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SCIENCE DIRECT®

Environment International 29 (2003) 201–211

ENVIRONMENT INTERNATIONAL

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Ecological effects of sulfur dioxide, fluorides, and minor air pollutants: recent trends and research needs

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Abstract

The regulation of the emissions of 'traditional' primary air pollutants (fluorides, sulfur dioxide) has changed the pattern of exposure of ecological systems, with greatly reduced exposure close to sources, but with a smaller effect in some remote areas. Measurements show that recovery is occurring at some sites, in fresh water chemistry (reduced acidity) and in sensitive biota (sustainable fish populations). However, the pattern of change in exposure has not always been simply related to emission reductions. An understanding of responses to recent changes will improve our predictions of the response to future emission changes, both locally and globally.

As exposure to 'traditional' pollutants is reduced, the potential for other pollutants to have effects becomes more evident. In the aqueous phase, we need to understand the role of soluble and suspended organics, but this also means explicit recognition of the possibility of phase exchange, and the role of photolytic reactions on plant, soil, and water surfaces. Do highly reactive free radicals in the atmosphere, formed by the action of sunlight on volatile organic compounds, have direct effects on plants? Organic compounds and heavy metals may be bioactive as gases and particles, but for many potentially toxic compounds, the experimental evidence for biotic response is very limited.

To evaluate the potential effects of pollutants, we need to understand the pathways by which airborne pollutants enter and react within ecosystems. For vegetation, we have to consider bidirectional fluxes, and distinguish among uptake through stomata, through leaf surfaces, or through roots. There are several challenges for the future. (1) Can we devise experiments that permit exposure of vegetation to gases, particles, and/or aqueous pollutants at 'realistic' concentrations? (2) Can we include the potential interactions with photolytically derived free radicals, and the dynamics of exchange? (3) How do we allow for responses to pollutant mixtures, or the simultaneous exposure to pollutants in gas, particle, and aqueous phases? The recognition of the importance of the dynamic exchange of pollutants between phases will be the key to the development of effective experimental approaches to evaluating cause–effect relationships between pollutant mixtures and ecosystem responses.

Keywords: Sulfur dioxide; Sulfate; Trends; Recovery; Uptake pathways; Air pollution

1. Introduction

This paper addresses the recent trends and future prospects for research into the ecological effects of air pollution not connected with nitrogen or ozone, which are addressed elsewhere in this volume (Adams, 2003, Davison and Cape, 2003, Fuhrer and Booker, 2003; Grantz et al., 2003; Laurence and Andersen, 2003).

Traditionally, the 'acid rain' debate focussed on the ecological impact of sulfur dioxide emissions. The earliest studies of the acute and chronic effects of sulfur dioxide, close to emission sources, go back several centuries, and what might be termed 'modern' studies were already in place by the end of the 19th century. Concerns over the effects of long-range transport on fresh water chemistry and biology were voiced about 50 years ago, and drove the 'acid rain' debate in the 1980s. In North America and Europe, emission reductions were negotiated internationally, and have led to a significant decrease in sulfur dioxide emissions. The other major pollutant clearly related to industrial activity, from brick making and aluminium production, is fluoride. The ecological effects were already well known over 30 years ago, and because there was a clear cause–effect relationship (fluoride accumulates in plants), action was taken to remove most fluoride emissions at their source.

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0160-4120/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0160-4120(02)00180-0

As emissions of these 'traditional' pollutants have decreased, the potential for other airborne pollutants to be recognized as having harmful ecological effects has increased. Attention is now turning to the possible effects of substances that are present at much smaller concentrations in the atmosphere than the major air pollutants, but which may (unchanged, or after metabolism) accumulate in ecosystems and be augmented through food chains. These 'new' pollutants may be present in the atmosphere as gases, or in the particulate phase, either as solids or adsorbed on the surface of particles. This paper will consider the role of some 'new' pollutants in the gas phase, and in aqueous solution as rain, cloud, or dew.

2. Sulfur dioxide

2.1. Emissions

Emissions of SO_2 in North America and Europe rose rapidly after the Second World War, and peaked in the late 1970s. Since then, changes in industrial practices and the introduction of emission controls have led to emission reductions (Fig. 1). Since 1980, there has been a consistent decrease in emissions in both North America and Europe. The most stringent controls were in Europe, both in the European Union (EU) and in the wider geographical area covered by European Monitoring and Evaluation Programme (EMEP), which extends to the European parts of the former Soviet Union, and from the Arctic to the Mediterranean Sea. The rate of reduction in Europe has been greater in the past decade, with overall emission reductions in 1998 (relative to 1990) at 43% over the EMEP area and 52% over the 15 Member States of the EU. This compares with around 17% over North America (United States and Canada) over the same period (Tarrason and Schaug, 2000). The introduction in 1995 of the Phase I of the US Clean Air Act Amendments of 1990 made only a small blip in the overall US emissions (Lynch et al., 2000), although regional effects in North Eastern United States were more obvious (Shannon, 1999). Per capita emissions in North America in 1998 were still significantly greater than in Europe (68 g year^{-1} SO_2 in North America, cf. 21 g year^{-1} SO_2 in EU, ca. 30 g year^{-1} SO_2 in EMEP area).

