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Dry deposition of reduced nitrogen

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ABSTRACT

The paper reviews the results of measurements of ammonia (NH_3) exchange and considers the application of this information in approaches to modelling atmospheric NH_3 inputs to ecosystems. Ammonia dry deposition is seen to be highly dependent on land management and the magnitude of agricultural nitrogen inputs. Efficient dry deposition is observed to many semi-natural and forest ecosystems, with typical deposition velocities (V_d) in the range 5–50 mm s^{-1}. By contrast, intensively grazed pastures and fertilized arable croplands frequently show net NH_3 emission, with fluxes dependent on the form of N input, environmental conditions (temperature, wetness) and plant growth stage. Other factors affecting the exchange of NH_3 with ecosystems include the existence of an NH_3 "compensation point" within plant tissues and interactions with acid gases such as SO_2. Available information on NH_3 exchange over the sea and aquatic water bodies suggests that both emission and deposition can occur depending on NH_3 air concentrations and water compensation points. Approaches to mapping NH_3 dry deposition include inferring deposition from monitored air concentrations and values of V_d ("inferential technique"), and atmospheric transport models. The former may be more site specific, but is limited by lack of NH_3 concentration monitoring, while the latter provides good regional coverage, but poor estimates of actual inputs to specific ecosystems (grids often >50 km $\times$ 50 km). A possible advance is to apply the air concentration field outputs of large scale transport models, with locally derived V_d, though this fails to treat the significant local variability in NH_3 emissions and air concentrations. An improvement would be the further development of local scale atmospheric transport models (e.g., 5 km $\times$ 5 km grids) incorporating land use information and ecosystem specific V_d on a fine spatial scale.

1. Introduction

The major forms of reduced nitrogen in the atmosphere are gaseous ammonia (NH_3) and particulate ammonium (NH_4^+). Other organic forms also exist, such as amines, but the concentrations of these components are generally negligible by comparison (Van der Eerden, 1982). Processes controlling the dry deposition of NH_4^+ aerosol have been are considered in another recent review (Ruijgrok et al., 1993), so that the main focus here is on gaseous NH_3.

While many pollutant gases such as SO_2, NO_2 and HNO_3 are consistently deposited, NH_3 is both emitted from and deposited to land and water surfaces. As a consequence, this paper discusses the processes controlling the net NH_3 flux in either direction. This is necessary because parameterization of NH_3 dry deposition in long range transport models depends on the integration of each of these land/sea surface, atmosphere processes. Nevertheless, because NH_3 deposition to semi-natural ecosystems, forests and sensitive water bodies is of special interest for comparison with critical loads, particular attention is given to these surfaces.

The main aim of this paper is to summarize results in a form useful for incorporation in

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regional mapping of deposition. For this purpose use of the resistance analysis of pollutant transfer (see, Duyzer and Fowler, 1994; Erisman and Baldocchi, 1994) is desirable, and where possible results are expressed here as deposition velocities (V_d) and canopy resistances (R_c). Studies of ammonia surface exchange have been made using micrometeorological, chamber and throughfall measurements, and these have been reviewed in detail elsewhere (Freney and Simpson, 1983; Schjørring, 1991; Lövblad and Erisman, 1992; Sutton et al., 1993d). Micrometeorological measurements are given most attention here, since these provide the best approach for estimating fluxes and resistances in the field, though each of the other methods have proved useful for examining processes controlling exchange.

In the following sections NH_3 surface exchange is considered for the range of European ecosystems: intensively grazed grasslands, agricultural croplands, semi-natural ecosystems and forests, and water surfaces. This is followed by a consideration of NH_3–SO_2 co-deposition and other uncertainties, examples of measured air concentrations, and a discussion of approaches to modelling regional NH_3 dry deposition.

