Chapter 2:

Deposition Fluxes of Air Pollutants to Terrestrial Surfaces in Europe

David Fowler, Jan Willem Erisman, Mark Sutton, Eiko Nemitz, Kim Pilegaard,
Martin Gallagher, Juha-Pekka Tuovinen, Jan Duyzer, Ludger Grünhage,
Ulrich Dämmgen and Stanislaw Cieslik

Summary

Further studies of deposition fluxes have focussed on the behaviour of ammonia, and have shown major variations depending on land use and land cover, on scales of 1 km x 1 km or even below this. Another recent finding with important policy implications is that the deposition of sulphur dioxide to vegetation is critically influenced by the availability of ammonia. Decreases in the ratio of sulphur dioxide to ammonia increase the efficiency of sulphur dioxide deposition.

2.1 Introduction and policy relevance

The deposition of pollutant gases and aerosols to the terrestrial surface represents the main sink for atmospheric pollutants and determines their atmospheric lifetime and travel distance. Deposition to the surface also represents potentially damaging inputs to ecosystems, buildings and other potentially sensitive targets at the surface. Thus the processes occurring at the interface of the atmosphere and the earth's surface are central to the science and applications to quantify effects of deposited pollutants. The underpinning science includes micrometeorology, plant physiology, microbiology, soil physics and chemistry and has been the focus of the individual projects within EUROTRAC-2. In general, the field measurements have been directed towards the understanding of processes at the interface between soils, vegetation and the atmosphere. The analysis and interpretation of field data and development of models has been focussed on estimating the deposition of the pollutants responsible for acidification, eutrophication and ground level ozone, and exceedances of Critical Loads and Levels. There have therefore been considerable policy orientated applications of the research in the synthesis and interpretation of the measurements. The current understanding of chemical, physical and biological mechanisms which regulate the fluxes has developed rapidly during EUROTRAC-2. This development has been in part due to the existence of a network of European research groups from the earlier EUROTRAC activities.

The direct link between assessments of terrestrial effects of the pollutants and the activities of this theme of EUROTRAC-2 science brings policy advice to governments into the applications of the research. Many of the research projects within the subproject BIATEX-2 have been specifically developed to underpin policy development. The current effects assessment for pollutants contributing to acidification, eutrophication and photochemical oxidant effects rely heavily on Critical Loads and Critical Levels methods (Posch *et al.,* 2001). In the case of the pollutants responsible for acidification and eutrophication, the spatial and temporal patterns of deposition are required to identify areas of exceedance of Critical Loads. The parameterisations derived from BIATEX-2 are also required to model future air quality and deposition patterns resulting from proposed emission controls.

In the case of effects of ozone on terrestrial ecosystems, the current Critical Levels methodology to assess terrestrial effects on the basis of a simple measure of exposure above an arbitrary threshold (AOT40) is subject to many uncertainties and the development of a flux-based assessment method is in progress, drawing the results of current EUROTRAC-2 research rapidly into policy applications. The deposition maps and parameterisations for Europe are central to policy development within the member states of Europe and within the UNECE and the EU.

2.1.1 Policy issues

The work on deposition processes within EUROTRAC-2 was focussed on improving the underlying scientific understanding. However, the priorities for the work were set by the funding agencies at national level and within the EU. The specific policy issues included

- Controlling emissions of reactive nitrogen: Developing and testing models to quantify net fluxes of ammonia over canopies of vegetation. This very specific research was vital to quantify the nitrogen inputs from the atmosphere to vegetation as a part of the assessment of eutrophication of European terrestrial ecosystems. The work required high quality field measurements of deposition and emission fluxes and the development of models incorporating all of the new understanding.
- Non-linearities: The relationship between emission and deposition patterns at regional scales contains significant non-linearities due to atmospheric processing and surface phenomena. This work addressed the non-linearities in emission and deposition patterns for sulphur in Europe due to interactions of sulphur dioxide and ammonia on the surfaces of vegetation. Such processes need to be understood to quantify the effects of changing chemical climate of the atmosphere over Europe on the patterns and effects of the individual pollutants.
- Ozone: The objective of reducing the effects of ozone on vegetation requires an improved method of assessing exposure and effects. The current method (AOT40), which is a simple measure of exposure to concentrations of ozone above an arbitrary threshold (40ppbv), has been shown to provide incorrect regional patterns of the risk of damage to vegetation in Europe. The damage to vegetation by ozone is primarily caused by stomatal uptake of ozone, and this research was directed to quantifying the different sites of ozone uptake in vegetation from measurements and models.

- Particles: The deposition rates of particles need to be known to model their fate and effects and current estimates of the dependence of particle deposition on particle size and the aerodynamic roughness of the landscape are very uncertain. This work therefore concentrated on understanding these relationships for the most uncertain of the terrestrial surfaces, trees and forests.

2.1.2 Concepts and terminology

The science of surface-atmosphere exchange and its application to describe pollutant deposition and the emission of biogenic compounds has its own vocabulary. In addition, a common framework for the analysis of the pathway of the exchange process between terrestrial surfaces and the free atmosphere has been developed. The widely applied **resistance analogy** is used to separate surface and atmospheric processes within the overall transfer scheme, and to identify the role of different physiological, chemical and physical processes in the land-atmosphere transfer of gases and particles. The conceptual framework for this approach is shown in Figure 2.1, in which a resistance model is used to describe the surface-atmosphere exchange of ammonia. The advantage of the approach is that the very different stages in the transfer of plant physiology and surface chemistry can be clearly separated, to show how changes in surface conditions influence their respective resistance components and the overall exchange. The total resistance to transfer between a reference height in the atmosphere and the surface is obtained by dividing the potential difference (i.e. concentration) at the reference height in the atmosphere by the deposition flux and has units of seconds per metre ($s\ m^{-1}$). The reciprocal of the total resistance has dimensions of velocity and is widely known as the **deposition velocity** (v_d). The terms deposition velocity and resistance are used extensively in this chapter; however, the individual applications to describe different gases require slightly different formulations, to allow for the fact that some of the pollutants are deposited while others exhibit both deposition and emission from terrestrial surfaces. In situations when a trace gas may be emitted or deposited from terrestrial surfaces due to the competition between surface processes generating the gas competing with deposition to the same surfaces, then a **compensation point** may exist. The compensation point is defined as the concentration at the surface at which no net vertical exchange takes place. For deposition to the surface, the flux is proportional to ambient concentration and the deposition velocity is simply the constant of proportionality. For emission of trace gases, the emission is proportional to the concentration difference between the site of production (in soil or vegetation) and the reference level in the atmosphere. Some of the pollutants undergo extensive processing in liquid films on the external surfaces of vegetation, so that chemical schemes have been incorporated within the simple resistance model, (e.g., Figure 2.8) but the overall concept remains common within the analysis.

The following summary, in which pollutants are considered separately for each of the policy issues, describes the issue and the science focus for each group of pollutants and the major developments in the science. The treatment is not complete as the scale of the task and the space allocated, preclude such detail. However, sufficient examples of the work are provided to show important developments in the science and their application in policy development.

2.2 Ammonia

Among the pollutants contributing to eutrophication and acidification, ammonia (NH_3) is unique in dominating the deposition and terrestrial effects of deposited nitrogen within sensitive plant communities. It is also the pollutant subjected to the least control throughout Europe. Among the European countries, the Netherlands has been alone in attempting large-scale reductions in emissions from agricultural activities, the major source. The ambitious attempt to reduce NH_3 emissions in the Netherlands has not, so far, yielded the expected reductions, in part due to an incomplete understanding of the underlying science during the policy development. However the implementation of a national policy provided an important focus for the research and synthesis of monitoring data and modelling and valuable progress has been made in reducing the scale of emissions in the Netherlands. As many European countries within the UNECE convention, signed at Gothenburg in 1999, are committed to reduce emissions of NH_3, it is important to identify the developments in the science during EUROTRAC-2 to show whether the current understanding will deliver adequate predictions of deposition (and emission) fluxes and their effects for a range of scenarios.

The main developments of the science of NH_3 exchange between terrestrial ecosystems and the atmosphere have provided the following:

- Extensive sets of NH_3 flux measurements over crops, forest and other semi-natural vegetation communities (mainly for Northern Europe) to test and develop improved models of the exchange process.
- Development of bioassays to quantify the NH_3 compensation point of vegetation
- Measurements and models of the interaction of NH_3 fluxes with concentrations and fluxes of nitric acid (HNO_3), sulphur dioxide (SO_2) and aerosol ammonium nitrate (NH_4NO_3) over vegetation
- Extensive national networks for NH_3 and aerosol NH_4 measurements to improve the resolution of concentration and deposition maps for these pollutants
- Development of a two path canopy compensation point model (Figure 2.1).
- Development of a surface chemistry chemical model to simulate the uptake and release of NH_3 from vegetation.
- An extensive new literature of NH_3 exchange and modelling at the local and regional scale

2.2.1 Background

Emissions of ammonia have increased substantially during the past century. This has led to both increases in NH_3 and ammonium (NH_4^+) concentrations in the atmosphere and to increased deposition of reduced nitrogen (NH_x=NH_3 + NH_4). The exchange fluxes of NH_3 with vegetation are bi-directional, this gas is unique among the major pollutants in being both emitted by and deposited onto vegetation. The fluxes of NH_3 are of interest for both intensively managed, agricultural land and unfertilised, semi-natural land. On the one hand, agricultural vegetation contributes NH_3 emission to the atmosphere, together with emissions from livestock husbandry and some non-agricultural sources. Conversely, semi-natural vegetation in Europe largely acts as a sink for NH_3, which together with other inputs of atmospheric nitrogen compounds may cause both acidification and eutrophication of sensitive habitats.

The bi-directional nature of NH_3 fluxes is a particular challenge for generalisation, being highly variable in space and time and closely coupled to both environmental conditions (such as temperature, wetness and the presence of other pollutants) and vegetation differences (such as habitat type, fertilisation, cutting, soil type, etc). However despite this variability, substantial progress has been made in quantifying NH_3 exchange through a combination of measurements and modelling activities. Substantial efforts have been made under the EUROTRAC-2 subprojects BIATEX-2 and GENEMIS, linked to the EC project GRAMINAE [GRassland AMmonia INteractions Across Europe] (Sutton *et al.,* 1999).

2.2.2 Experimental strategy

GRAMINAE has provided the first European perspective on NH_3 exchange with grasslands and included measurements in an East-West continental transect across Europe. The main effort has been to use micrometeorological methods to determine NH_3 fluxes and relate these to environmental and management conditions, including a comprehensive suite of interpretative measurements such as plant and soil nitrogen parameters (Sutton *et al.,* 2001). In addition to using micrometeorological gradient methods, a substantial effort was placed to develop the state-of-the-art in Relaxed Eddy Accumulation (REA) measurements of NH_3 fluxes (e.g., Erisman *et al.,* 2001, Nemitz *et al.,* 2001a). The purpose of this was to allow single-height flux sampling that could eventually (by applying REA at several heights) be applied to improve the quality of flux measurement methods.

The direct flux measurements have been complemented by studies of NH_3 exchange fluxes and bioassays conducted under controlled conditions to examine the mechanisms regulating fluxes (Schjoerring *et al.,* 1998). The work has led to the refinement of a range of models, building on core bi-directional resistance models for NH_3. The range of models includes analysis of within-canopy NH_3 cycling and interconversion between gaseous NH_3 and aerosol NH_4^+ in relation to surface fluxes (e.g., Sutton *et al.,* 2000), a model integrating NH_3 exchange with ecosystem functioning in grasslands (Riedo *et al.,* 2002) and refinement of atmospheric dispersion models for NH_3 at local and regional scales (e.g., Loubet *et al.,* 2001).

The GRAMINAE Integrated Experiment, which was hosted by the Federal Agricultural Research Centre (FAL) at Braunschweig during 2000, was a major activity bringing together over 50 scientists in the field to investigate the wide range of issues governing NH_3 exchange with grasslands.