In Asia, data are now becoming available for the whole region and disaggregated into individual countries (Streets et al., 2000). Emissions of SO_2 in the mid 1980s were similar to those in the United States and the 15 countries that now constitute the European Union, with China contributing around two-thirds of the total. In contrast to the decreases seen in the west, overall emissions have increased by around 16% between 1990 and 1998, although there are indications that the introduction of controls on the sulfur content of coal has slowed the rate of increase in emissions. Per capita emissions are still much smaller than for Europe and North America, amounting to around 12 g year^{-1} SO_2.

2.2. Air concentrations and dry deposition

The reduction in emissions of SO_2 has varied across regional scales within countries, as well as between countries, as industrial practices have changed (e.g., major changes in heavy industry in eastern Europe) and emission controls have been selectively introduced. The consequent effects on measured air concentrations have also varied regionally, but with an overall decrease in average concentrations that has generally been greater than the decrease in emissions (Tarrason and Schaug, 2000; USEPA, 1998). However, this decrease has been seen most noticeably in urban areas, both in the United States and in Europe, predominantly from the larger decrease in emissions from low-level sources associated with domestic and industrial oil and coal burning rather than from major point sources. The rate of removal of SO_2 from the atmosphere by dry

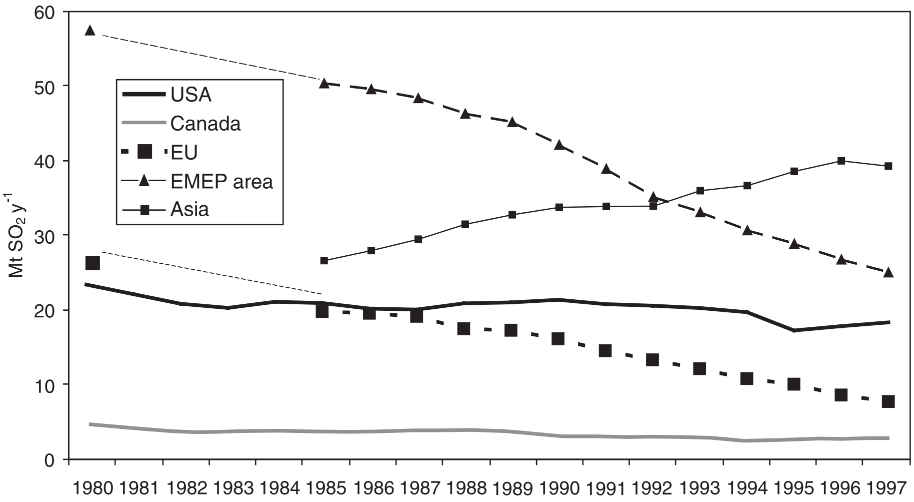

Fig. 1. Comparison of SO_2 emission trends: Europe, North America, and Asia (Tarrason and Schaug, 2000; Streets et al., 2000).

deposition may also have increased as air concentrations decreased in the source areas. Recent measurements suggest that average deposition velocities in Central England have increased as the SO_2/NH_3 ratio has fallen (Fowler et al., 2001). Geographical trends across Europe also imply that the surface resistance to dry deposition of SO_2, which is one of the major factors influencing the overall dry deposition rate, depends on the relative concentrations of SO_2 and NH_3 (Fowler, 2001). A smaller SO_2/NH_3 ratio permits a greater fraction of SO_2 to dissolve in surface water because the self-limiting acidity produced is neutralized by the presence of NH_3. These interdependencies between SO_2 and NH_3 concentrations, and their effect on dry deposition (in addition to factors such as surface wetness) are currently not well represented in dry deposition models. These models attempt to estimate regional dry deposition patterns and sulfur budgets using air concentration fields derived from models and/or measurements. Unfortunately, there are no long-term measurements of gas fluxes (as opposed to gas concentrations) to demonstrate the changes implied by the studies cited above.

2.3. Direct effects of SO_2 on vegetation

The acute and chronic effects of SO_2 on vegetation, which were observable close to emission sources in Europe, North America, and Japan from the start of industrialization, have largely disappeared. However, rapid industrialization in other parts of the world is leading to localized and regional air concentrations of SO_2 well in excess of thresholds for vegetation damage. To a large extent, improvements in air quality in such regions will only be achieved by localized emission reductions because the effects are driven by gaseous SO_2 rather than by long-range transport of sulfate.

2.4. Sulfate deposition and consequences for freshwater acidification

Further from sources, the wet deposition of sulfate dominates the deposition processes, and routine measurements of sulfate in precipitation show downward trends across North America and Europe (Hedin et al., 1994; Nilles and Conley, 2001; Tarrason and Schaug, 2000). Across Europe, the average sulfate concentration in rain has fallen more slowly than emissions, while in the United States, average sulfate concentrations have fallen more rapidly than emissions (Fig. 2). However, the average numbers conceal very large regional differences in the trends in sulfate concentration and deposition, and are to some extent determined by the locations of the sampling sites relative to emission sources. In general, in the more remote areas, wet deposition of sulfate has decreased more slowly than the emissions. For example, in the UK, four regions showing different temporal trends in rainfall sulfate concentrations between 1988 and 1997 have been identified. In the southeast, the region containing most of the SO_2 emissions, nonsea sulfate concentrations fell on average by 1.6 μM $year^{-1}$ (from 41 to 25 μM) whereas at remote northwestern sites in Scotland, the trend was only 0.25 μM $year^{-1}$ (Fig. 3) (Monteith and Evans, 2000).

