozone depletion due to the use of certain aerosol propellants in homes, to ecosystem damage due to the emission of acidifying compounds in a neighbouring country.

1.3.7 Synergy of Weather Factors

Weather factors mostly act on monuments in a synergistic way. The simultaneous action of temperature and water in repeated freezing/thawing cycles is a typical example of a situation which is very dangerous for wet porous, brittle and quasi-brittle materials. The interaction of temperature and moisture causes repeated and uneven volumetric changes and results in material deterioration and propagation of defects such as cracks. In combination with abrasive particles, the wind can cause remarkable surface erosion (e.g. on monuments in sandy deserts). However, there are numerous other examples: moisture and deposition mechanisms, wind plus water plus pollutants forming weak acids and penetrating into materials.

In recent years it has become clear that there may be one more climatic parameter that must be considered, that is the long-term fluctuations in climate included the long-term trends which are generally grouped together as the "greenhouse effect". A method of examining responses of building and materials to future climates is to review information on the sensitivity of materials to the present climate. However, this shows that there is a substantial lack of understanding and information. Some of the problems stem from the ever-present problem of linking accelerated laboratory testing to performance under atmospheric conditions. Consequently, it is impossible to quantify the impact of a temperature rise of a few degrees, a 10% increase in UV-dose, a 10% change in driving rain, etc. It is said that the climate of a city such as Amsterdam will change into the present climate of Paris but at present it would be difficult to indicate differences in the durability of materials in these two cities.

The effect of climate on construction can be tackled from two directions and both seem to have roles in future research. The first is usually termed "top down" and concentrates on making inventories of failures that occur (or have occurred) in the building stock. Analysis of this type of data can identify the parameters that seem to be associated with failure – for example rain penetration of building fabric – and also indicate how design guidance can be amended to overcome potential problems. Naturally, this type of approach is often closely linked to other research topics, in particular those associated with designing for durability and predicted service life.

The second approach is termed "bottom up" and concentrates on the analysis of mechanisms by which agents (wind, rain, etc.) give rise to failure. At first this approach can seem likely to give more generally applicable results as it is more theoretically based and may well involve modelling of some form. However, experience in other fields, including the climate change modelling, has shown that the width and complexity of the models, combined with many parameter uncertainties, can lead to substantial error bars on the final results. The "top down" approach tends to be more empirical and, although less widely applicable, may give more meaningful and useful results.

The EU-funded "Noah's Ark Project" (ISAC, 2004) assessed a number of factors associated with future climate change which are likely to have an impact on building deterioration at different temporal and spatial scales. It is accepted that trends in atmospheric composition and microclimate parameters will affect the fundamental processes causing damage to building materials, and that increasing atmospheric concentrations of carbon dioxide and other trace gases alter air chemistry and influence chemical reactions. In general, higher temperatures will influence chemical reactions, as well as reduce the effects of thaw-freezing cycles in many environments, while regions with stable cold weather could experience increased thaw-freezing cycles. Alteration in seasonal and annual rainfall will change the length of time during which surfaces are wet, affecting surface leaching and the moisture balance that influences material decay processes.

Although legislation has greatly reduced concentrations of "traditional" air pollutants in cities, the changing climate may enhance the effects of some of them. In particular, changes in wetting and drying cycles on building surfaces may alter the deposition of acidic gases onto the surface. Longer sunlight hours can increase the photochemical degradation of polymers used in both modern construction and the restoration of ancient buildings.

The explanation of damage to cultural heritage buildings from air pollution requires an understanding of many processes, from the details of the building to the nature of the sources of pollution which impact it. The range of interactions is shown diagrammatically in Fig. 1.1. These issues and procedures are developed later in this book.