2.2.3 Results and discussion

The work in the recent GRAMINAE project has built on the findings of the former EXAMINE project (Sutton *et al.,* 2000), which developed models for assessing NH_3 bi-directional exchange. A key advance was the development of the 'canopy compensation point' resistance model, which allowed competition between deposition to plant cuticles and bi-directional exchange with a stomatal compensation point (χ_s) (Sutton *et al.,* 1995). With the recent work, this has been extended to a 2-layer model including bi-directional exchange with the soil surface (Nemitz *et al.,* 2001b). Figure 2.1 shows the 2-layer model, which is considered to provide a balance between simplicity and detail that is suitable for incorporation into more general models. Other NH_3 resistance models have been developed which address specific questions, as summarised by Sutton *et al.* (2001) and Nemitz *et al.* (2001b).

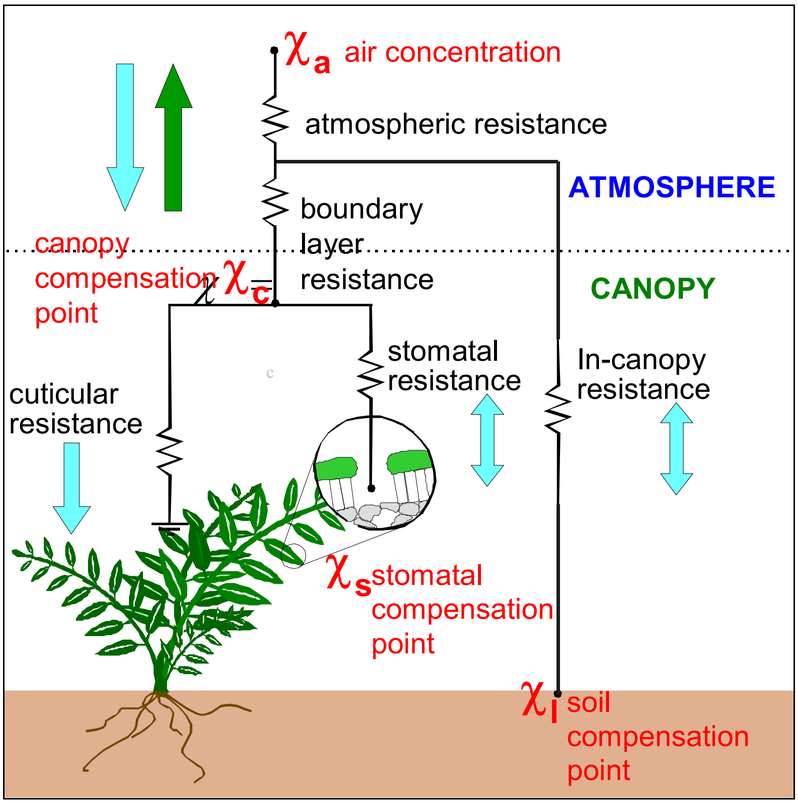

Figure 2.1. Two-layer canopy compensation point model of NH_3 exchange. Contrary to resistance models of pollutant deposition, the air concentration is not assumed to be zero at the surface, and instead of a canopy resistance (R_c), the surface concentrations χ_s, χ_l and χ_c are calculated. (From Sutton *et al.*, 2002).

The simpler bioassay: total foliar [NH_4^+], has been shown to correlate well with apoplastic [NH_4] and NH_3 emission (see Figure 2.2).

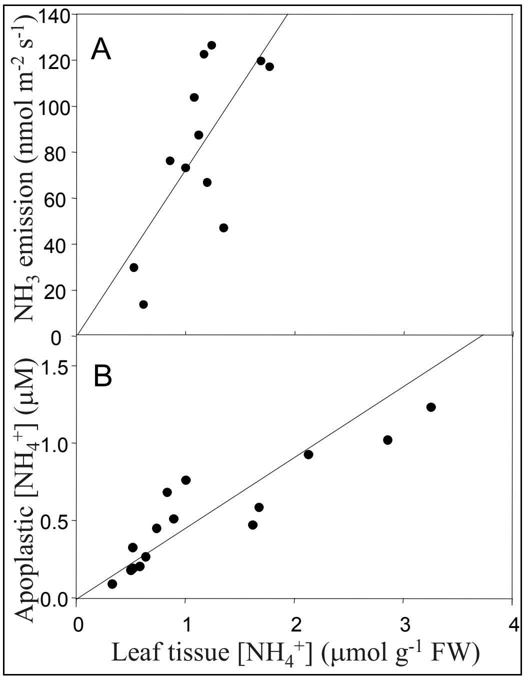

Figure 2.2. Comparison of two bioassays to estimate the stomatal compensation point (χ_s) in grass leaves (Mattsson and Schjoerring 2002). In principle, apoplastic [NH_4^+] is the most suitable bioassay. However, the simpler bioassay of total foliar [NH_4^+] is also found to correlate with NH_3 emissions (A) and apoplastic [NH_4^+] (B). (From Sutton *et al.*, 2002).

While micrometeorological measurements provide estimates of net NH_3 fluxes in the field, controlled studies are useful to provide data to parameterise the compensation point models. For example, cuvettes can be used to determine χ_s directly, by measuring the NH_3 flux under a range of NH_3 concentrations. Where the cuticular resistance (R_w) can be shown to be negligible, the NH_3 concentration at which the flux is zero equates to χ_s (Schjoerring *et al.,* 1998). Bioassays of χ_s have also proved useful since these are much easier to perform than gas exchange measurements. In a now standard method, leaves are impregnated with an isotonic solution and this is subsequently extracted by centrifugation to estimate apoplastic pH and [NH_4^+], which are the aqueous concentrations relevant to the sub-stomatal cavity (Schjoerring *et al.,* 1998). The ratio [NH_4^+]/[H^+], referred to as Γ_s is directly scalable to χ_s but avoids the temperature dependence of NH_x solubility. Currently, there is debate regarding the absolute magnitude of the bioassay estimates, although there is consensus that they provide a useful comparison between treatments. An example of the micrometeorological measurements made in the GRAMINAE transect and the application of the single-layer canopy compensation point model is shown in Figure 2.3. The NH_3 flux is mostly toward deposition prior to the cut, following which NH_3 emissions increase substantially. Following fertilisation, the fitted Γ increased by a factor of 63 compared with prior to the cut, and this reflects a combination of both increased Γ_s and Γ_g, where the latter is the ratio [NH_4^+]/[H^+]

at the soil surface. Given that only three fixed values of Γ are applied in the model, the close fit to the measurements indicates the controlling importance of humidity (on R_w) and canopy temperature (on χ_s), together with wind speed and stability as they affect R_a and R_b.

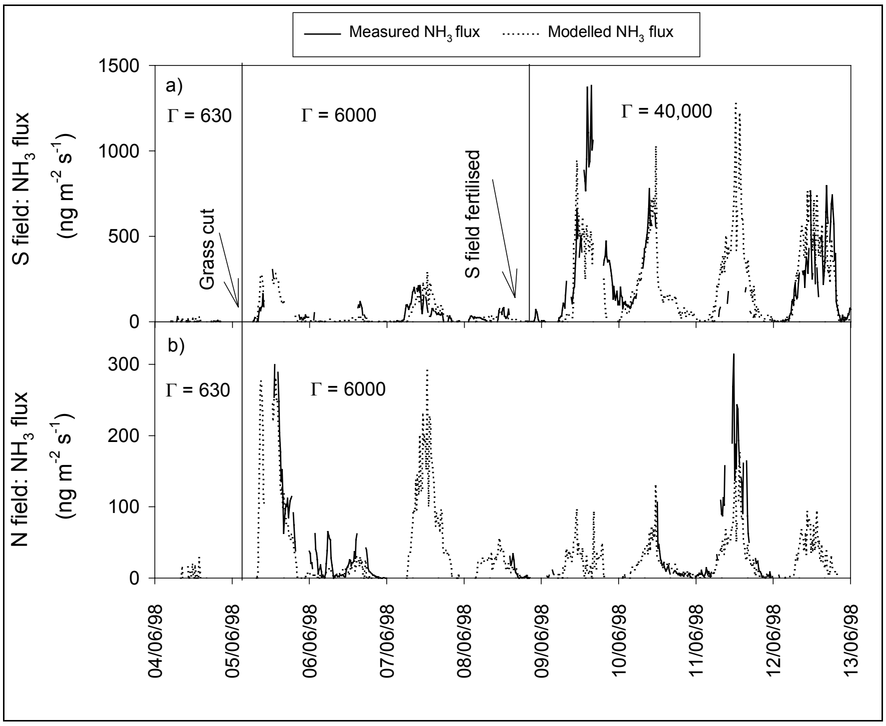

Figure 2.3. Comparison of fluxes measured at the Scottish GRAMINAE site with the 1-layer canopy compensation point model. The results are split between periods with wind from fields north (N) and south (S) of the measurement point since the N field was not fertilised within the period shown. (From Sutton *et al.*, 2002).

The fluxes measured in the GRAMINAE transect may be used to assess the effect of climate differences across Europe. This is possible, for example, in comparing semi-natural grasslands such as an acid peatland in Scotland with the Hungarian “puszta” grassland. Overall, the average rate of deposition (flux / concentration) was smaller to the Hungarian grassland, which reflects a more continental climate with drier conditions in summer and frozen conditions in winter. By contrast, the Scottish semi-natural grassland is wet or subject to high humidity at canopy level for much of the year, leading to smaller canopy resistances. In most cases, however, the effect of different climate between sites was masked by differences in management practices of grasslands. Hence the largest NH_3 emissions were recorded for the Dutch intensive grassland, while the second largest emissions were found for the Dutch semi-natural grassland (which was grazed by wild geese in winter). A semi-natural Mediterranean rangeland (light grazing) in Greece also showed NH_3 emissions even when not fertilised, but conversely, on an annual basis a fertilised grass-clover pasture in Switzerland was found to be a weak sink for NH_3.

Given the variability of fluxes with management, and the empirical nature of the fitted compensation point values (Figure 2.3), a major effort was placed to measure the compensation point of the vegetation based on ecosystem functioning in relation to carbon (C) and nitrogen (N) cycling. For this purpose the PaSim model (a dynamic grassland ecosystem model), was extended to incorporate more detailed modules for plant N and soil surface N fluxes (Riedo *et al.,* 2002). Plant N was separated into three pools: structural N, symplastic (intra-cellular) N and apoplastic N.

The PaSim model can be used to examine the interactions of management, climate and NH_3 fluxes. In particular, the understanding developed may be used to consider methods to reduce NH_3 emissions. An example of this is the effect of delaying fertilisation following cutting, since this gives the sward time to recover, and should allow an increased fraction of the fertiliser-N to be retained in the plant soil system. Initial analysis with PaSim showed that a two-week delay in fertilisation reduced annual NH_3 emissions at the Scottish site by 15%, with the only cost being a 4% reduction in dry matter production. This is an obviously policy relevant result which, through the UNECE Ammonia Expert Group, has been included in the revised Technical Annex on Ammonia Abatement under the Gothenburg Protocol.

The GRAMINAE Integrated Experiment has provided internationally the most detailed and robust dataset on NH_3 exchange with grassland. The comparison of four continuous gradient systems provided estimates of NH_3 fluxes on a 15-minute basis for three weeks and these show clearly the effect of management, with increased emissions following cutting and then further increases following N fertilisation. The comparison of continuous REA methods provided more variable results, reflecting the more demanding analytical challenge of this approach (since smaller NH_3 concentration differences must be detected than with the gradient method). One of the advantages of REA, however, is that a referencing mode can be implemented at automated intervals, with random switching between inlets, which can be used to correct sampling bias between the inlets (Nemitz *et al.,* 2001a).