These reductions in wet deposition have led to some recovery from acidification in freshwaters in North America and Europe, at least as far as chemical changes are concerned. Sulfate concentrations in freshwaters generally decreased more in the 1990s than in the 1980s (Stoddard et al., 1999), but this was not always matched by an increase in alkalinity. Alkalinity increased in most of the acidified freshwaters in Europe, but in only one of five regions in North America. While the reduction in emissions of SO_2 in Europe has been much greater than in North America, there has also been a significant decrease in the wet deposition of

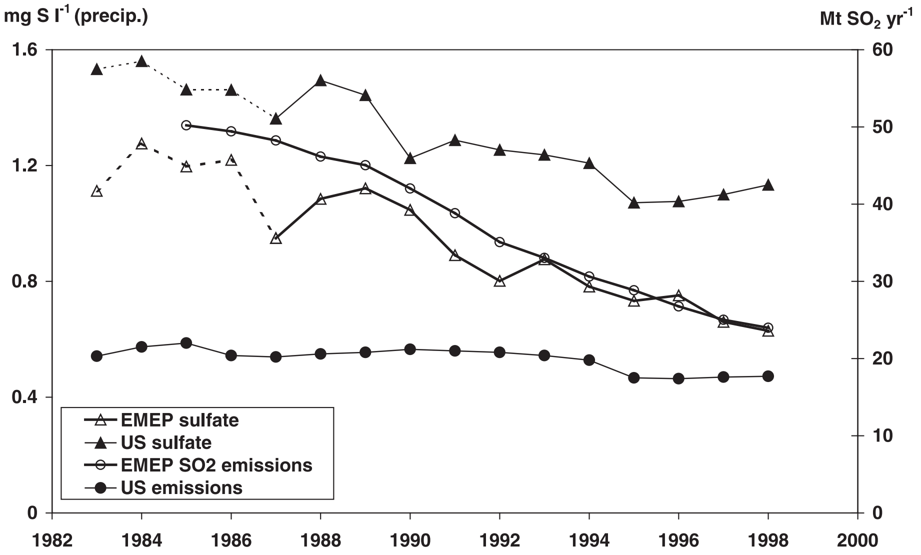

Fig. 2. Average precipitation sulfate concentrations, and total SO_2 emissions in the EMEP area and the United States. Dashed lines indicate fewer than 38 sites (EMEP) or 180 sites (United States) (Tarrason and Schaug, 2000; USEPA, 1998).