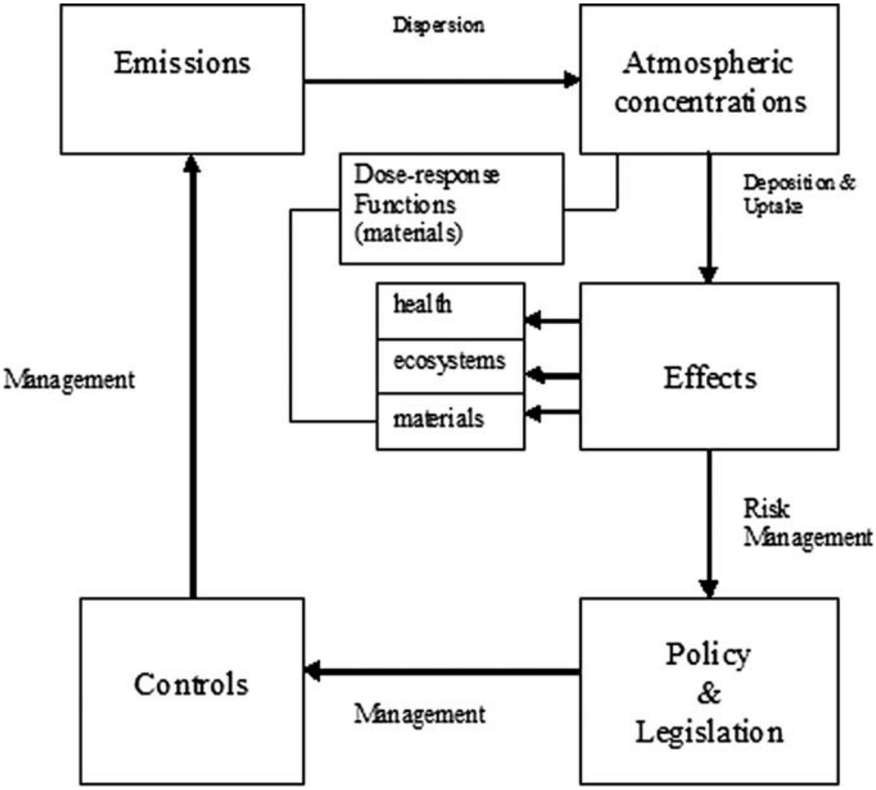

Fig. 1.1 Processes involved in the damage caused by exposure to air pollution

1.4 Pollutant Characteristics

Three broad but useful classifications of atmospheric pollutants are given here.

1.4.1 Natural or Anthropogenic

“Pollutants” from natural sources include lightning, volcanic eruptions, natural microbiological processes in the soil (bacterial action), wind-blown soils and animals. Pollutants from anthropogenic sources, i.e. from man-made activities such as energy generation, transport and domestic functions, include sulphur oxides, nitrogen oxides, hydrocarbons and heavy metals. Most atmospheric pollutants have both natural and anthropogenic sources. However, management and control options for natural source emissions are limited so most emphasis is placed on the identification and control of anthropogenic emissions.

1.4.2 Primary or Secondary

Primary pollutants are those emitted directly to the atmosphere by natural or anthropogenic sources. Secondary pollutants are those produced in the atmosphere by chemical reactions between the primary pollutants, generally in the presence of sunlight. Ozone (O_3) is an example of a secondary pollutant.

1.4.3 Gaseous or Particulate

Some air pollutants exist in the gaseous phase at ambient temperatures, e.g. NO_2, SO_2 and O_3. The normal definition of particulate includes both the liquid and solid forms of matter. Airborne particulate matter includes any material that can be transported through the atmosphere by wind and air movements including particulate matter up to 1 mm in diameter, though most particles in the ambient atmosphere are significantly smaller than this.

Here we focus on the most important transboundary pollutants that cause acidification (and therefore damage to materials), but also eutrophication and ground-level ozone. These are in turn sulphur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matter (e.g. PM_{10}) and precursor pollutants that cause ground-level ozone (O_3).

1.5 Emission Inventories

In order to calculate changes in emissions to see if international and national emission agreements have been met, government bodies regularly compile and update databases of emissions, called emission inventories. These inventories give emission totals per year for atmospheric pollutants, a breakdown of source contributions and often projections into the future based on the impact of current or future policies. Emission rates are often mapped showing how rates vary on a grid basis or per administration area, country or state. Sources of pollutants are categorised into three types: point sources (those occurring at a particular point, e.g. from industry), line or mobile sources (from transportation) and area sources (from diffuse emission points occurring across a wider area, e.g. agricultural or space heating emissions). Geographical information systems (GIS) are often used to compile the databases of emission sources and rates on a spatial scale and allow for easy mapping or manipulation of the data to show changes over time or compare source contributions.