As part of the assessment of spatial variability, the FIDES model (Loubet *et al.,* 2001), which incorporates a canopy compensation point model (as shown in Figure 2.1), was applied. In this approach, an enhancement of concentration above background, at a given distance from a source of known location, is used to: a) calculate the emission required to explain the concentration enhancement, b) simulate the downwind profile of NH_3 concentration. An example comparison of the three different approaches (gradient, REA and FIDES surface dispersion estimates) to calculate NH_3 flux at Site 1 is shown for 3 days after fertilisation in Figure 2.4. Extremely close agreement is observed on 9 June, while 8 June illustrates the benefits of comparing different approaches. On 8 June, two of the gradient systems (both at Site 1) suggested high fluxes, while the other two gradient systems (one each at Site 1 and 2) suggested much lower fluxes. Without independent support it was impossible to favour any system and the average was calculated, as shown by F_{AGM} in Figure 2.4. From the two independent systems (REA and FIDES surface dispersion), it can be seen that the mean F_{GRAD} is larger and that the lower gradient estimates were more representative.

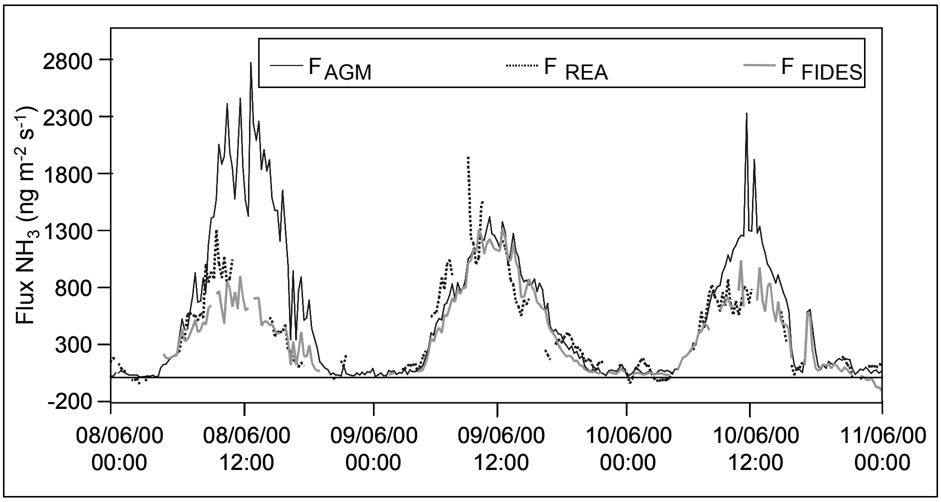

Figure 2.4. Comparison of three different micrometeorological approaches to measure NH_3 fluxes: AGM, Aerodynamic Gradient Method (mean estimate from 4 continuous systems); REA, Relaxed Eddy Accumulation (UMIST/CEH system); FIDES, Application of mean measured $[NH_3]$ at 1 m and 47 m in the FIDES near source dispersion model. There was wide discrepancy within the gradient systems on 8 June, (two high and two low estimates), the REA and FIDES estimates agree with the two instruments that gave lower values for this day. (From Sutton *et al.*, 2002.)

A key aim of the experiment was explicitly to measure horizontal concentration changes and determine errors in vertical fluxes. Classically, this is an issue avoided by micrometeorologists, as it is well established that advection leads to errors in flux measurements. However it must be recognised that advection is a normal feature of the rural landscape and that an "ideal micrometeorological site" is, in fact, the exception. It might be argued that advection and surface–atmosphere exchange should be studied separately to simplify the problem. However this fails to provide information on the interaction between the two issues. Given the uncertainties, such effects of "complex terrain" were set as a priority issue for BIATEX-2.

Following fertilisation the advection error would lead to underestimation in fluxes (in the case where the error is not calculated and the appropriate correction made). Conversely, where advection from the farm is the main effect, NH_3 emission from the field would be overestimated or deposition underestimated. This is a finding of general importance, especially for semi-natural ecosystems in the vicinity of NH_3 emission sources, such as nearby farms. In addition to flux measurements underestimating deposition, the advection errors also apply to inferential models of deposition, which use site-based NH_3 concentration monitoring data as input. Within a few 100 m of a large farm source, such as at Braunschweig, the advection error could account for an additional 5 kg N per hectare per year.

2.2.4 The problem of scale in assessing impacts of NH_3 effects on semi-natural plant communities

The basic pattern of NH_3 spatial variability has major implications for NH_3 policy. Deposition is typically calculated at a 50 km resolution across Europe, within the EMEP model, or at a 5 km resolution in national assessments

(NEGTAP 2001). However, both these scales hide substantial spatial variability, as indicated by the example of a field-level critical load exceedance map for a location in central England (Figure 2.5, Dragosits *et al.,* 1998).

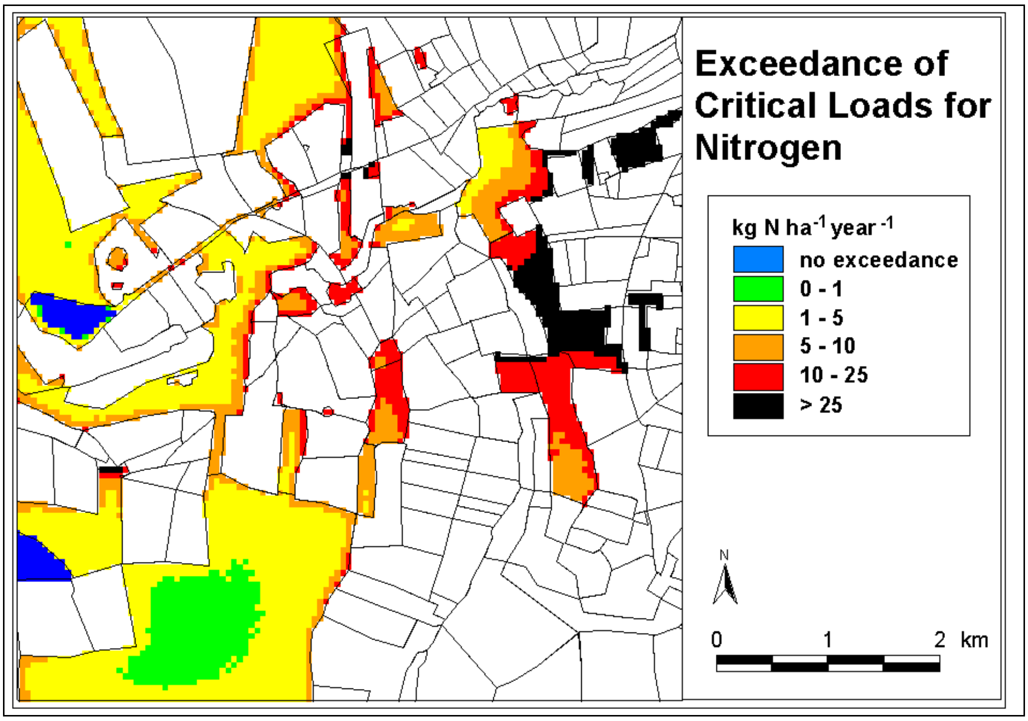

Figure 2.5. Model estimation of the local variability in exceedance of the critical load for nitrogen, accounting for variability in NH_3 emissions, land-use dependent deposition and critical loads at the field scale. Results from the LADD model at 50 m resolution for an area of 5 km x 5 km in central England (Dragosits *et al.,* 2002).

Very large critical loads exceedance occurs near large farms, while larger exceedance is also seen adjacent to agricultural fields. The very large local variability in NH_3 emission and deposition creates hotspots of deposition occurring within tens of metres downwind of major agricultural sources. These hotspots of deposition are invisible in 50 km resolution maps generated for Europe, and even 5 km maps produced for national assessments are unable to capture the fine structure of the exceedances. The result is that the current assessments of ecosystem effects at European and national scale underestimate the magnitude of exceedance for eutrophication of semi-natural plant communities. If it is considered that national emission reductions planned under the Gothenburg Protocol and the National Emissions Ceilings (NEC) Directive are of the order of 20-30%, it can be quickly seen that the intense local exceedance shown in Figure 2.5 will not be solved by average reductions of this magnitude. The national policies currently agreed are insufficient to allow sustainability of such vulnerable ecosystems from the threat of nitrogen deposition. By contrast, the high spatial variability points also to the benefits of spatial policies (c.f. Bleeker and Erisman, 1998) that encourage a local spatial separation between NH_3 source areas (such as intensive livestock farming) and vulnerable ecosystems.

Ammonia remains the major cause of eutrophication over extensive areas of semi-natural vegetation in Europe, and it is clear that similar problems occur in North America although concern there appears to be focussed on areas in which specific issues have been identified, including the Neuse river in North Carolina and eutrophication of substantial areas of the Sierra Nevada mountains in California. The underlying scientific understanding has developed and models are now available to quantify emission and deposition fluxes at a scales as fine as 1 km x 1 km. However uncertainty in the fluxes at this scale remain very large, and such fine scale maps of concentration and deposition must be supported by dense networks of monitoring instruments and very good spatial information on agricultural activity. The major developments in understanding NH_3 exchange provide the means of quantifying the terrestrial inputs to sensitive ecosystems, allowing for the first time for the nutritional state of the vegetation. The importance of NH_3 as a contributor to eutrophication (and to acidification) throughout Europe will further raise the scientific and political importance of NH_3 during the coming years.

2.3 Sulphur dioxide

Despite the three decades of research on the deposition of sulphur dioxide (SO_2), important developments continue to be made in understanding the processes of exchange at the surface. Much of the policy development in Europe to reduce the effects of acidification has focussed on the control of SO_2, and the developments in understanding have been incorporated into long range transport models and impact assessment. It is therefore important to outline these developments.

Emissions of SO_2 throughout western Europe declined by approximately 80% since the peak in emissions in the early 1970s, largely through the effects of legislation following the observations of widespread acidification in northern Europe. The chemical climate of the boundary layer during the early years of this period was dominated by SO_2 and the ratio of SO_2:NO_2 was generally in excess of 2 across large regions. Similarly, the ratio SO_2:NH_3 was in excess of 5 over the emission areas of Germany, Belgium and central and eastern England. The velocity of SO_2 dry deposition in these conditions was measured and found for most vegetation and soil surfaces to be between 3 mm s^{-1} and 8 mm s^{-1} (Garland, 1983). The extensive measurements of SO_2 dry deposition during EUROTRAC-2 were made by more advanced techniques, largely developed within the EUROTRAC science community, allowing continuous measurement of the flux. These measurements showed that the deposition velocity was increasing with time, even though concentrations were declining. The apparent paradox is explained quite simply, the main limitation to the deposition of this reactive gas is the chemical limitation at the surface. As most surfaces of vegetation are wet with dew, rain or ‘effectively wet’ with layers of water molecules adsorbed onto foliar surfaces, the solution and reaction of SO_2 at the surface depends on the pH of the water layer, which in turn is regulated by the availability of NH_3 and SO_2, (Erisman *et al.*, 1998a). Thus the gradual change in the ratio of SO_2:NH_3 has increased the rate of removal of SO_2 at the surface (Fowler *et al.,* 2001). The field data obtained largely at the continuous flux monitoring stations in the

Netherlands at Speuld forest, at Melpitz in Germany, Sutton Bonington in England and Auchencorth Moss in southern Scotland have been used to demonstrate these changes and the underlying mechanisms.

Table 2.1. Changes in canopy resistance r_c for SO_2 deposition to cereals, 1970 to 2000.

Concentrations	**1970-1975**	**1995-2000**
SO_2 (μg m^{-3})	47.9	3.3
NH_3 (μg m^{-3})	~5.0	5.0
r_c (sm^{-1})	130	80

The data presented in Table 2.1 show that with the reduction in ambient concentration from 48 μg m^{-3} to 3.3 μg m^{-3}, the surface resistance declined by approximately 40%. These measurements were made at the same site, over the same crop species and over the same period of the year (Fowler *et al.,* 2001). The major change in conditions which regulate the surface resistance is the relative amount of SO_2 and NH_3 at the surface, which changed from 2.6 to 0.5. This change in relative amounts of SO_2 and NH_3 has accelerated the local decline in SO_2 concentration, such that large areas of rural Europe are now remarkably free of SO_2 and the crops require sulphur fertiliser to avoid nutrient deficiency.