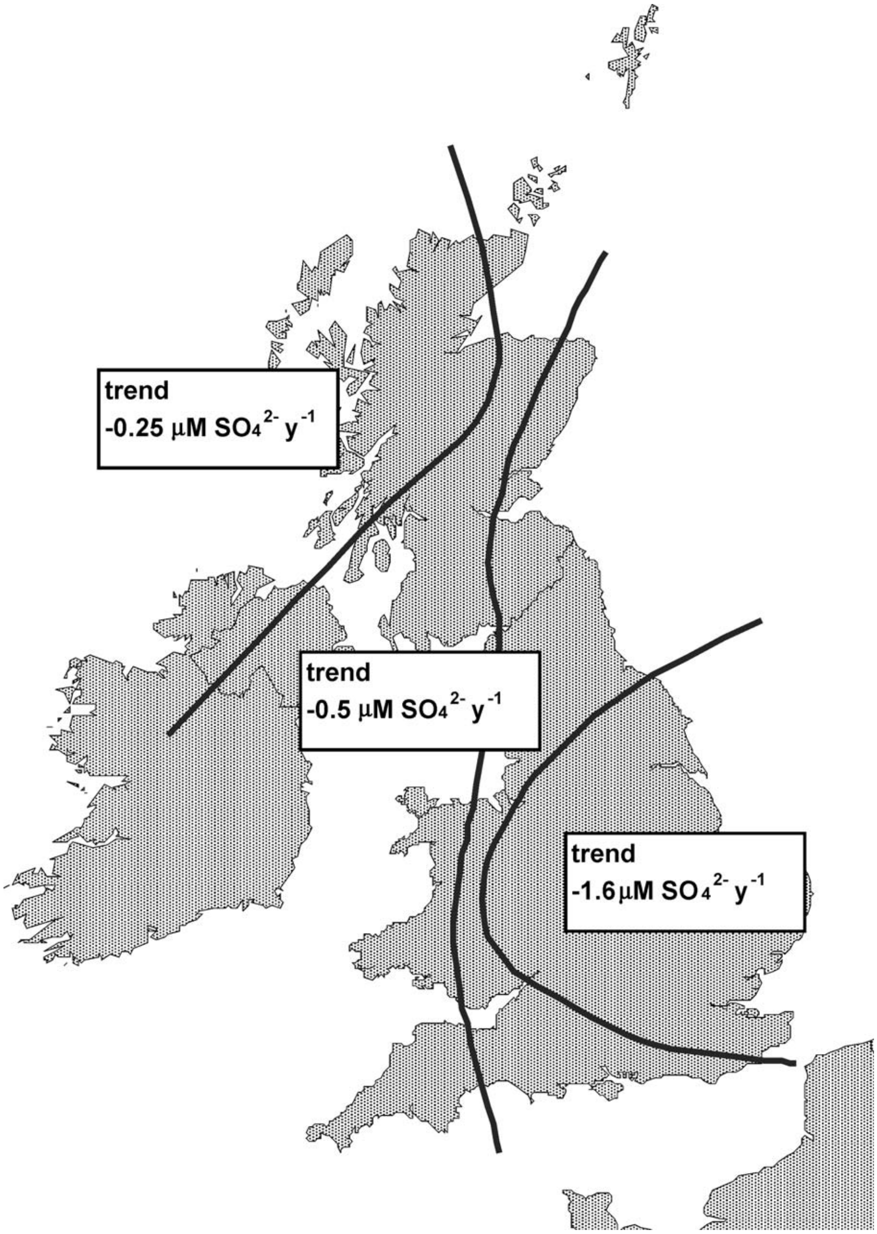

Fig. 3. Trends in annual nonmarine SO_4^{2-} concentration in precipitation between 1988 and 1997 across groups of sites based on an objective hierarchical clustering of trends. The main source region for SO_2 emissions is in Southeastern England (redrawn from Monteith and Evans, 2000).

base cations in all the regions (except in Great Britain), as noted earlier by Hedin et al. (1994). This decrease in base cation deposition was more pronounced in North America than in Europe in the 1990s. The consequent impact of the reduction in sulfate deposition on freshwater chemistry has therefore been less than might have been expected.

The reduction in wet deposition of base cations has compounded a problem caused by the progressive leaching of calcium and magnesium from soils in the affected areas. Sulfate ion leaching in acidified soils is associated with free acidity and aluminum, rather than being balanced by base cations. Hovmand (1999) calculated the cumulative wet and dry deposition of S to a spruce forest in Denmark. He showed, in the 90 years up to 1995, that the amount of S deposited (as equivalents) was between two and three times the total base cation (Ca, Mg, K) content currently available in the forest soil. Where weathering rates are very small and/or base cations are not available (as in the sandy soil of his study), it is likely that even the most optimistic scenarios for emission reduction will not restore the base cation content of the soil in a reasonable time. This suggests that the legacy of a century of industrial activity is a permanent change in soil and freshwater status.

2.5. Biological consequences of emission reductions

The clearest evidence that improvements in water quality have led to biological recovery comes from northern

Europe. In Norway, as early as the mid 1990s, changes in invertebrate populations in freshwaters led Raddum and Fjellheim (1995) to suggest that the observed increase in invertebrate diversity was probably a result of the reductions in acid deposition. More recently, there have been significant increases in the densities of brown trout in the Gaular and Vikedal rivers that are moderately acidic river systems in Western and Southwestern Norway (Hesthagen et al., 2001). Similarly, the river Otra (also in Southwestern Norway) again can support a native salmon population (Kroglund et al., 2001). In Sweden, Lake Orvattnet has begun to recover from acidification, based on a study of diatoms and perch populations (Ek et al., 1995). More recently, the successful reproduction of perch has been taken as an indication of the recovery of fish populations in the acidified lakes of Southern Finland (Nyberg et al., 2001). In Great Britain, although chemical recovery has been less clear-cut than in Scandinavia (Monteith et al., 2001), biological recovery is occurring in at least two chronically affected areas of the UK (Juggins et al., 1996).

In North America, the large emission reduction from smelting operations at Sudbury (Canada) has led to the recovery of acidified freshwaters in the region. This, admittedly extreme, situation has given some idea of the time scales involved in the process. Keller and Yan (1998) suggested that about a decade is sufficient to permit a substantial recovery of zooplankton communities. Presumably, the recovery of fish stocks takes a little longer. This may explain why, in a recent survey of freshwaters in Nova Scotia, there was no significant time trend in the population densities of 10 fish species between 1982 and 1996 (Watt et al., 2000), despite a significant decline in sulfate concentrations.

2.6. Nonlinearity and conclusions for future research

The nonlinearity in the relationship between emissions and both dry and wet deposition on a regional scale has important implications for ecological effects of emitted SO_2. The historical problems of acute and chronic SO_2 damage to vegetation, soiling of buildings, and human health effects of sulfuric acid smog have largely disappeared from the industrialized source regions. However, the reductions in sulfate deposition to remote areas, where soil and freshwater acidification has resulted in the loss of fish and other biota from lakes and rivers, have been smaller than anticipated. The reasons for this nonlinear behavior are not fully understood, but have been attributed to several causes: (1) long-range transport of anthropogenic sulfate and natural sources, contributing a significant ‘background’ deposition; (2) the removal of oxidant limitation in the conversion of SO_2 to sulfate during atmospheric transport; and (3) changes in the rates of dry deposition of SO_2 related to the availability of ammonia in the boundary layer. The complexities of the atmospheric chemistry of SO_2 oxidation and the effect of emission controls on NO_x and VOCs have been explored recently by Stein and Lamb (2000) for a particular event in the United States.

Source–receptor models have been introduced to target future emission reduction strategies so these strategies will be most effective (e.g., the UN Economic Commission for Europe, Warren and ApSimon, 2000; the RAINS-ASIA model, Shah et al., 2000). The strategies rely on the models to include all the processes that control the transport, reaction, and deposition of SO_2 from source to receptor. Simple parameterisations of the processes, whether of dry deposition or atmospheric chemistry, that rely on the processes being independent of emission strength and air concentration of SO_2 are not secure. There is evidence that reaction and deposition rates are not linearly dependent on air concentrations, and cannot be treated as constants over time. Moreover, there are still very few field data to provide a framework for developing more responsive model parameterisations, at concentrations that are relevant to today’s emission levels and concentrations. Given the regional diversity in factors such as NH_3 emissions, cloud frequency, cloud water pH, oxidant availability, and surface wetness, we cannot safely assume that even well-structured models, shown to work well in one region, can be simply translated to a different region of the world. Nor can they be translated to a time in the future where many of the controlling factors may be significantly different from the present.