2. Exchange over intensively grazed grasslands

Intensively grazed grasslands represent a net source of NH_3 to the atmosphere. As such, this exchange is normally included in mapped NH_3 emission inventories (e.g., Buijsman et al., 1987; Kruse et al., 1989; Asman, 1992) and used as an input to atmospheric transport models (e.g., Sandnes and Styve, 1992; Asman and van Jaarsveld, 1992). Other NH_3 emissions included in inventories are losses from animal houses, stored livestock waste and following slurry spreading. Animal houses and manure storage represent point sources, while slurry spreading is an intermittent source. By contrast, field losses from grazing animals occur over both extended time periods and large ground areas. Exchange over grazed fields is therefore also relevant when calculating dry deposition in atmospheric transport models, since it is important that the same land area and exchange is not treated twice.

Field measurements of ammonia fluxes over grazed pastures show annual emissions in the range 1 to 40 kg N ha^{-1} yr^{-1} depending on animal type, sward N fertilization and timing of grazing. For example measurements in the UK by Jarvis et al. (1989) showed losses of 7, 9 and 25 kg N ha^{-1} for May to October over rotationally grazed beef cattle pasture with fertilization of 170, 210 or 420 kg N ha^{-1} (Table 1). This response was well supported by measurements of Bussink (1990) who observed NH_3 losses of 8 and 40 kg N ha^{-1} for a similar period, from rotationally grazed cattle pasture fertilized with 250 and 550 kg N ha^{-1}. Emissions were also estimated on a per animal basis providing an average loss of up to 0.04 kg N $animal^{-1}$ day^{-1}. By contrast to cattle, NH_3 emissions from sheep grazed pastures are much smaller, with Jarvis and Pain (1990) reporting

Table 1. *Examples of average NH_3 emissions from cattle and sheep pastures in relation to N fertilization inputs; further data provided by Jarvis and Pain (1990)*

Management	Total NH_3 emission kg N ha^{-1} yr^{-1}	Emission per animal g N day^{-1}	Ref.
Beef cattle: rotational grazing			Jarvis et al. (1989)
grass-clover ($\equiv$ 170 kg N ha^{-1}) + 0N	7	5.0	
grass + 210 kg N ha^{-1}	9	9.0	
grass + 420 kg N ha^{-1}	25	18.0	
Dairy cows: rotational grazing			Bussink(1990)
grass + 250 kg N ha^{-1}	8	14.0	
grass + 550 kg N ha^{-1}	41	42.5	
Sheep: continuous grazing			Jarvis and Pain (1990)
grass + 0 kg N ha^{-1}	4	0.2	
grass + 420 kg N ha^{-1}	9	1.2	

annual emissions of 4 and 9 kg N ha^{-1} yr^{-1} for continuously grazed sheep pasture receiving 0 or 420 kg N fertilizer ha^{-1} yr^{-1}. Maximum daily emissions have been estimated at 2.8, 2.3 and 0.4 kg N ha^{-1} day^{-1} for dairy cattle, beef cattle and sheep respectively (Jarvis et al., 1989). It should be noted that emission rates are highly dependent on environmental conditions, especially windspeed, temperature and wetness. In addition to these maximum figures, periods of deposition also occur, both on daily scales and seasonally. Hence, during the non-grazed winter period for many cattle pastures, NH_3 deposition is likely for much of the time, though measurements are needed to confirm this.

3. Exchange over agricultural croplands

As with grazed pastures, both NH_3 emission and deposition occur over agricultural croplands. A summary of micrometeorological NH_3 measurements over croplands is given in Table 2, and this shows above canopy fluxes in the range -120–1100 ng NH_3 m^{-2} s^{-1}. The magnitude and direction of the fluxes may change on hourly, diurnal and seasonal scales. This depends on environmental conditions, crop growth characteristics and timing of fertilizer applications.