Similar links between the surface or canopy resistance and the ratio of SO_2 to NH_3 are seen in the data from Speuld forest in the Netherlands (Figure 2.6, Erisman *et al.,* 1998a). The measurements are shown in Figure 2.7, in which the canopy resistance is small, consistent with the relative abundance of NH_3.

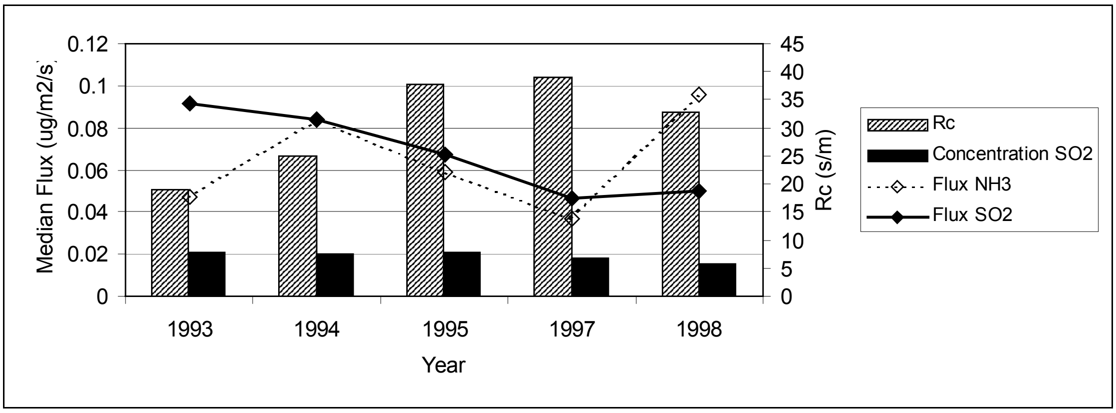

Figure 2.6. Annual dry deposition fluxes of SO_2 and NH_3 and canopy resistances for SO_2 at Speuld Forest from 1993 to 1998 (From Erisman *et al.,* 1998a).

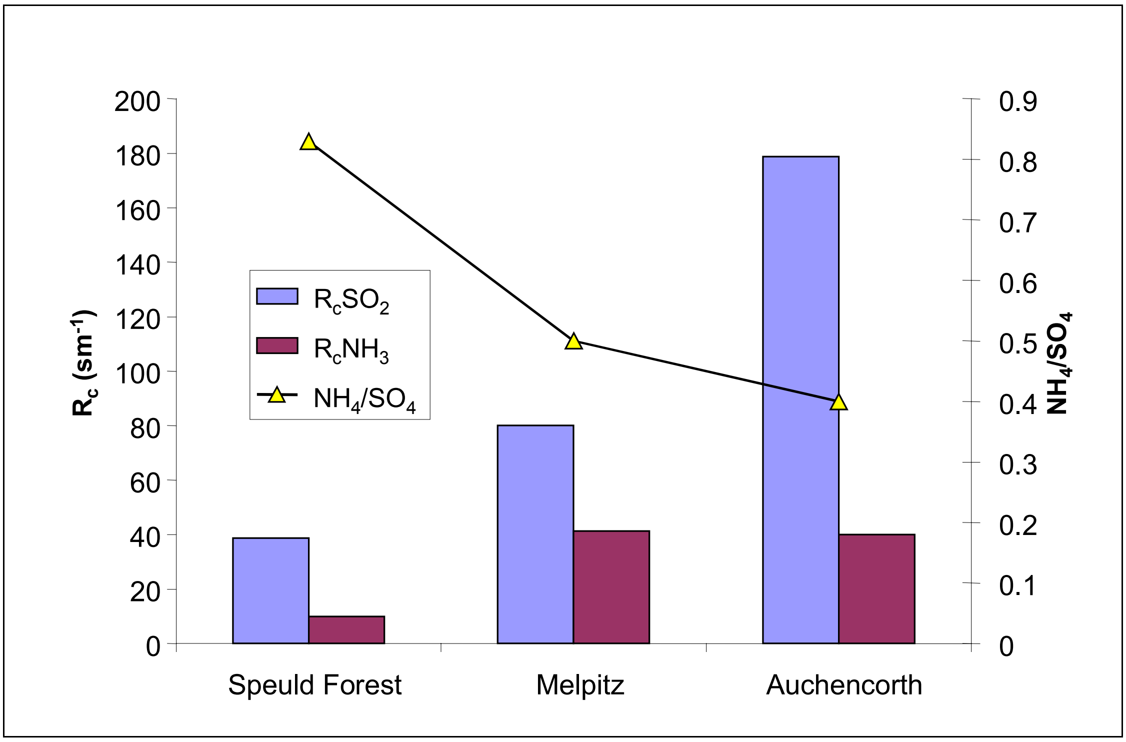

Figure 2.7. The long term surface resistance for SO_2 deposition (R_cSO_2), NH_3 deposition and the ratio of ambient concentrations of NH_4/SO_4 at three long term flux monitoring sites in Europe (from Erisman *et al.,* 1998b).

These data show the coupling between the chemical climate and the rate of surface exchange of SO_2. The underlying chemistry on vegetation surfaces is, in principle very well known. However, it has taken many years to develop and apply methods to monitor long term fluxes and to separate the chemical effects at the surface from all the other causes of variability in deposition rates in field conditions. The synthesis of this work includes the development of a dynamic model of the interaction of NH_3 and SO_2 on the deposition process, to enable the responses of changes in the two pollutant concentrations to be studied (Flechard *et al*., 1999).

The model calculates the concentrations of gas phase pollutants in equilibrium with dissolved phase gases in surface water on foliage and allows for diffusion through the plant cuticle and gas phase diffusion via stomata. The model is described in detail by Flechard *et al.* (1999). The model is initialised using measured rainfall chemistry at the study site, assuming that a substantial rain event (>3mm) washes soluble contaminants from foliage and provides a liquid film of known composition for the start of the simulation. The model then uses measured gas concentrations and meteorological variables to simulate the trace gas exchange over the following dry period. Figure 2.8 shows the model schematically.

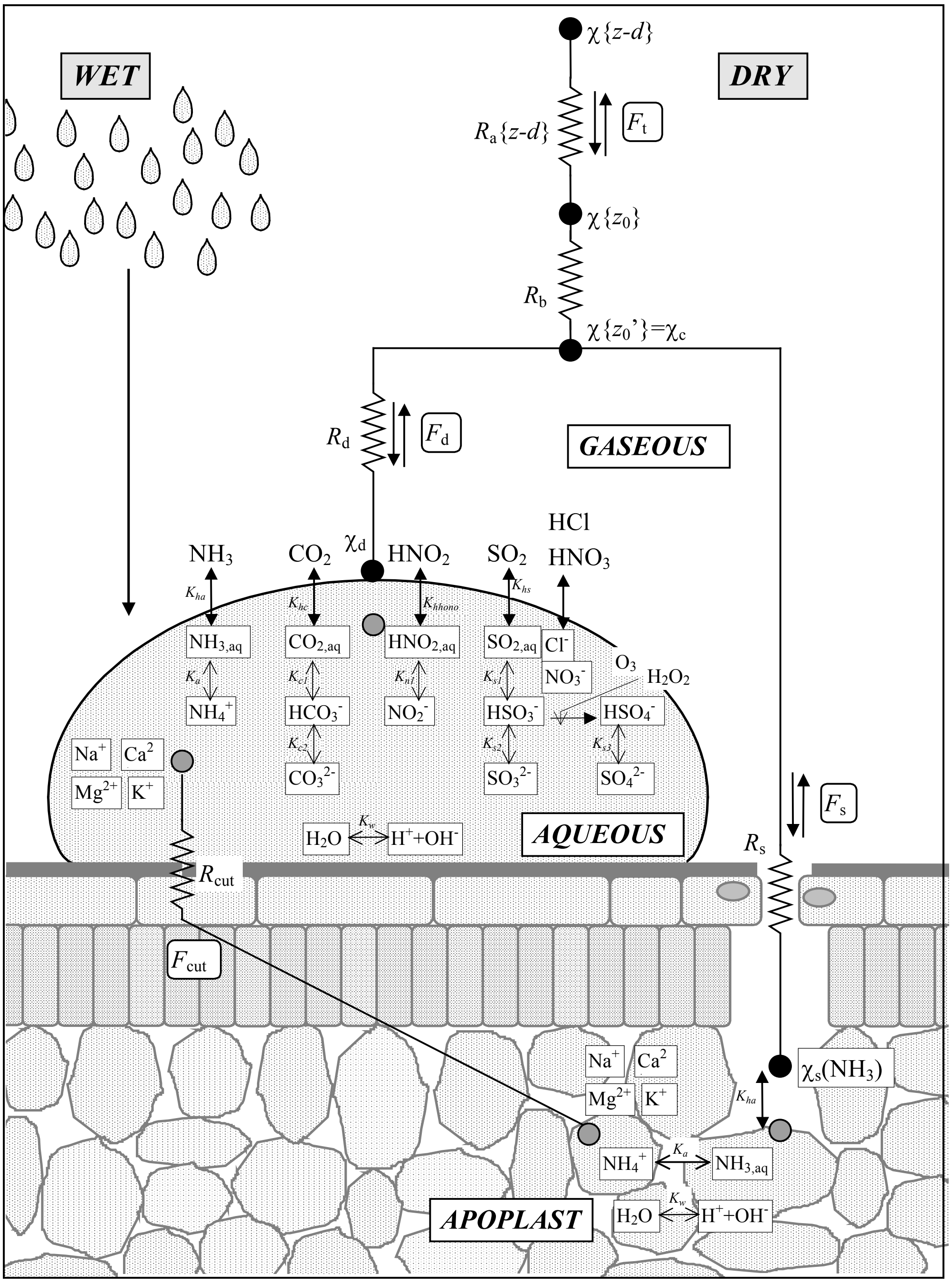

Figure 2.8. A schematic representation of the dynamic canopy compensation pollution model for SO_2 and NH_3 exchange over vegetation (from Flechard *et al.*, 1999).

To illustrate the model characteristics and the dynamic response to changing ambient concentrations of SO_2 and the effect of NH_3 on the SO_2 flux, a 5 day period (21-3-95 to 26-3-95) has been simulated, as shown in Figure 2.9. The measured and modelled SO_2 fluxes track each other reasonably closely and both show values substantially smaller than Fso_2 max (the maximum flux possible for the given rates of turbulent exchange).

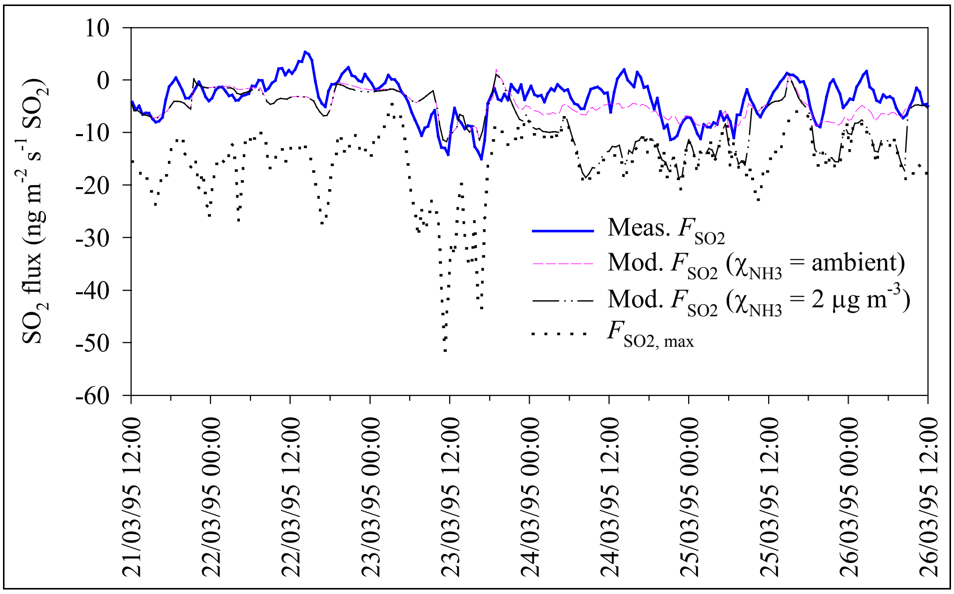

Figure 2.9. A comparison between measured and modelled SO_2 fluxes at Auchencorth Moss over the period 21-3-95 to 26-3-95 showing the influence of increasing ambient NH_3 concentration on SO_2 flux (from Flechard *et al.*, 1999).