3. Fluoride

Fluoride damage around aluminium smelters, brick works, and phosphate fertilizer factories has been recognized for over a century, and stimulated research on biological effects that led eventually to the development of air quality guidelines. More is known about the biological effects of fluoride on vegetation than any other air pollutant. The most recent summary of symptoms and sensitive species is that of Weinstein et al. (1998). Air quality guidelines were originally developed in the United States, with one of the earliest collations of data made by McCune (1969a,b). Sensitive species, such as *Gladiolus* and some conifers, were identified, and attempts were made to relate the onset of symptoms to exposure times at different air concentrations of HF. The lowest concentrations that produce visible injury are around 0.3 $\mu g\ m^{-3}$, if the exposure time is sufficiently long.

Air concentrations have fallen rapidly with the advent of cleaner technologies. It is estimated that the emission per tonne of aluminium produced has fallen by a factor of 100 over the last 50 years. However, incidents still occur, often as the result of accidental releases, and these can cause localized acute injury for several square kilometers around the source. There is also a potential problem from the increased use of cryolite as a pesticide in the United States, to the extent that it may be a more widespread source of fluoride in the environment than HF from industry.

Although fluoride emissions from industry are no longer a major issue in North America and Europe, there is growing evidence of the pollutant effects of fluoride in developing countries. Where studies have been made, for example in Brazil (Klumpp et al., 1996) using 'traditional' bioindicator species, the risk to vegetation has been quantified. Local plant species are also being screened as potential bioindicators more suitable for the tropics (Klumpp et al., 1995).

More recently, concern has been raised over the potential for the accumulation in sensitive ecosystems of fluorinated breakdown products from CFC replacements. Measurements of trifluoroacetate (TFA) in the environment have shown its ubiquity. However, the amounts measured are considerably larger than can be explained simply as resulting from the breakdown of CFC replacements in the atmosphere. The issues and a risk assessment are presented on the web site of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) (http://www.afeas.org/wetlands.html), which provides references for further reading. The risk assessment suggests that the predicted TFA concentrations are much lower than the 'no-effect concentrations' derived for several plant species (Boutonnet et al., 1999). However, direct experiments on the effects of TFA on plants have shown that different species do not necessarily respond to this pollutant in a way that reflects their response to more 'traditional' air pollutants. This result shows that we cannot assume that the knowledge base derived from the last few decades of air pollution research can be utilized directly to predict the effects of 'new' pollutants.

4. New pollutants

The debate concerning the potential effects of TFA on the environment raises much wider issues about how we identify sensitive plant and animal species, and sensitive ecosystems when challenged by a chemical that is totally foreign. Now that the threat posed by 'acid rain' is seen as being understood, if not yet fully dealt with, attention is moving to the potential harmful effects of less concentrated, but more widespread pollutants, particularly if there is evidence for bioaccumulation over long time scales. Some of these pollutants cannot be described as 'new' issues; there is a longstanding body of research on pesticides and pesticide residues, and their toxicology. These studies, however, have largely focussed on the higher sections of the food chain. Vegetation is not usually perceived to be at risk of direct effects, and is often assumed to be a passive accumulator—and used for monitoring air concentrations (e.g., DDT and secondary products in pine needles; Strachan et al., 1994).

However, questions still arise about the interactions between plants and pollutants other than the major ions in rain, or the major inorganic pollutant gases and particles. Although one might assume that the major uptake pathways of the 'traditional' pollutants such as SO_2, O_3, NO_x, or NH_3 are well understood, after decades of research, there still exist perceptions about their interaction with plants that color our approach to 'new' pollutants.

5. Pollutants in solution

The issues surrounding the occurrence and potential effects of TFA in the environment are mirrored in concern over the role of trichloroacetate (TCA). Since the early work of Frank et al. (1990), who postulated a role for TCA as a contributor to 'forest decline' in Germany, measurements of TCA in air, rain, vegetation, and soil have been made across the world (McCulloch, 2002). As has been found for TFA, there appears to be much more TCA in the environment than can be accounted for on the basis of the atmospheric oxidation of chlorinated hydrocarbons—Frank's original hypothesis. Measurements have shown that TCA can be formed in soil by microorganisms, using chloride ion as substrate. A recent mass budget for a forested watershed in Scotland found that the soil and vegetation stock of TCA was very much larger than the input fluxes (in rain, in cloud, and by dry deposition) and output fluxes in the drainage stream (Reeves, 2000). Earlier studies suggested that the major uptake pathway into foliage was via the roots, but the recent work points to a more complex behavior, with removal processes in foliage balancing root uptake. A related laboratory experiment found significant direct uptake by the above ground parts of spruce seedlings. The particular interest was the apparent large uptake by the stem, rather than the needles. Trichloroacetic acid is a strong acid, and should be fully ionized in rain, cloud, and dew. Therefore, it should behave like the major pollutant anions, nitrate and sulfate.