Estimates of UK emissions are calculated annually on a 1×1 km square grid scale as the National Atmospheric Emissions Inventory (NAEI), by AEA Technology for the UK's Department for Environment, Food and Rural Affairs (DEFRA). Changes in annual emissions are predicted into the future, and also given for each year back to 1970 to show patterns over time. The European Environment Agency's Topic Centre on Air Pollution compiles an emission inventory on a 50×50 km square grid scale. The European Monitoring and Evaluation Programme (EMEP-Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe, formerly the CORINAIR inventory) maps emissions across Europe from ten internationally agreed source categories (UN/ECE SNAP nomenclature/source sectors).

The United States Environment Protection Agency (USEPA) National Emission Inventory (NEI) 2002 database includes four of the six criteria pollutants (CO, NO_x, SO_2 and particulate matter (PM_{10} and $PM_{2.5}$)). The NEI also includes emissions of volatile organic compounds (VOCs), which are ozone precursors, emitted from motor vehicle fuel distribution and chemical manufacturing, as well as other solvent uses. VOCs react with nitrogen oxides in the atmosphere to form ozone. Ammonia (NH_3) is also an additional pollutant included in the NEI.

Emissions inventories at a finer spatial scale (0.5 or 1 km square) have been compiled for urban areas and major conurbations. For example, emissions per 1×1 km square grid have been compiled for London since 1993, initially as the London Energy Study, giving emissions of CO_2 and SO_2. Now greatly improved and expanded to 27 pollutants, the London Atmospheric Emissions Inventory (LAEI) compiled by the Greater London Authority (GLA) gives emissions for a base year of 2004. Emission inventory summary data is available to the public and has been used here to examine the main air pollutants and consideration of their sources and emission rates.

1.6 The Main Air Pollutants

This section reviews the main air pollutants responsible for damage to materials, with a summary of their physical and chemical properties. Emission rates are presented. Data for the UK are presented as examples; similar trends are experienced by many other countries.

1.6.1 Sulphur Dioxide

The most important natural sources of sulphur dioxide, SO_2 (and of other sulphur compounds) are volcanoes, during both active and dormant periods. Globally, these contribute perhaps 20% of the world's total sulphur emissions. However, in both developed and less-developed countries, particularly in urban areas, emissions that arise from the combustion of solid fossil fuels are of prime concern. Coal and oil both contain sulphur in varying amounts, and both therefore produce sulphur dioxide when burnt. The average sulphur content of British coal is 1.7%, and that of heavy fuel oil about 2–3%. By contrast, natural gas contains negligible amounts of sulphur.

A summary of the sulphur dioxide yearly emissions since 1970 in the UK is shown in Fig. 1.2

Since 1970 there has been a substantial overall reduction of more than 74% in SO_2 emissions. Reductions in public power, commercial, residential and industrial emissions, changes in fuel use and increasing use of abatement equipment have led to this fall. Emissions of SO_2 from solid fuel use have declined by 84% since 1970 and those from petroleum by 95%. However, coal combustion is still the main source – it accounted for 76% of the 2003 UK SO_2 emissions, for example. The most important factors in the fall in emissions from petroleum use are the decline in fuel oil use and the reduction in the sulphur content of gas oil and diesel fuel. The reduction in the sulphur content of gas oil is particularly significant in sectors such as domestic heating, commercial heating and off-road sources where gas oil is used extensively. The emission profile exhibits a steady decline between 1970 and 2004 with the exception of small peaks in 1973 and 1979 corresponding to the harsh winters in those years and a short period at the end of the 1980s when emissions were relatively constant from year to year. The two main contributors are solid fuel and petroleum products.

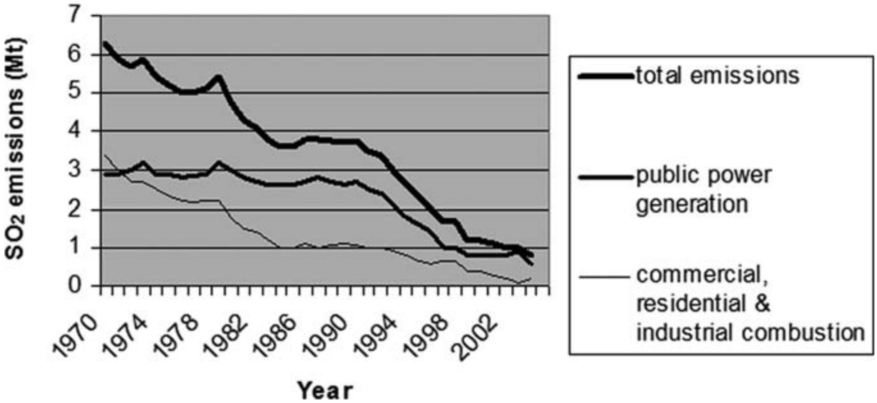

Fig. 1.2 Annual emissions of SO_2 in the UK. (NAEI, 2008)