Policy Relevance

The policy relevance of interactions between SO_2 and NH_3 and the developments in understanding are that the non-linearities in the spatial relationships between emission and deposition due to these effects can now be quantified and used to assess the overall effects of control measures on exceedances of Critical loads and levels. The effects on rates of deposition have been quantified, modelled and the effects on regional deposition rates explored.

2.4 Nitrogen oxides

The research on surface exchange of nitrogen oxides during the last five years has been a relatively small component of the research programme. The major sinks for NO_2 in vegetation are known to be stomata and there is no significant uptake on external surfaces of vegetation. The research question addressed has been the sources and sinks of NO_x (=NO+NO_2) in forest ecosystems. The problem arises from the simultaneous emission of NO by forest soil and the deposition and reaction of NO_2 within forest canopies, which make it difficult to quantify the net sink or source strength of forests for boundary layer NO_x. Thus the policy relevant developments in understanding NO and NO_2 exchange in recent years have been restricted to forest ecosystems. These ecosystems were targeted because the interaction of the soil emissions of NO with the NO_2 uptake by the forest canopy and O_3 fluxes precluded reliable quantification of deposition fluxes. Furthermore, some forest ecosystems appear to be amongst the most sensitive to the effects of eutrophication, and are therefore a focus of interest for effects assessment.

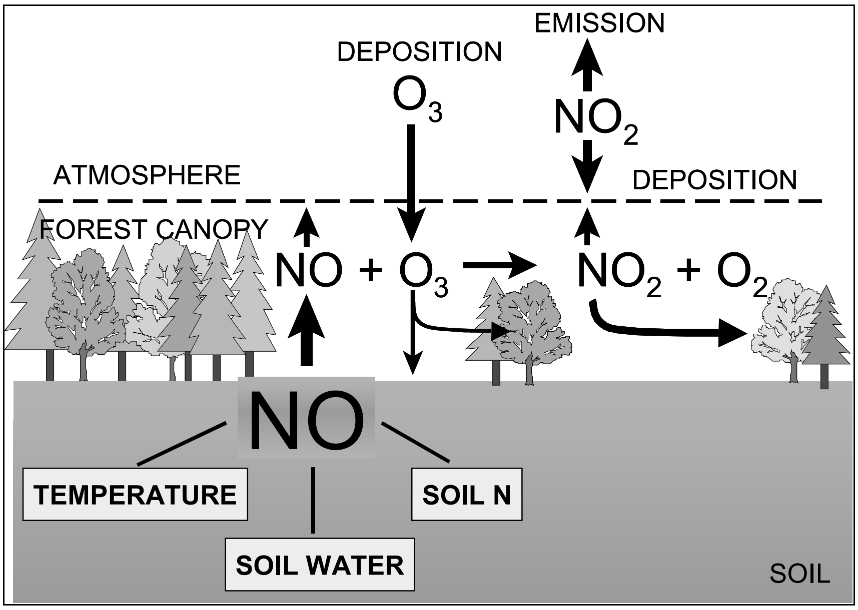

Figure 2.10. The interaction of soil emission of NO with NO – O_3 reaction within canopy and NO_2 uptake by stomata and the net exchange of NO_x above forest canopies.

The processes regulating the net exchange of NO_x between forests and the atmosphere have been identified, and the work shows that forests may be either a source or a sink for NO_x, depending on the magnitude of soil NO emissions and recapture of NO_2 by the forest canopy. The process is shown schematically in Figure 2.10, and key developments have been the simultaneous measurement of NO fluxes from soil, the fluxes of NO_2 and O_3 above canopy and the development of a dynamic model for the fluxes and chemistry within forest canopies (Figure 2.11) (Duyzer *et al.*, 1995, 1998; Walton *et al.*, 1997).

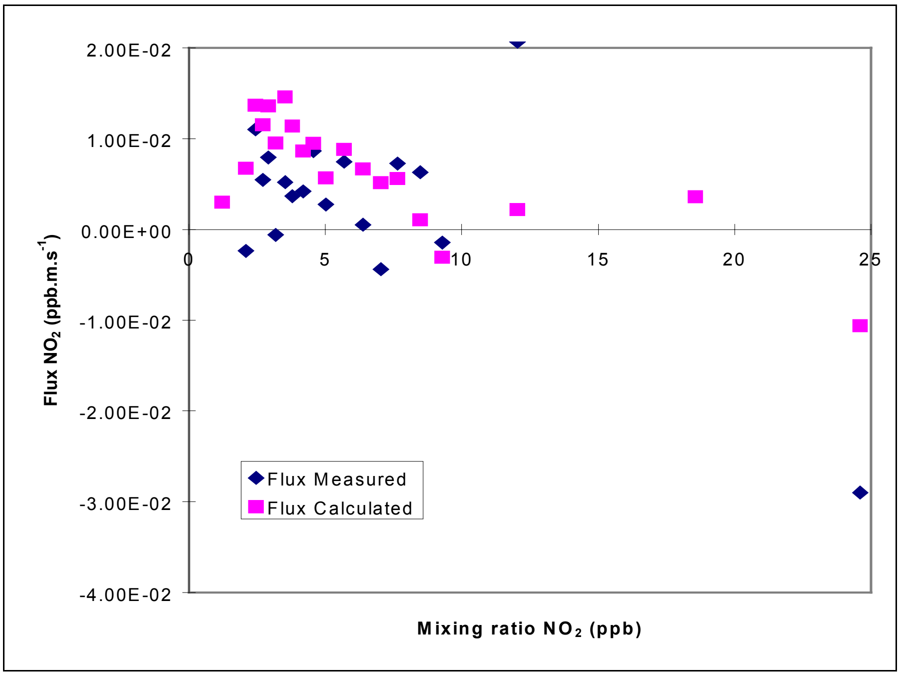

Figure 2.11. Fluxes of NO_2 observed above Speuld Forests (Duyzer *et al.,* 1995).

Policy Relevance

The consequence of soil emissions of NO and within-canopy conversion of the NO to NO_2 by reaction with O_3, is that this produces a within-canopy source of NO_2. The within-canopy source of NO_2 interacts with the NO_2 from above the forest canopy to determine the net exchange above the forest. At very small ambient NO_2 concentrations, the forest may therefore be a source of NO_x to the lower atmosphere, as the emission of NO from soil and conversion to NO_2 within canopy exceeds the uptake by the canopy, and NO_2 is emitted by the forest. At larger ambient NO_2 concentrations, the forest becomes a net sink, as stomatal uptake of NO_2 from above canopy sources exceeds the NO emission from the soil. The importance of these processes for environmental policies are that forests may be much smaller sink for NO_2 than has been assumed earlier and spatial patterns of N deposition within Europe will need to be revised.

2.5 Ozone

Ozone remains a key pollutant across Europe, with widespread exceedances of thresholds for effects on vegetation, human health and materials. The substantial reductions in emissions of O_3 precursors achieved to date have reduced peak concentrations in large areas of Europe, but, in addition to the remaining exceedances of environmental thresholds, there is evidence that background O_3 concentrations are increasing (NEGTAP 2001). The deposition of O_3 to vegetation and soil represents the main sink for ambient O_3 and is a very important parameter in long range transport models. The flux of O_3 into vegetation also represents the main pathway for damage to crops and semi-natural vegetation.

2.5.1 Ozone flux and AOT40

While the deposited flux of ozone into stomata has been shown to be the primary cause of the yield loss of agricultural crops, indices of exposure such as the AOT40 are generally applied in effects assessment. Several problems with the AOT40 approach have been identified. In particular, this index is simply the product of concentration above a threshold and time and takes no account of the physiological conditions in vegetation or environmental conditions. In the case of high irradiance, O_3 concentration and temperature conditions, when the stomata within a canopy of vegetation may be closed to conserve water, the uptake flux of O_3 may be very small, yet the AOT40 index would be accumulating large values. Thus there is concern that effects assessments based on the AOT40 are at best very uncertain, and appear to yield an incorrect regional distribution of the risk of damage to vegetation in Europe. Work during recent years has provided the models necessary to quantify the stomatal flux and provide a more appropriate measure of ozone.

The development of an O_3 flux based assessment requires the models to calculate stomatal uptake from readily available land-use data and meteorological variables, and the field data to test the models. Recent work by Tuovinen *et al.* (2001) and by Emberson *et al.* (2000), show good agreement between modelled and measured O_3 fluxes for several important crop and semi-natural species. As an example, the comparison is shown in Figure 2.12 for Scots pine in Finland.

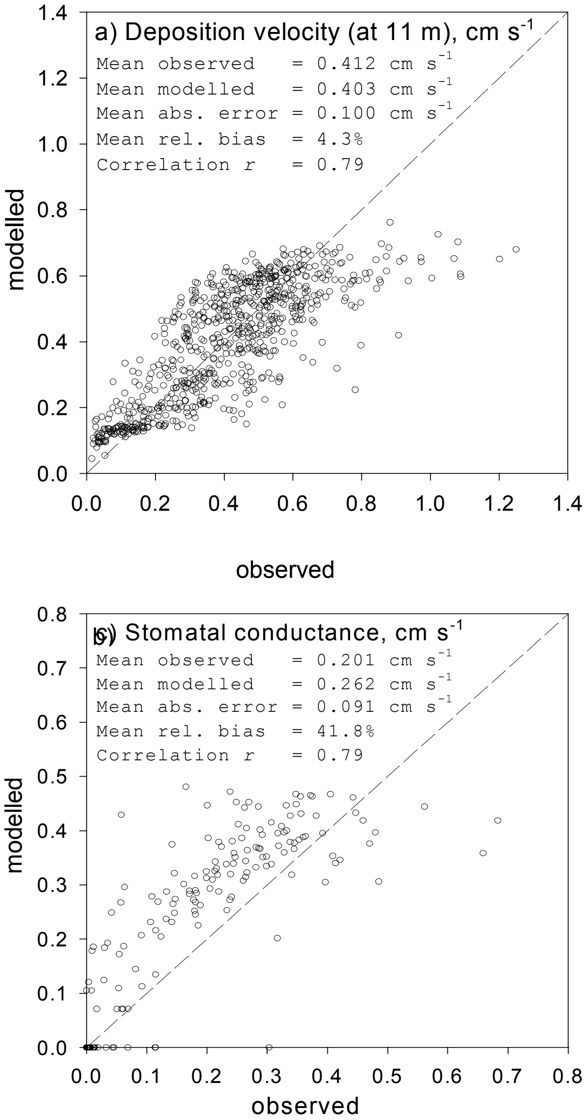

Figure 2.12. A comparison of the modelled dry deposition velocity (a) and canopy stomatal conductance (b) with those derived from O_3 and H_2O flux measurements over a Scots Pine forest at Mekrijärvi in July 1995 (23–27 July for G_{sto}); mean abs. error = arithmetic mean of $|x_{mod}–x_{obs}|$, where x_{mod} and x_{obs} are the modelled and observed quantity in question, respectively; mean rel. bias = arithmetic mean of $2(x_{mod}–x_{obs})/(x_{mod}+x_{obs})$ for non-zero x_{mod} and x_{obs} (Tuovinen *et al.,* 2001).