Although there have been many 'acid rain'-related studies of foliar leaching and ion exchange at leaf surfaces, following the early work of Tukey (1970) and others, very few have considered the possibility of direct uptake of ions by stem tissue, rather than through leaves. Isotope studies using ^{15}N-labelled nitrate and ammonium showed much greater uptake of both ions by twigs than by needles in Norway spruce (Wilson and Tiley, 1998). The stem may also be a major source of leached cations. Leachings of magnesium and potassium ions from whole spruce shoots and detached needles were similar, but there was no detectable leaching of calcium ions from needles despite a large loss rate from whole shoots (Mitterhuber et al., 1989). Even the potential for foliar exchange is idealized, based on laboratory experiments. The well-developed waxy cuticles on the leaves of higher plants do restrict water and ion transport across the leaf surface, but the 'waterproof' nature of this barrier is rarely perfect. Even on intact leaves, there can be considerable variation across an individual leaf (Leyton and Juniper, 1963). Natural abrasion can lead to

30-fold increases in ion uptake by leaves (Hoad et al., 1992), even for anions that by conventional wisdom are not efficiently transported across the leaf cuticle (Riederer, 1989).

These illustrations point to the care that must be taken when attempting to understand the uptake pathways of water-soluble pollutants, even those that are fully ionized in solution. Many organic solutes may be present in nonionic form, and are therefore more likely to interact directly with the hydrophobic waxes and leaf cuticle, as well as stem tissue. Concentrations need not be small relative to inorganic pollutants. Recent measurements of the total N content of rainfall in Britain between May and November 2000, using protocols designed to minimize biological activity during or after sampling, indicate that soluble organic N can account for up to 35% of the total N in rain (Cape et al., 2001). The chemical composition of this dissolved organic nitrogen (DON) is not known, but the observations are not isolated—a literature survey conducted as part of the above study identified over 60 references to DON measurements in rain. Although some of the reported DON concentrations may have arisen from artefacts in measurement and chemical analysis, recent reports using rigorous sampling protocols (Scudlark et al., 1998) indicate that the occurrence of DON in rain is widespread.

Surfactants are wet-deposited pollutants that cause direct damage to vegetation, associated with salt injury. Most reports are from coastal areas where storms blow suspended surfactant-laden sea spray inland (Grossoni et al., 1998). The potential for organic solutes to alter the surface activity of water droplets, and therefore enhance the direct effects of ionic pollutants, has been recently demonstrated in the measurement of the surface tension of polluted cloud droplets (Facchini et al., 2000).

6. Pollutants in both gas and aqueous phases

While experiments to investigate the effects of solutes such as TCA or surfactants on plants can be conducted relatively simply, much greater care must be taken when using aqueous solutions of volatile solutes. These solutes may be inorganic or organic, and the volatility may depend on solution pH. In this context, there is an increasing literature on the occurrence and concentrations of small organic acids (formic, acetic, oxalic) in the atmosphere, both in the gas phase (and particle phase for oxalic acid) (Hofmann et al., 1997) and in solution. Although not present in as large concentrations as inorganic acids, their rapid disappearance from rain samples (Ayers et al., 1998) implies that they are a useful energy source for microorganisms, and may affect the microflora on plant surfaces, with possible consequences for surface wettability (Knoll and Schreiber, 2000).

6.1. Gas–aqueous equilibria

There are several instances in the literature where the dynamic equilibrium between the gas and aqueous phases has not been properly appreciated. In closed systems, the chemical equilibria involved can be used to extract useful cause–effect information (Cape, 1984) (Fig. 4). More importantly, experiments to test cause–effect hypotheses have sometimes ignored the simple chemistry of water-soluble gases, and may have inferred incorrect conclusions as a result. In open systems, for example, there is likely to be a loss of volatile solutes from artificially applied solutions (as simulated rain or mist) that may give rise to unrealistically high concentrations, up to ppmv levels. The released vapor may then enter stomata directly, a pathway

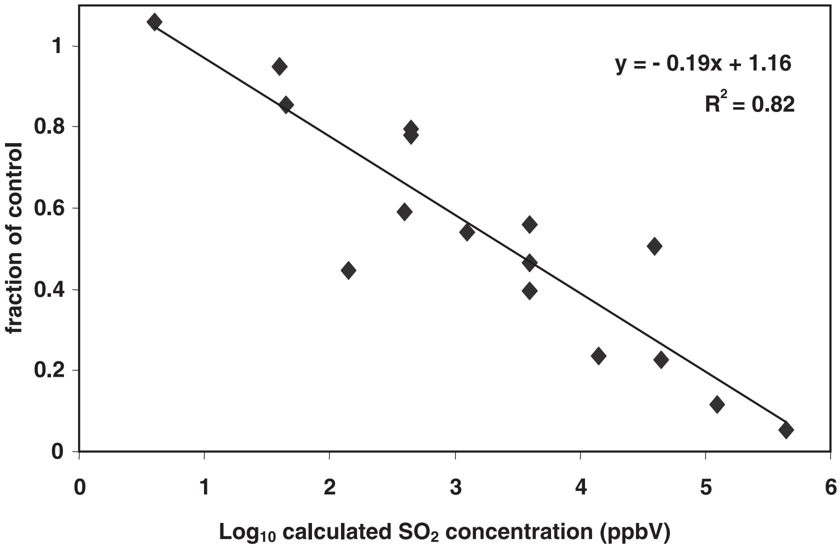

Fig. 4. Reduction in photosynthesis (measured by incorporation of $^{14}CO_2$) of Scots pine needles exposed to bisulfite solutions in a closed system at a range of different pH values, showing the benefit of utilising the phase partitioning behavior of SO_2 as a function of pH (Cape, 1984).

that is probably not available to solutions in the absence of surfactants (Schönherr and Bukovac, 1972), and confound the objectives of the experiment. Although weak acid solutes such as bisulfite or nitrite have obvious related gas phases such as SO_2 or HNO_2, even highly soluble solutes such as nitric acid or ammonia may be released as vapors as droplets evaporate (Milford et al., 2000).