The effect on ground-level concentrations has been compounded by the change in fuel use patterns that has been going on since the Clean Air Acts of 1956 and 1968. Not only has the burning of coal and oil (once widespread in domestic, commercial and industrial space heating and process use) declined sharply, but electricity generation has been concentrated in large power stations in predominantly rural areas. As a consequence, emissions from low and medium level (in terms of stack height) sources have been replaced by high-level emissions. Higher SO_2 concentrations can therefore be found near coal-fired power stations. There are still a few towns in the UK where the burning of coal for domestic heating produces high concentrations of SO_2 locally, e.g. Belfast City.

It seems likely that national emissions will decline still further as a result of the continued rollout of flue gas desulphurisation in power stations and the replacement of coal by natural gas and imported coal for electricity generation. Relatively small, local sources can have a disproportionate effect on ground-

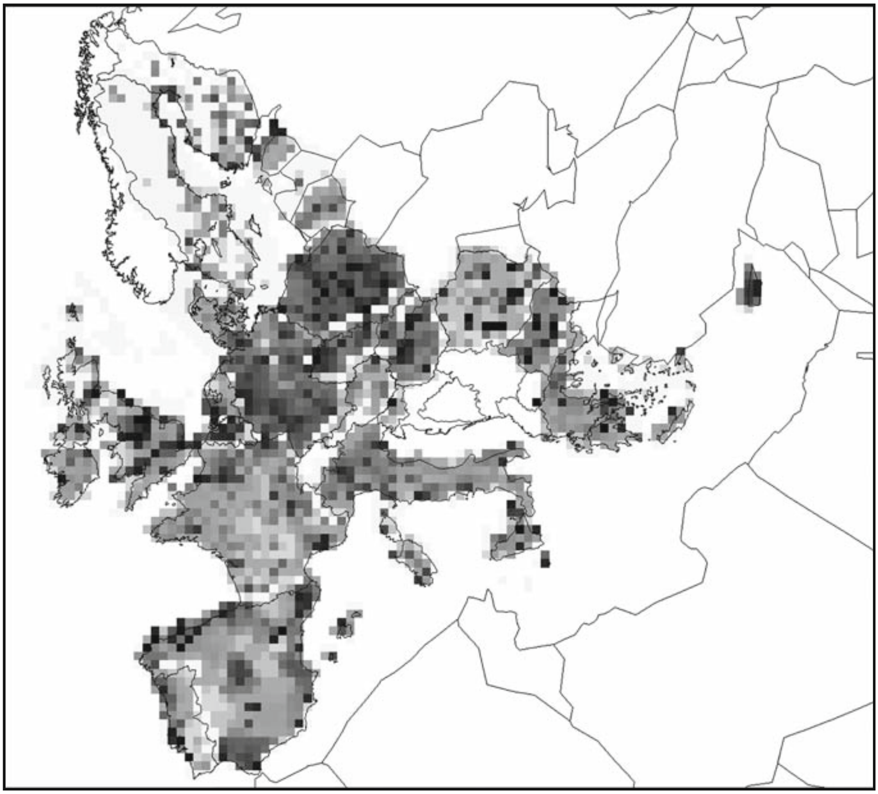

Fig. 1.3 SO_x Emissions per 50 km square grid for the 27 EU countries in 2004 in mega grammes. (EMEP, 2006)

level concentrations, particularly during a high-pollution episode, which occurs as a result of an inversion trapping the emissions from low-level sources within a shallow mixing layer. SO_2 emissions contributed to a number of severe smog pollution episodes in the 1950s and 1960s, for example, the Great Smog in London in December 1952 where industrial and domestic coal burning during a period of cold temperatures and an inversion layer trapped emissions at low levels. Very poor visibility and high levels of SO_2 (up to 3.7 mg m^{-3}) and black smoke (above 4.5 mg m^{-3}) led to up to 4000 extra deaths from respiratory diseases (Anderson, 1999). This was a major drive for government action and helped shape modern air pollution legislation in force today.