The use of a flux-based approach requires further work and comparisons of the model with many other species, but this approach offers important progress towards a new assessment of O_3 effects on vegetation in Europe.

2.5.2 Non-stomatal deposition

For the total deposition of O_3 to terrestrial surfaces, the other important development has been the partitioning of the surface deposition between stomatal uptake and deposition to the external surfaces of the vegetation. An important finding from this work for boundary layer O_3 concentrations is that the non-stomatal deposition flux is the dominant term for most surfaces, and that the rate of non-stomatal deposition varies with the physical conditions at the surface.

At its simplest the non-stomatal O_3 flux may be estimated from the measurement of nocturnal O_3 fluxes. From measurements over moorland vegetation in southern Scotland, recent measurements show that, with a median canopy resistance for r_{ns} of approximately 300 s m^{-1}, the annual non-stomatal ozone deposition at this site would be about 50 kg O_3 per hectare annually. The total deposition at the site, derived from the flux averaged from the entire four year data set, is 77 kg O_3 per hectare annually. Thus 65% of the total flux of ozone to the site is non-stomatal. A more precise separation of the stomatal and non-stomatal flux is possible during periods when the vegetation is dry and high quality water vapour fluxes are available at the site. Then making the reasonable assumption the water vapour flux is dominated by evapotranspiration in these conditions, the non-stomatal flux can be obtained by difference.

From a substantial data set during the summer over moorland, the variation in non-stomatal O_3 deposition surface resistance with other environmental variables can be tested. In Figure 2.13 the effect of solar radiation on non-stomatal surface resistance is shown, revealing a much faster rate of leaf surface reaction with O_3 at high irradiance.

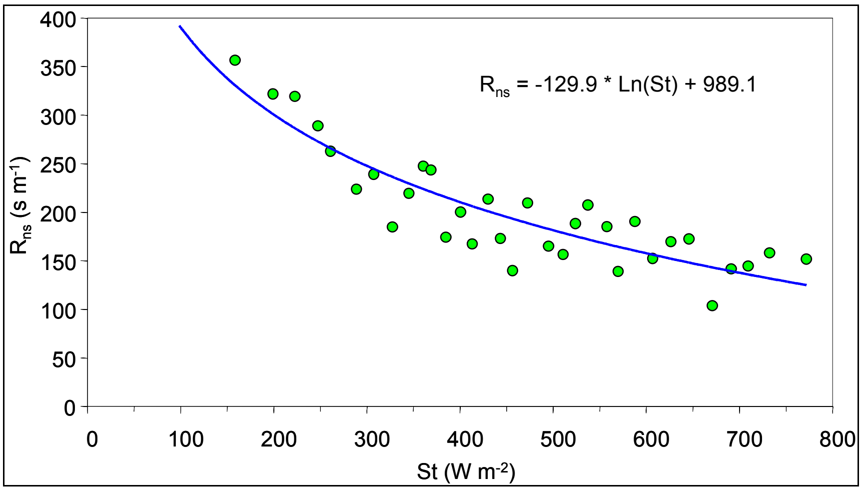

Figure 2.13. The relationship between canopy resistance for non-stomatal O_3 deposition (R_{ns}) and global radiation (St_t) for Auchencorth Moss, daytime data, (Fowler *et al.,* 2001).

The effect may be simply considered to be the temperature dependent reaction of ozone with surfaces of vegetation and, as such, an effective activation energy for the process may be estimated from an Arrhenius plot of the data (Figure 2.14). The surface resistance for non-stomatal O_3 deposition (R_{ns}) decreases with temperature from 400 s m^{-1} at 0°C to 200 s m^{-1} at 15°C in dry conditions and is consistent with a temperature dependent surface reaction of O_3.

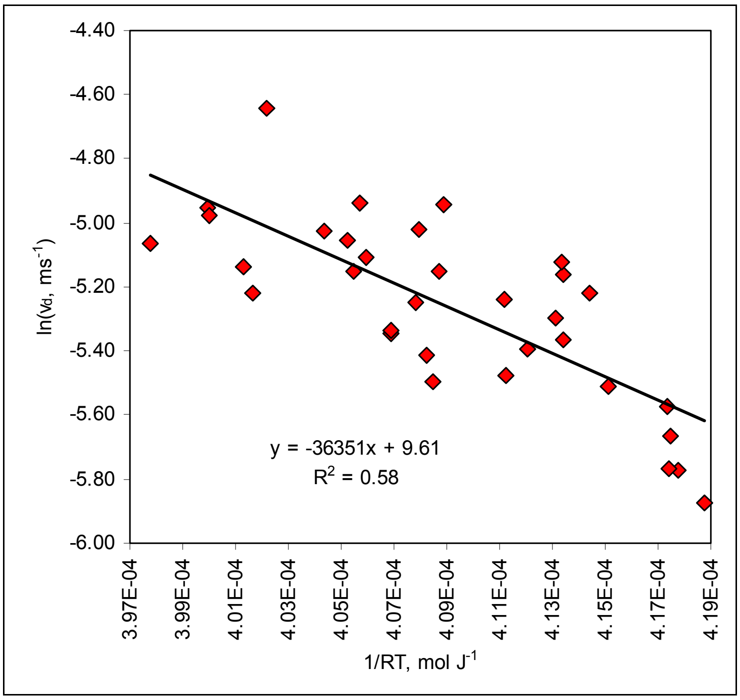

Figure 2.14. A plot of LnO_3 deposition velocity against 1/RT to estimate activation energy for non-stomatal O_3 deposition to vegetation from O_3 flux measurements at Auchencorth Moss. (Fowler *et al.,* 2001).

2.5.3 The importance of stomatal and non-stomatal fluxes

The physiological role of the ozone deposited to external surfaces of vegetation remains unknown. It is possible that ozone plays an important role in the ageing of epicuticular wax and other cuticular components of leaf surfaces. However the crop loss associated with exposure to elevated ozone is primarily due to stomatal uptake.

Policy relevance

The development of an alternative, flux based approach to replace AOT40 for assessment of the effects of O_3 on vegetation is a very important step. The other major development is the separation of the surface O_3 flux into stomatal and non-stomatal components, and the demonstration that non-stomatal deposition is very variable. The continuous flux measurements show that the majority of the ozone deposited is non-stomatal. For models of boundary layer or surface concentrations in long-range transport models, it is the non-stomatal term which dominates the surface flux which requires detailed attention. To date, non-stomatal ozone fluxes have been treated as a constant in most models.

2.6 Particle deposition

The accurate quantification of deposition rates of particles is a necessary prerequisite for modelling of air quality, long-range transport and radiative forcing potential. Despite their importance, the size-dependence of deposition rates is poorly understood, and therefore their atmospheric lifetime remains uncertain. One of the principal reasons why progress has been slow is the limited quality of instrumentation suitable for micrometeorological flux measurements. Also, the modellers are often unaware of the limited quality of the available emission inventories and deposition parameterisations they rely on. As a result, not many groups have been working on the measurement and parameterisation of the surface/atmosphere exchange of particles, although the field is currently gaining momentum, driven by the health impact.

Here we present a summary of recent advances in the micrometeorological measurement of surface/atmosphere exchange of particles, covering three aspects: recent instrument development, new datasets and new parameterisations.

2.6.1 Deposition rates to forest

At the end of BIATEX-1 a compilation of the size-dependent deposition rates to forests, derived with various methods, consistently revealed much larger deposition rates in the diameter size range 0.1 to 2 µm than predicted by current theoretical approaches (Gallagher *et al.*, 1997). These fast deposition rates appear to be in contradiction to the global residence time of radioactive material (Garland, 2001). Using the naturally occurring, particle-bound tracer ^{210}Pb, a product in the ^{238}U decay series with a half-life of 22.3 years, long-term averages of deposition rates can be derived from inventories of ^{210}Pb in the vegetation and the soil underneath, if the ecosystem has not been disturbed for (ideally) four half-lives (Fowler *et al.*, 1998). While micrometeorological techniques require large homogeneous surfaces, the ^{210}Pb inventory method can be applied for example to small groups of trees. Measurements under urban grassland and woodland at three sites in Birmingham and at Rothamsted, UK, revealed deposition rates of 2 to 4 mm s^{-1} to grass and 7 to 11 mm s^{-1} to forest and support the greatly enhanced deposition rates to rough surfaces (Figure 2.15).

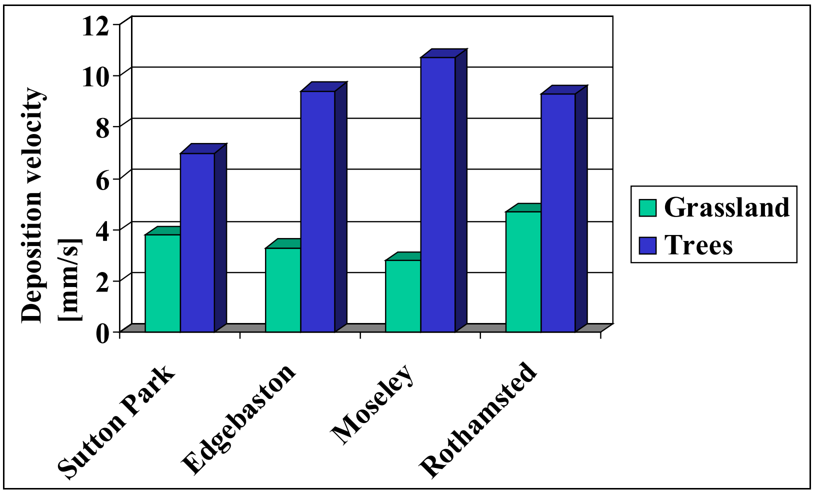

Figure 2.15. Deposition rates to grass and woodland at three undisturbed sites in Birmingham and at Rothamsted, derived with the ^{210}Pb inventory method.

2.6.2 Deposition rates to short vegetation

By contrast to the large deposition velocities (V_d) found for forests, the deposition velocity to a Scottish moorland, measured with two different optical particle counters during three periods (Figure 2.16a) agreed well with the unmodified model description of Slinn (1982). Similar datasets were obtained for deposition to long and short grassland during the BIATEX-2 experiment of the EU GRAMINAE project above an experimental grassland in Braunschweig, Germany. The measurements were combined with existing datasets to derive a logarithmic relationship between the deposition velocity of particles in the diameter range 0.1 to 0.2 µm on the surface roughness height (z_0) (Figure 2.16b; Gallagher *et al.*, 2002). For larger particles the relationship is less well defined and still subject to investigation.