Ammonia emissions from fertilizer application depend on the type of fertilizer used. For example, large losses may follow urea application (>10 μg m^{-2} s^{-1}, Freney and Simpson, 1983), while other fertilizers such as NH_4NO_3 give much smaller maximum losses. Most of the fertilizer emission occurs in the first few days following application. In addition to direct fertilizer losses, Harper et al. (1987) have suggested that for annual crops longer term net emission and deposition relates to N shortage and surplus in the plants over the growing season. They observed elevated emission for several weeks following fertilization (N surplus period), deposition during the vegetative growth phase (N in demand), and emission during

Table 2. *Examples of micrometeorological flux measurements of NH_3 exchange over agricultural croplands; note: negative fluxes denote deposition to vegetation*

Plant canopy	Conc. NH_3 (μg N m^{-3})	Above canopy fluxes (ng NH_3 m^{-2} ground s^{-1})	Ref. and notes
grass + clover	≈ 2	35–121 flux at soil: 80–1600	Denmead et al. (1976). Ungrazed pasture.
wheat (*Triticum aestivum*)	≈ 10 ≈ 10 25–35 10–18	pre-fertilization: 315 post-fertilization: -70–1060 vegetative growth stage: -70 grain filling stage: -24–790	Harper et al. (1987). Fertilized with 112 kg N ha^{-1} as NH_4NO_3. Integrated emission over growing season ≈ 15 kg N ha^{-1}
range of grass and crop surfaces	mean: 1.5	-24–120 mean: 38	Harrison et al. (1989)
grass and barley (*Hordeum vulgare*).	0.0–1.0	grassland summer: -1–22 grassland winter: -35–-5 barley summer: -5–24	Sutton (1990), Sutton et al. (1993c). Fertilized with 100–150 kg N ha^{-1} as NH_4NO_3. Integrated emission over year estimated as ≈ 0.4 kg N ha^{-1} yr^{-1}
alfalfa (*Medicago sativa*)	1–7	-170–840	Dabney and Bouldin (1990). Largest emission following hay cutting.
wheat	1–5	-15–31	Meixner et al. (1991)
barley	1–2	-60–180	Schjørring et al. (1993a). Fertilized with 40, 120 or 160 kg N ha^{-1} as NH_4NO_3. Integrated emission over growing season 0.6–1.3 kg N ha^{-1}
wheat	2–4	vegetative growth: 24–120	Schjørring et al. (1992). Integrated emission over growing season ≈ 7 kg N ha^{-1}

senescence and grain filling (N re-mobilized to grain). Similar effects of N supply have been observed in chamber experiments, such as by Whitehead and Lockyer (1987), who found N fertilization to reduce gaseous NH_3 uptake in Rye-grass. The seasonal effect has also been supported by field measurements of Schjørring et al. (1993a), who found an increased emission in June to August, which they related to senescence induced nitrogen re-mobilization (Schjørring et al., 1993b).

Onto this seasonal pattern may be superimposed the effects of environmental conditions. As with grazed fields, emission is favoured in warm dry conditions, and deposition favoured when the ground is wet (Harper et al., 1987; Dabney and Bouldin, 1990; Sutton, 1990; Sutton et al., 1993c). These effects result in hourly variation of NH_3 fluxes, as well as favouring emission in summer and deposition in winter. Over plant canopies the main source of NH_3 emission is from leaf tissues, via stomata. Emission is therefore expected to be largest in the day-time when stomata are open. Denmead et al. (1976) also found large soil emissions of NH_3, which were possibly associated with decomposing vegetation, but found that these were largely recaptured by vegetation above. In the absence of plants, larger soil emissions may occur immediately following fertilization, though at other times NH_3 emission is unlikely for soils with pH <7–7.5, as mineralized NH_4^+ is bound into soil colloids or nitrified.

The potential for crops to emit NH_3 depends on the concentration of NH_4^+ in plant tissues. From Henry's Law the NH_4^+ corresponds to an equilibrium NH_3 concentration within the substomatal cavities of leaves. This is called the compensation point (Farquhar et al., 1980), since where it equals the air concentration there is a balance between emission and deposition processes. When NH_3 air concentrations are smaller than the compensation point, emission occurs, and when they are larger, deposition occurs. During senescence of annual grain crops, degradation of proteins leads to formation of NH_4^+, which increases the compensation point and favours NH_3 emission (Morgan and Parton, 1989; Schjørring et al., 1993b). The total senescence emission depends on the N source-sink processes within the crop, in particular the amount of tissue N and the efficiency of its re-utilization in grain. Hence large NH_3 emissions may be expected where high initial N fertilization is followed by poor growing conditions during grain filling. Such effects may cause large year to year variation in net NH_3 fluxes (Schjørring et al., 1993a).