European emissions (Fig. 1.3) reflect areas of power use and production. Cities in Spain, for example, can clearly be seen. SO_2 emissions are higher generally in Eastern European countries, due to coal-fired power stations and the relatively high sulphur content of coal sourced locally. This has implications for cultural heritage in cities like Prague for example, as historic buildings are exposed to higher SO_2 concentrations.

1.6.2 Nitrogen Oxides and Nitric Acid

There are a number of nitrogen oxides (NO_x), but the one of principal interest as an air pollutant likely to have adverse effects on human health and soiling properties is nitrogen dioxide (NO_2). Other nitrogen oxides such as N_2O_3 and N_2O_4 are of lesser significance as air pollutants. Nitrous oxide (N_2O) is of some interest as a greenhouse gas, while nitrogen pentoxide (N_2O_5) and nitrogen trioxide (NO_3) are important in the atmospheric chemistry of pollution episodes. Nitrogen compounds are also contributors to the wet and dry deposition of acidic compounds on vegetation and buildings.

The oxide emitted to the atmosphere in the largest amounts is nitric oxide (NO), which is itself relatively innocuous. However, it is readily oxidised – by, for example, ozone – and is the immediate source of most atmospheric nitrogen dioxide. The fraction of nitric oxide that is converted to nitrogen dioxide by ozone and the speed of the reaction depend upon the concentrations of the two reacting gases. The reaction is fast and, provided the concentration of ozone is sufficient, is substantially complete within a minute or so. In locations such as busy roads where the nitric oxide concentration is high, the local concentration of ozone may be insufficient to complete the reaction. Much of the nitric oxide may therefore travel downwind of its source and reach relatively clean air before more ozone becomes available. The NO/NO_2 ratio is therefore significantly larger in urban than in rural areas.

Nitric oxide and nitrogen dioxide are known collectively as NO_x, and it is usual to express NO_x as the NO_2 equivalent in estimates of emissions by mass. In the atmosphere, nitric acid is present in very minute quantities as a gas or vapour, produced by reactions between atmospheric oxidants and emitted nitrogen oxides. Typically, emitted NO_x is converted to nitric acid within a day or less. The atmospheric removal processes for gaseous nitric acid are by wet and dry deposition. The estimated half-life and lifetime for dry deposition of nitric acid are 1.5–2 days and 2–3 days respectively, and there is also efficient nitric acid removal during episodic precipitation events. Nitric acid reacts with gaseous ammonia to form particulate or aerosol nitrate, which in turn is removed by wet and dry deposition of the particles. The average half-life and lifetime for particles in the atmosphere are about 3.5–10 days and 5–15 days respectively.

1.6.2.1 Sources of Atmospheric NO_x

The most important natural sources of NO_x are volcanoes, lightning and bacterial action (natural microbiological processes in the soil) and on a global scale these far outweigh anthropogenic sources. However, in urban areas the emissions arising from the combustion of fossil fuels are of most concern.

Any combustion process may produce nitrogen oxides from the oxidation of nitrogen in the air or, less importantly, in the fuel or other material being burned. The most important man-made sources are the combustion of fossil fuels in power generation and the combustion of petrol and diesel in vehicles. Other relatively minor contributions to the atmosphere come from non-combustion industrial processes such as the manufacture of nitric acid, the use of explosives and welding operations.

Estimates of UK NO_x emissions during the period 1970–2004 and source apportionment are given in Fig. 1.4. It can be seen that the main sources are power stations and road transport; the latter and coal combustion combined to account for 54% of UK emissions in 2003. Emissions from power stations have remained fairly constant during the period, only decreasing from the end of the 1990s from improvements in abatement technology. Those from road transport steadily increased from about 0.6 Mt in 1970 to 1.3 Mt per year in the early

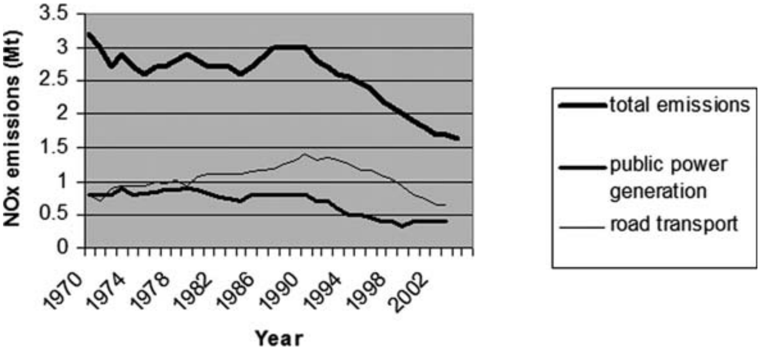

Fig. 1.4 Annual UK NOx emissions and proportion from sources. (NAEI, 2008)