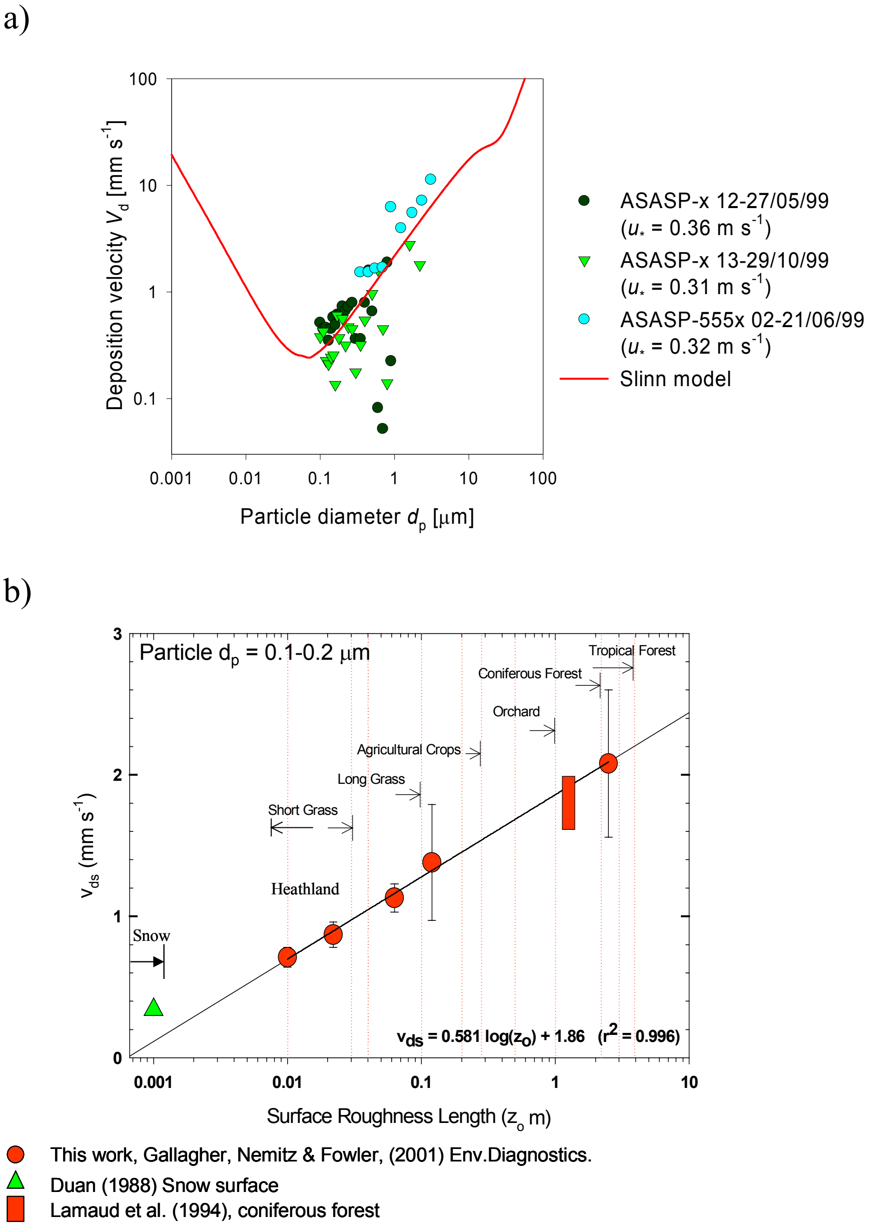

Figure 2.16. (a) Size-dependent deposition rates of particles to Scottish moorland vegetation measured with two different particle counters. (b) Deposition rate of accumulation mode particles in the diameter range 0.1 µm < d_p < 0.2 µm as a function of surface roughness length (z_0) (Gallagher *et al.*, 2002). From Nemitz *et al.*, 2002a).

2.6.3 Total particle fluxes dominated by nucleation mode particles

As indicated by Figure 2.16a, optical sizing techniques are currently limited to particles greater than 0.1 μm diameter and, until recently, only very limited measurements were available regarding the deposition rates of smaller, so-called nucleation mode particles. Although these small particles carry little *mass*, they can grow into the accumulation mode through coagulation and uptake of secondary material from the gas phase, and they usually dominate the particle *number* distribution. Consequently, the total number flux will be dominated by these small particles. Buzorius *et al.* (1998) pioneered the application of condensation particle counters (CPCs) with a lower cut-off diameter of typically 2 or 11 nm and an upper size limit of about 2 μm for eddy-covariance flux measurements.

Although the response time of the instrument is relatively slow, such systems are appropriate for measurements above rough vegetation or from tall towers. This methodology has now been adopted by other groups to measure fluxes over grass, moorland, forests, water, ice and in the urban environment (Beck *et al.*, 2001; Nilsson and Rannik, 2001; Dorsey *et al.*, 2002; Nemitz *et al.*, 2002b; Held and Klemm, 2002).

However, since these measurements were made during nucleation events, during which number concentrations were dominated by particles < 20 nm, they may be further enhanced by the increased diffusivity of these small particles, which is responsible for the increase of the V_d for small particles (cf Figure 2.16a).

2.6.4 Composition resolved particle fluxes

It is likely that deposition rates of particles depend on their chemical composition. For example inorganic hygroscopic particles have the potential to grow as they approach the humid vegetation canopy so that their effective deposition velocity is governed by a different size than is measured well above the surface. Instruments for composition resolved particle fluxes are required to study this effect and to quantify the contributions of particles to the inputs of atmospheric pollutants to sensitive ecosystems. One new development for the measurement of composition resolved particles fluxes is a gradient system utilising the ECN Steam Jet Aerosol Collector (SJAC; Slanina *et al.*, 2001). Figure 2.17 shows an example time series of NH_4^+ deposition measurements to a Dutch heathland, in comparison with individual runs using filter-pack gradients, which are prone to underestimate the NH_4^+ concentration due to volatilisation losses.

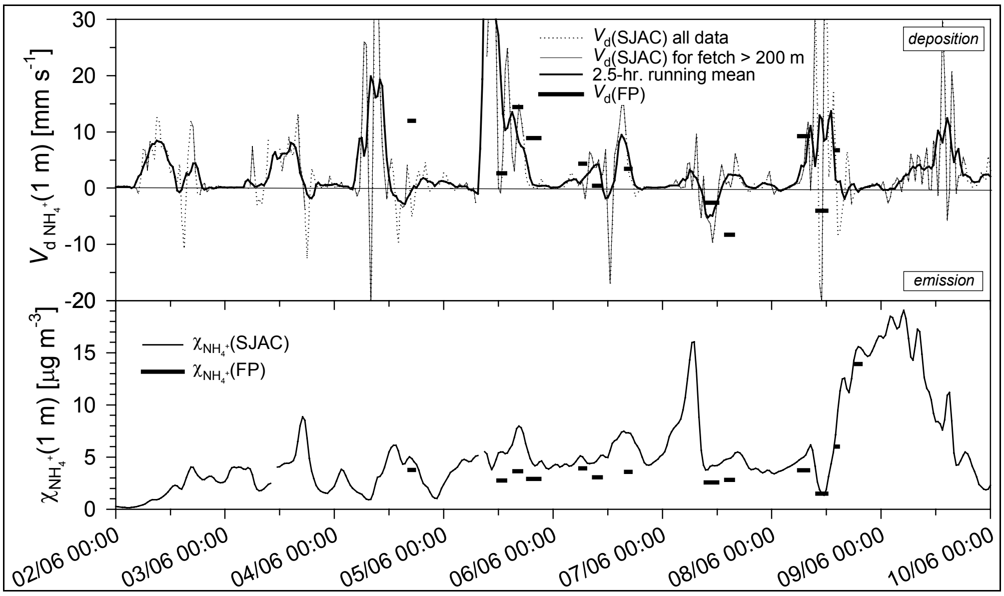

Figure 2.17. Example time-series of NH_4^+ concentrations and deposition velocities measured with a two-height Steam Jet Aerosol Collector (SJAC) above heathland, compared with individual filter-pack (FP) runs. (From Nemitz *et al*., 2002a).

Policy relevance

The improved parameterisation of aerosol deposition velocity has a direct application in long range transport models of the major pollutants, and therefore into policy. The strong new evidence of greatly enhanced particle deposition onto woodland and forest has application in the mitigation of human health effects of aerosols in urban areas by tree planting schemes. The new data provides for the first time the means to quantify the response of aerosol concentration to tree planting.

2.7 Monitoring and modelling of biosphere / atmosphere exchange of gases and aerosols

Deposition of air pollutants is an important loss process for pollutants from the atmosphere and can cause severe damage to ecosystems. The loss from and the emission to the atmosphere are also important for modelling of long-range transport of secondary formed particulate matter. Furthermore, fluxes of ozone are relevant for determining critical thresholds for effects. In order to develop effective emission reduction options and to monitor the progress in terms of reduced deposition levels, a combination of modelling and measurement activities is needed. The measurements serve as independent checks on the modelled concentration and deposition fields and they serve as understanding of surface exchange processes. Models serve to keep the link with emissions and to assess effective abatement strategies. Furthermore, there is a need for tools to scale results up to sites where no measurements are available. Deposition can occur as wet, dry and cloud/fog deposition. Wet deposition in Europe is routinely monitored in existing networks, e.g., ECE-EMEP, but this is not the case for dry and cloud/fog deposition of gases and particulate matter, which are much more difficult to measure. On average in Europe, dry deposition accounts for about 20% of the total deposition with a range of 10-90%. Dry deposition is site specific, determined by factors such as roughness of the surface, surface wetness, climate and environmental factors. Total (throughfall) deposition in forests is routinely measured at more than 400 intensive monitoring sites of the UNECE/ Forest monitoring programme (de Vries *et al.*, 2001). Apart from these monitoring programmes, several EU projects and EUROTRAC activities have contributed to the needs of monitoring and modelling of surface exchange of trace gases and particles. A (limited) overview of the monitoring activities, modelling activities and evaluation of model results are given below.

2.7.1 Wet deposition

Wet deposition is routinely monitored at about 90 EMEP sites distributed over Europe and in several national monitoring networks. Van Leeuwen *et al.* (1996) compiled a wet deposition map of Europe based on these measurements. Since then this exercise has not been repeated. At Schagerbrug, a grassland close to the Dutch shore, a comparison experiment was conducted of samplers used in different national and EU monitoring networks (Draaijers *et al.*, 2001). More than 90% of the samplers used are bulk samplers collecting dry deposition on the funnels. These samplers therefore overestimate the wet deposition flux by 5-40%, depending on the location, climate, sampler construction and component. The results show that for bulk precipitation fluxes the required accuracy of 10% or less is realised for only 5-40% of the participating countries, depending on chemical component. Bulk precipitation fluxes of NO_3^-, NH_4^+, H^+ and Kjeldahl-N generally could be determined with a greater accuracy than bulk precipitation fluxes of SO_4^{2-}, Na^+, Cl^-, Mg^{2+}, Ca^{2+}, alkalinity and H^+. Bulk precipitation fluxes of K^+ generally had the lowest accuracy. These results show that wet deposition, the dominant input to ecosystems, is not determined accurately enough for trends.

2.7.2 Dry deposition

Long-term flux monitoring stations for SO_2, NO_x, O_3 and NH_3 have been developed (Erisman *et al.*, 2001). Such sites have provided the major progress in understanding the processes which regulate long-term surface-atmosphere fluxes. The development of models used to calculate regional and site specific inputs of sulphur and nitrogen have relied heavily on these long-term measurements. The measurements show that SO_2 fluxes over most of Europe are regulated by chemical processes within surface films of water, which in turn is strongly influenced by the presence of NH_3. Dynamic models which simulate the process have been developed and, where sufficient chemical and micrometeorological data are available, these models quantify the net exchange of SO_2 and NH_3. For NH_3, parameterisations of the bi-directional plant-atmosphere exchange and the influence of management options have been included in the models (Sutton *et al.*, 1998). The parameterisation of the dry deposition velocity for gases and particles was based on Erisman and Draaijers (1995) and was further developed using recent literature (e.g., Brook *et al.*, 1999; Wesely and Hicks, 2000). The models have been applied over European scales for annual deposition estimates of sulphur and nitrogen inputs (see below).

2.7.3 Total deposition

Currently throughfall measurements are made at about 400 Intensive Monitoring plots to estimate the site specific inputs of nutrients in European forests (de Vries *et al*., 2001). Throughfall data are a measure for the soil load of pollutants. Because of canopy exchange processes, the data can not directly be used for atmospheric deposition (Erisman and Draaijers, 1995). Canopy exchange models have been developed to overcome this problem (Draaijers *et al*., 1996). By applying such models an estimate of total deposition can be obtained, but the uncertainty is still relatively high. The measurements are relatively cheap and easy to perform, and are therefore suitable to obtain spatial variation in deposition.