From a modelling perspective it is desirable to formalize such measurements into the usual resistance analogy framework. The deposition velocity provides a rate of deposition normalized for air concentration ($\chi\{z\}$) and is calculated as $V_d\{z\} = -\text{flux}/\chi\{z\}$, where z is a reference height above the ground. It is assumed that the concentration at the absorbing surface is zero, so that V_d is independent of χ. However, where both emission and deposition occurs over agricultural vegetation, V_d is dependent on χ, and is therefore less useful. Nevertheless, the resistance approach may still be applied to estimate the maximum possible exchange velocity, $V_m\{z\} = 1/(R_a\{z\} + R_b)$, where $R_a\{z\}$ and R_b are the atmospheric and quasi-laminar sub-layer resistances respectively. The existence of the compensation point over croplands could, in principle, be used to model NH_3 exchange. This has been estimated from chamber studies but is found to be very variable, in the range $1 -> 30\ \mu g\ NH_3\text{–}N\ m^{-3}$ (Farquhar et al., 1980; Morgan and Parton, 1989) as a consequence of the factors discussed above. The compensation point (denoted χ_s) may also be estimated from micro-meteorological measurements using the resistance framework:

$$\chi_s = \chi\{1\text{ m}\} + \text{flux}[R_a\{1\text{ m}\} + R_b + R_s], \qquad (1)$$

where $\chi\{z\}$ and $R_a\{z\}$ are set here to 1 m, and R_s is the bulk stomatal resistance (Dabney and Bouldin, 1990; Sutton, 1990). Micrometeorological measurements in dry summer conditions by these authors have provided χ_s in the range 2–7 μg $NH_3\text{–}N\ m^{-3}$. However, χ_s is not accessible in wet conditions as leaf surface deposition dominates. Nevertheless, a net canopy compensation point ($\chi\{z'_o\}$) may be estimated by considering only the atmospheric resistances in eq. (1) and removing R_s. This provides the net potential of the canopy to emit NH_3.

Clearly all these interactions are complicated to model in detail so that current long term estimates are very simplified and extremely uncertain. Harper et al. (1987) in the USA and Schjørring et al. (1992, 1993a) in Denmark have provided net emission estimates for 3–4 month (spring–summer)

growing seasons of 15 and 0.5–7 kg N ha^{-1} respectively for grain crops. Extended periods of deposition are expected in winter, so that annual emission is less than these estimates. Including exchange processes over the whole year Sutton et al. (1993c) estimated annual net NH_3 emission over a UK fertilized grass crop to be <1 kg N ha^{-1} yr^{-1}.

4. Deposition to semi-natural ecosystems and forests

By contrast to agricultural croplands, semi-natural (unfertilized) ecosystems and forests generally show NH_3 dry deposition (Table 3). For example, over Dutch heathland Duyzer et al. (1987) recorded a mean deposition velocity of 19 mm s^{-1}. They also found enhanced V_d when the vegetation was wet, showing smaller R_c (mean 9 s m^{-1}) than for dry vegetation (mean 28 s m^{-1}). Over upland moorlands Sutton et al. (1992a) observed similar rapid deposition with a mean R_c of 6 s m^{-1}, though no clear effect of surface wetness was found at their more humid sites. In both of these examples the measured R_c were much smaller than stomatal resistance for NH_3 uptake (R_s, typically 50–300 s m^{-1} in day-time) so that most of the NH_3 must have been deposited onto leaf surfaces. If uptake had been through stomata alone, deposition would have been much slower, with $V_d < 10$ mm s^{-1}.

These results also show that the net canopy compensation point for semi-natural ecosystems is frequently negligible. The canopy compensation point estimate, $\chi\{z'_o\}$, is closely related to R_c since both account for the difference between V_d and the maximum rate of deposition possible by turbulence. Hence, where R_c is zero, so is $\chi\{z'_o\}$. In the results of Sutton et al. (1992a) the mean $\chi\{z'_o\}$ for measurements at 4 sites was 0.01 μg NH_3–N m^{-3}. A larger compensation point may still exist within plant stomata but this is presumably short circuited by deposition to the leaf surface.