1990s, when they constituted about 50% of the total. Road transport emissions then decreased to around 0.6 t/y today as emissions from petrol engines have declined since the introduction of catalytic converters in the early 1990s. EC Directives on exhaust emissions required mandatory fitting of a catalytic converter (a three-way catalyst, TWC) to all new petrol engine cars throughout the European Union from 1993. NO_x emissions from such cars (expressed in terms of grams per kilometre averaged over the whole TWC car population) are generally at least 10 times lower than from cars without converters. As almost all of the petrol vehicle fleet now has TWCs, the maximum pollution benefit of this technology has been observed and only a relatively small reduction in NO_x emissions will occur in the future as older cars are taken out of service. A 75% reduction in NO_x emissions resulted from this action.

Recent research has highlighted the increasing importance of directly emitted NO_2. There is evidence for significant amounts of NO_2 being emitted directly from the tailpipes of diesel vehicles, especially when slow moving, with levels possibly as high as 25% of total NO_x emissions in mass terms. These primary emissions have a significant impact on roadside NO_2 concentrations in areas where the proportion of diesel vehicles is large (DEFRA, 2004).

Fuel use and population density also drive the spatial pattern of NO_x emissions as Fig. 1.5 shows for emission densities across the United States. Similar patterns occur for all other industrialised nations.

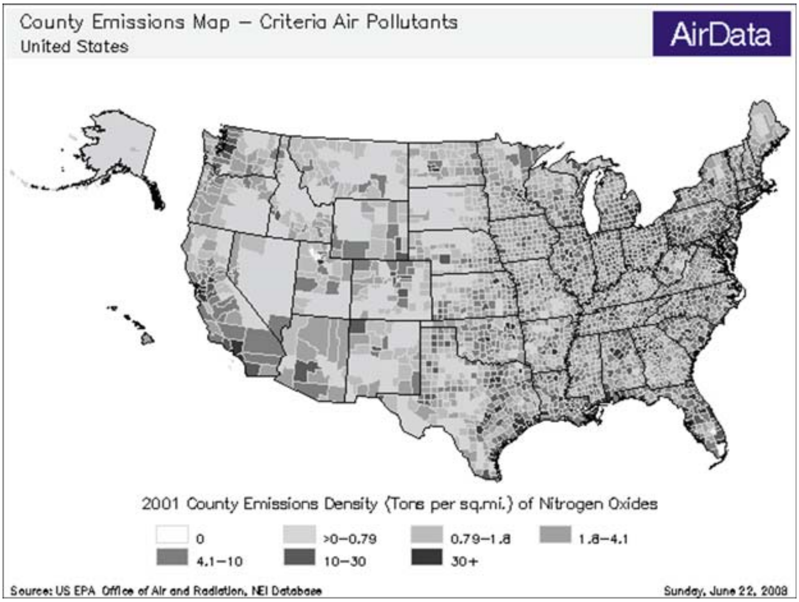

Fig. 1.5 Nitrogen dioxide emissions in the US in 1999. (EPA, 2008)

1.6.3 Particulate Matter

Particulate matter is a term that represents a wide range of chemically and physically diverse substances that can be described by size, formation mechanism, origin, chemical composition, atmospheric behaviour and method of measurement. The concentration of particles in the atmosphere varies across space and time and as a function of the source of the particles and the transformations that occur to them as they age and travel.

There are a number of ways of measuring the amount of PM in the air, which has resulted in a number of different ways of expressing the data. Historically, measurements focused on a weight measure, total suspended particulate (TSP), which was often averaged over seven days, or measured “smoke” as a proxy for particulate. The levels of smoke or black smoke in the atmosphere were measured as an indicator of the concentration of particles in the air. In the UK a measurement of black smoke has been the traditional technique as an indication of the level of PM in the air and is still used in the Automatic Urban Network (AURN) and EU Directive monitoring networks. The method consists of drawing air through a white filter paper and measuring the darkness of the stain produced by use of a reflectometer. A standard calibration curve is used to convert the reflectometer measurement into a nominal mass concentration of the airborne particles, referred to as the “black smoke concentration”. The method is defined by British Standards (BSI, 1969). The validity of the results depends upon the fraction of carbonaceous (i.e. black) material in the sample. The standard calibration curve is valid only for particulate material of the type that existed in UK urban areas up to the early 1960s, and nowadays there is no reliable relationship between black smoke and gravimetric measurements (Bailey and Clayton, 1982). The relationship between TSP and PM_{10} is controlled by the size distribution of the airborne particles, and is therefore very variable.