2.7.4 Modelling of deposition

There are several approaches to model ecosystem inputs: a) long-range transport modelling based on emission estimates and b) using measurements of concentrations and meteorological data to estimate deposition, or a combination of the two. Within BIATEX-2 a range of different approaches has been used. As an example, the combined measurement and modelling approach has been chosen to maintain the link with emissions and at the same time obtain ecosystem specific deposition estimates using EDACS (European Deposition of Acidifying Components on a small Scale) (Erisman and Draaijers, 1995). This model has been improved by ECN and meteorological input is updated, based on data from the European Centre for Medium-range Weather Forecasts (ECMWF). Concentrations of gases and aerosols are derived from the EMEP model. Wet deposition is derived from measurements and dry deposition is estimated using modelled concentrations with the EMEP model and land use specific dry deposition velocities calculated with ECMWF meteorology and a dry deposition module (Figure 2.18). Every 6 hours the ECMWF meteorological data is used to calculate a deposition velocity for each grid or each plot. The deposition velocity is combined with a concentration to estimate the flux. An annual flux is the summation of all 6-hour values. The model input and output is flexible and depends on the land use information that is used. Currently land use maps for Europe ($l/6^o$ x $1/6^o$) and for Germany (1 km x 1 km) are available. By using calculated concentration maps, the relationship between emissions and deposition is maintained and scenario studies, budget studies and assessments can be carried out on different scales.

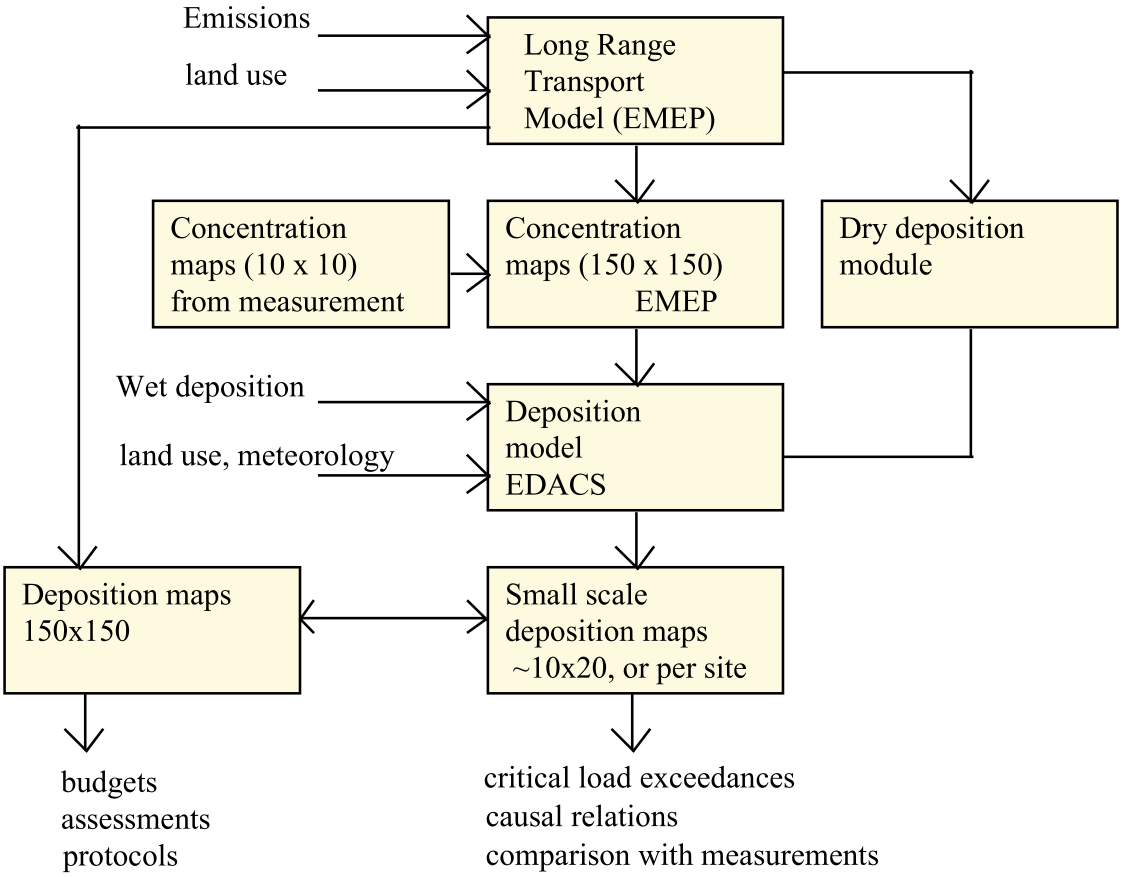

Figure 2.18. Outline of method to estimate local scale deposition fluxes. (From Erisman *et al*., 2002).

In this approach, site-specific calculations are made using site specific information available for the Intensive Monitoring plots. Figure 2.19 shows the model comparison with throughfall measurements at the plots. The correlation for sulphur is small (Figure 2.19a). This is especially due to an overestimation of sulphur deposition at a few sites. These sites are all located close to or in the Black triangle. It appears that the DEHM model (described by Brandt *et al*., 2001) overestimates SO_2 concentrations in these areas because of the resolution of concentrations. On average the modelled sulphur deposition and measured throughfall are comparable. The nitrogen deposition, both of NO_3 and NH_4 is considerably larger than the measured throughfall, although the correlation is larger than for SO_4 (Figure 2.19b, 2.19c). Specifically the reduced N deposition is higher by up to a factor of two, despite the high correlation.

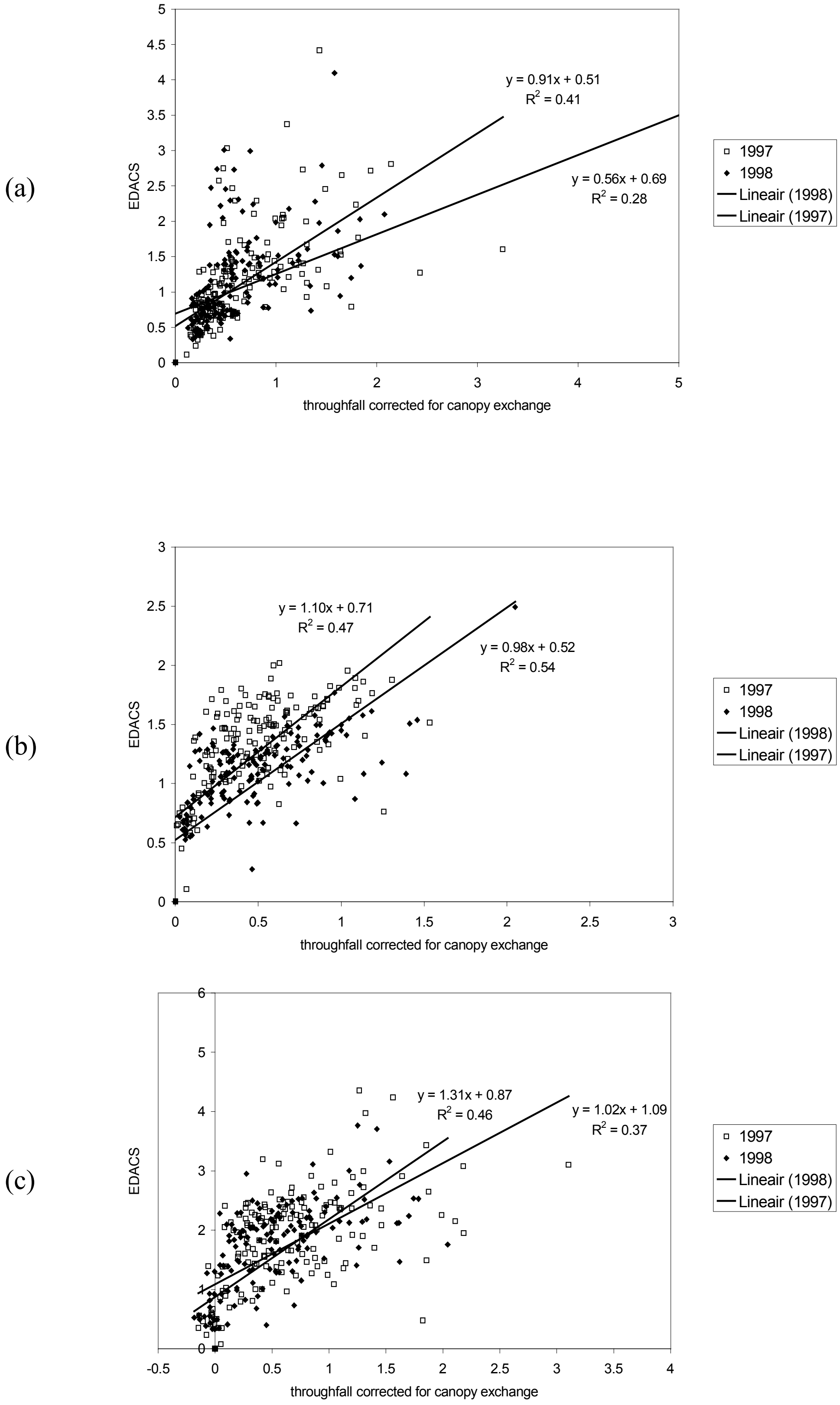

Figure 2.19. Comparison of total deposition calculated with EDACS (Erisman and Draaijers 1995) with throughfall measurements of (a) SO_4, (b) NO_3 and (c) NH_4. (From Erisman *et al.*, 2002).

Most of our present knowledge on atmosphere–biosphere exchange, stems from the 1980s and early 1990s, when acidification research was intensively conducted. Recently, most progress has been made on ammonia exchange and on monitoring of dry deposition. Examples of the value of deposition monitoring are that non-linearity in the emission–deposition relationship at the country scale has been identified for sulphur emission and deposition and the discovery of a major discrepancy in the atmospheric budget of ammonia over the Netherlands has been identified. Monitoring of fluxes has become possible, but the uncertainty is still very high, especially for wet deposition and the deposition of reactive gases and particles. Fluxes of ozone and inert gases, such as CO_2 can easily be monitored. Progress has been made in the recognition and understanding of O_3 uptake at surfaces. For modelling of the surface exchange of gases, there is lack of parameterisation of dynamic processes, occurring for example with surface wetness. Furthermore, the modelling of the bi-directional nature of gas exchange (nitrogen compounds) and the external surface uptake of O_3 should be improved.

2.8 Tools

Research in surface-atmosphere exchange processes requires its specialist tools for the developments over the last decade. These include:

- Specific instruments to measure fluxes or concentrations in the field. In particular the improved understanding of NH_3 exchange has depended heavily on the development of continuous annular denuder instruments, the development of high quality passive sampling methods for NH_3 monitoring networks and extensive research and monitoring networks in the Netherlands, Denmark and the UK. The development and application of Tunable Diode Laser spectroscopy for the measurement of trace gas fluxes by eddy co-variance methods.
- The development of a range of new micrometeorological methods to measure field and landscape scale fluxes of a wide range of pollutant gases and particles. These include eddy co-variance for reactive gases, conditional sampling methods for Relaxed Eddy Accumulation methods, boundary layer budget methods and tracer ratio methods for reactive trace gases.
- New instrumentation and methods for the measurement of VOC emission fluxes from vegetation.
- Application of micrometeorological methods to quantify aerosol and trace gas fluxes over urban landscapes.
- Models to simulate NH_3 bi-directional exchange over vegetation, inverse Lagrangian methods for the interpretation of fluxes of ammonia from multiple sources within crop canopies. Process based modes containing a detailed surface chemistry scheme to simulate the interaction of soluble reactive gases with the micrometeorology over crop canopies.

- The development of long-term flux monitoring instruments and their application in Europe to provide 5 to 10 year continuous records of SO_2, NH_3, and O_3 fluxes at representative regional sites in Europe.

This short list of tools illustrates some of the main tools developed within the EUROTRAC research on deposition. The brief list is not intended to be complete or exhaustive, but to illustrate the main areas of development. The development of the scientific understanding has depended on these tools, and to an important extent the tools control and limit the developments in understanding. In particular the appearance of new, very sensitive instruments for trace gas measurement provides the key to developments in the scientific understanding.

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Chapter 2

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Chapter 3

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