6.2. The role of photolysis

The active role of UV light in aquatic systems is recognized as driving much of the chemistry that occurs in the uppermost surface layers of both marine and freshwater ecosystems (Cooper and Zika, 1987). However, the potential role for UV light to interact with terrestrial ecosystems has been largely ignored. Most studies of effects to date have been conducted in laboratories or controlled environment chambers, often under glass or plastic even if natural light is used. Commercial greenhouse glazing and most plastics do not transmit UV light effectively. While this may be of little consequence for plant growth (although surface structures may be sensitive to light quality; Cape and Percy, 1993), the potential for UV-initiated pollutant reaction at or with plant surfaces is ignored.

Probably any effect of UV light is restricted to the external plant surface, given that many leaf surfaces contain pigments that absorb UV before it can cause problems within the leaf (Baur et al., 1998). However, even leaf surface photochemistry may be relevant to studies of pollutant effects on plants. Recent work in Japan has demonstrated the potential for the production of highly reactive hydroxyl radicals (OH) in dew on leaf surfaces (Arakaki et al., 1999). The source of OH could be either photolysis of nitrous acid (HONO), dissolved in dew after night-time formation from reactions of NO_x, probably on aerosol, droplet, or leaf surfaces (Lammel and Cape, 1996), or photo-Fenton reactions of hydrogen peroxide catalysed by iron (Fe^{III}) and oxalate ions leached or dry deposited on the leaf surface. A well-replicated experiment in the field under UV-transmitting roofs showed significant reductions in net photosynthesis and stomatal conductance of Japanese red pine seedlings sprayed with dilute hydrogen peroxide/oxalate/Fe^{III} solutions before sunrise (Kobayashi et al., 2002). Hydrogen peroxide alone had no effect, reflecting earlier experimental studies with this oxidant on conifers (Cape, 1997).

7. Minor pollutant gases

In addition to the main components of gaseous oxidized and reduced nitrogen, sulfur dioxide, and ozone, there is a vast range of other gases present in the atmosphere at concentrations in the order of 1 ppbv. Some of these are naturally occurring biogenic hydrocarbons that interact directly with manmade emissions of NO_x and contribute directly to the problem of ozone production. However, there is little evidence in the literature for the potential direct effects of trace gases other than the ‘traditional’ pollutants. One might suppose that the reasons for this are the small concentration involved and the practical problem of measuring the air concentration reliably. At small concentrations, one might reasonably argue that effects on vegetation would be minimal since, by analogy with the major gaseous air pollutants, long-term exposure (weeks or more) to tens of ppbv is usually required to produce a clear effect on plants. There are two reasons for small concentrations of a gas in the atmosphere—small abundance or high reactivity. In the former case, the argument for low concentrations having little or no effect might be tenable in the absence of plant accumulation (as in the case of HF, where the ‘no-effect’ concentration is a few tenths of a ppbv). In the latter case, however, the chemical reactivity that leads to the short atmospheric lifetime of a pollutant may also apply to reactivity with vegetation. As an example, consider the potential for direct effects on vegetation of the OH radical. The concentration of this species in daytime is of the order of one part in 10^{13} (0.1 pptv), with a lifetime of a few tenths of a second. It is unlikely that OH radicals enter stomata, but they may be formed in the substomatal cavity by reaction of the longer-lived hydroperoxy radical (HO_2) with endogenous NO. We have no way at present of determining whether in fact such reactions of short-lived but reactive species are important in determining plant health in polluted atmospheres (Cape, 1997).

Even where there is evidence that a minor air pollutant has direct harmful effects on plants, the difficulty in making routine measurements often means that there are no reliable data for establishing the likelihood of plant damage occurring. For example, there have been several studies, with a long history, on the effects of peroxyacetyl nitrate (PAN) on vegetation (Cape, 1997)), but there are few routine measurements of PAN, especially in periurban regions where the concentrations might be expected to be the highest. Episodes of elevated concentration with several ppbv can arise even in regions, like central Scotland, that are not usually associated with photo-oxidant pollution (Cape and McFadyen, in press), so the likelihood of more widespread exposure to potentially damaging PAN concentrations is probably high.

The issues for future research involving minor air pollutants fall into two categories—absorption/emission by vegetation and soil, and direct effects on vegetation.

7.1. Exchange between the atmosphere and the ground

In the simplest case, the exchange of trace gases without reaction at the surface can be likened to simple partitioning between air and the surface, whether regarded as an undefined absorber or differentiated into different plant parts and soil. Organic compounds are known to accumulate in the lipophilic parts of vegetation—in general, the lower the vapour pressure, the greater the partitioning (at equilibrium) into the plant (Riederer, 1995). However, for semivolatile organic compounds (SVOCs), the rate of uptake may be very slow, so that equilibrium is not achieved in the lifetime of the plant. For volatile organic compounds (VOCs), the question of exchange between the atmosphere and the Earth's surface becomes relevant when considering the potential for VOCs to be reversibly absorbed over periods of minutes or hours, or in response to temperature cycling (Severinsen and Jager, 1998). Such processes, if of sufficient magnitude, could act to regulate dispersion, which in turn could influence atmospheric processes such as ozone formation.