In the last 15–20 years, studies have concentrated on different size fractions due to the nature, sources, behaviour and effects of the PM. The predominant particle mix in most cities is dominated by fine particles (less than 2.5 μm in aerodynamic diameter (see definitions later in this section), known as $PM_{2.5}$) generated by combustion sources, with smaller amounts of coarse dust (between 2.5 and 10 μm in diameter). Particles less than 10 μm in diameter (PM_{10}) are often measured that include both fine and coarse dust particles. More precisely, PM_{10} has been specified in terms of a sampling method for which the collection efficiency of particles of size˙10 μm is 50%. These particles pose the greatest health concern because they can pass through the nose and throat and get into the lungs. Particles larger than 10 μm in diameter that are suspended in the air are referred to as total suspended particulates (TSP). A number of size-selective inlets have been designed for the TSP monitors to capture particles, with a cut point of 10 μm.

PM_{10} has become the generally accepted measure of particulate material in the atmosphere in the UK and in Europe due to its well-documented association with adverse health effects. The main sources of primary PM_{10} are road transport

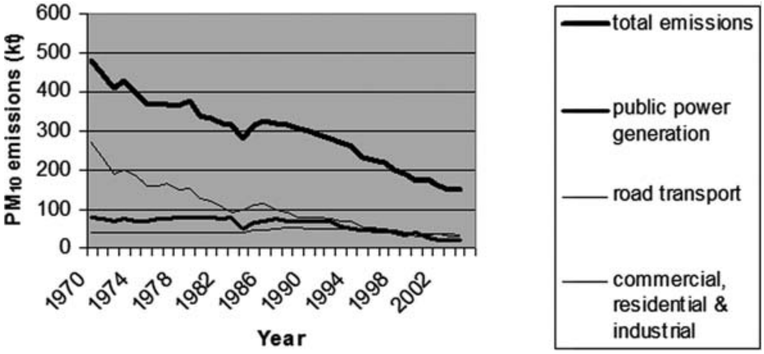

Fig. 1.6 Annual PM_{10} emissions since 1970 in the UK. (NAEI, 2008)

(all road transport emits PM_{10}, but diesel vehicles emit a greater mass of particulate per vehicle kilometre), stationary combustion (domestic coal combustion traditionally being the major source of particulate emissions in the UK) and industrial processes (including bulk handling, construction, mining and quarrying).

UK emissions of PM_{10} declined by 51% between 1990 and 2003, giving an emission total of 0.14 Mt in 2003 (Fig. 1.6). This reflects a trend away from coal use particularly by domestic users. Coal combustion and road transport together contributed 57% of UK emissions of PM_{10} in 2003. PM_{10} emissions from road transport have shown a steady decline across recent years. $PM_{2.5}$ emissions have also fallen, but by a smaller amount, with the largest source sector being road transport, accounting for 52% of the 2003 total emission. Black smoke emissions in the UK have significantly declined (by some 66% between 1970 and 2003). $PM_{2.5}$emissions in 2003 were estimated to be 152 kt although these estimates are based on old measurement data and are hence very uncertain. Domestic and commercial emissions have fallen from 263 kt (54% of the total emission) in 1970 to 41 kt (27%) in 2004 (NAEI, 2008).

Many of the atmospheric pollutants about which there is concern as to possible adverse health effects and of soiling are in particulate form. Lead and other heavy metals, asbestos and some of the polyaromatic hydrocarbons are well-known examples. The particulate material in the atmosphere consists of many chemically and physically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide range of sizes. They originate from a variety of sources – either emitted directly from, for example, vehicles and factories or formed in the atmosphere by the transformations of gaseous pollutants such as sulphur oxides, nitrogen oxides and volatile organic substances.

Attempts have been made in the past to classify disperse aerosol systems in gases on the basis of their nature, origin and particle size. None of these has been completely successful because of the indefinite character of many types of particulate clouds and the difference, often not clear cut, between scientific and