Few measurements that are relevant to ambient concentrations of VOCs in air exist, but increases in the sensitivity of gas chromatography mass spectrometry (GC-MS) and in sampling technology are beginning to provide some data (Kesselmeier and Staudt, 1999). The rate of uptake/release has also been measured for a few plant/VOC systems at close-to-ambient concentrations, and has been found to be very slow relative to the exchange (largely irreversible) of inorganic gases. Typical 'deposition velocities' are of the order of 10^{-5} m s^{-1} or less (Duyzer and van Oss, 1997). The extent of partitioning is also relatively small. Even with typical bioconcentration factors for VOCs of 10^2–10^3 (g m^{-3} leaf per g m^{-3} air), the proportion of the boundary layer burden of VOCs held by vegetation is small. Bioconcentration factors for SVOCs are larger, and the potential for bioaccumulation and concentration up the food chains has been well documented (Jones et al., 1999). The behavior of SVOCs, however, cannot be treated simply as a gas phase process, given that they are usually present in the atmosphere in both the gas and aerosol phase. The above generalisations, however, are based on relatively few measurements of a few VOCs/SVOCs with a few plant species. There is little information on potential interactions with more polar molecules (e.g., oxygenated or nitrated VOCs).

7.2. Effects of VOCs on plants

There have been few experimental studies of the direct effects of VOCs on plants at concentrations, or over time scales, relevant to atmospheric exposure (Cape, in press). Uptake and active metabolism have been observed for aromatic molecules such as benzene and toluene (Collins et al., 2000; Ugrekhelidze et al., 1997), but the relevance to ambient exposures is not known. The potential for using plants as absorbers of VOCs in buildings has also been studied, with varying success (Cornejo et al., 1999). However, the issue of the toxicity (or potential for causing changes in the plant) of the absorbed VOCs or their breakdown products has not been assessed. Recent studies at near-ambient (urban) concentrations of benzene and toluene have suggested that grass may actively metabolize or transport these compounds from leaves (Binnie et al., 2002). If metabolized, we do not know whether the product(s) is volatile, or toxic to the plant or to animals that might eat the plant. Mixtures of VOCs and NO_x in roadside air, polluted by vehicle exhausts, have been shown to change the structure of leaf surface waxes on conifers (Sauter et al., 1987). This effect is most likely caused by physical disruption of the crystalline structures by dissolution of the VOCs in the wax (Sauter and Pambor, 1989). Such surface degradation of wax structures has long been associated with polluted air, although the causal agent has usually been assumed to be SO_2 or O_3. Given the growing evidence that plants can utilize/break down VOCs, more research on the identity and fate of the reaction products is needed.

8. Conclusions and future research directions

8.1. Sulfur dioxide

The emissions reductions over the past 20 years in North America and Europe have led to decreases in air concentrations of the gas, and in the concentration and deposition of sulfate in precipitation. However, the benefits of emission reduction are not seen uniformly across the affected region. The reasons for this 'nonlinear' response in space (i.e., geographically) are beginning to be unraveled, but even after 30 years of intense research activity, we still know very little. There are several issues that need to be resolved:

- Up to what distance from major sources is the atmospheric conversion of SO_2 to sulfate limited by oxidant availability, and how will this change as protocols to limit oxidant production take effect?
- How important is NH_3 availability in regulating in-cloud oxidation?
- How important is NH_3, and specifically the NH_3/SO_2 ratio, in determining the rate of dry deposition of SO_2 at the ground?
- How do we incorporate the spatial and temporal variability of NH_3 into model parameterisations of dry deposition?
- In the longer term, how will distribution patterns of sulfate be changed by changes in cloud frequency and surface wetness as climate changes?

There is also a nonlinear response to emission reductions in time, as ecosystems begin to recover from historic accumulations of deposited S. Although recovery is beginning to be seen in some regions, there are several issues to be resolved:

- To what extent is the decrease in base cation deposition in precipitation slowing the response to decreased S deposition?
- What factors determine how quickly soil chemistry and fresh waters in affected regions will recover to their preindustrial state, if ever?

- What are the implications for eventual biological recovery?
- Can management practices speed up recovery, or be used to establish stable (resilient) ecosystems, even if the preindustrial conditions cannot be reestablished?
- In the light of the increasing emissions of SO_2 in regions where industrialisation is developing rapidly, can we recommend the most cost-effective methods of minimising the ecological impacts in both the short term and the long term?

8.2. New pollutants

Little is known about the atmospheric concentrations or vegetation responses to minor air pollutants. The challenges for the future may be summarized as follows:

- Can we predict, on the basis of plant physiology/biochemistry, whether a given substance is likely to be phytoactive?
- How do we construct experiments to test the short-term and long-term risks to vegetation posed by a given pollutant?
- How do we identify the components of ecosystems likely to be most sensitive to a new pollutant?
- Can inexpensive, robust technologies be developed for measuring exposure, or, ideally, the dose of a pollutant across wide temporal and spatial scales?
- How best do we use the measurable physico-chemical properties of a substance to predict the likely pathways of uptake by plants?

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