There are nevertheless exceptions to this general pattern as shown by results of Sutton et al. (1992b) and Erisman and Wyers (1993) in Table 3. These

Table 3. *Range of micrometeorological measurements of NH_3 dry deposition to semi-natural ecosystems and forests*

Ecosystems	Air concentration (μg NH_3 m^{-3})	Range of NH_3 fluxes (ng m^{-2} s^{-1})	Deposition velocity, V_d (mm s^{-1})	Canopy resistance, R_c (s m^{-1})	Ref. and notes
dry heathland	0–25	−190–−30	19		Duyzer et al. (1987)
dry surface				28	
wet surface				9	
unpland moorland	0.03–1.2	−64–0			Sutton et al. (1992a)
non-frozen			28	6	
frozen			9	50–200	
dry heathland	0.3–8.5	−90–22			Sutton et al. (1992b)
dry <70% RH			emission	—	day
humid >80% RH			0–15	0–100	day/night
dry heathland	0.5–40	−450–500	—		Erisman and Wyers (1993)
dry <70% RH				0–300*	
>70% RH or wet				0–100	
frozen				200	
neutral cut meadow	1.3–3.4	−60–−8	16	3	Sutton et al. (1993b)
coniferous forest	1–27	−1270–−290	32	4	Duyzer et al. (1992)
	0.1–25	−100	32	—	Wyers et al. (1992b)
	0–4		14–200	$R_b + R_c = 6$*	Andersen et al. (1993)

Notes: negative fluxes denote deposition; single values are means. * Calculated from their data; some runs indicated ammonia emission.

studies showed that larger R_c can occur, particularly when the air is very dry (RH < 60%) and in areas subject to large NH_3 concentrations. At such sites the leaf surface sink may become saturated, even allowing short periods of emission. A similar effect has been inferred from air concentration monitoring in a forest area, where air concentrations were suggested to be regulated by the forest NH_3 compensation point during dry summer time conditions (RH < 50%) in a continental climate (Langford and Fehsenfeld, 1992). The effect of humidity may result from the presence of salts on leaf surfaces from deposited gas and aerosol. At humidities typically >70% these deliquesce and may provide a micro-scale water-layer allowing extra deposition (c.f., Van Hove et al., 1989). In addition, Benner et al. (1992) have shown increased adsorption of water onto clean inert surfaces, with water-layer thicknesses ranging from 2–3 molecular monolayers at 50% RH to over 40 monolayers at approximately 95% RH. Temperature is also important, and measurements in Table 3 suggest that reduced rates of deposition may occur in frozen conditions or to snow surfaces, with R_c in the range 50–200 s m^{-1}.

Efficient deposition has also been observed over forests and several examples are summarized in Table 3. Because of increased turbulence over the rougher forest vegetation, atmospheric resistances for transfer (R_a, R_b) are much smaller than for short vegetation. With small values of R_c, this therefore allows much larger rates of NH_3 deposition to forests, with typical V_d in the range 10–100 mm s^{-1}. However, estimation of long term fluxes over forests becomes very sensitive to the value of R_c, providing a much larger uncertainty in the calculated deposition. The sub-layer resistance R_b is also a potential source of error since this is estimated semi-empirically. R_b gives a larger uncertainty for deposition to forests because of its increased contribution to the total resistance where R_a and R_c are small.

The contrasting exchange pattern of NH_3 over semi-natural ecosystems and forests compared with croplands may be related to the nitrogen status of these different communities. It is probable that the N fertilization of croplands increases the available N in plant tissues resulting in a larger compensation point. This provides a larger tendency for stomatal emission in croplands, with the NH_3 able to saturate or escape recapture by the leaf surfaces, allowing a net emission to the atmosphere for extended periods.

5. Exchange over sea and lake surfaces

Ammonia exchange over sea areas is relevant as an input to long-range transport models and ammonia budgets. In addition, deposition of NH_3 to sea and lake surfaces is important since N may be the limiting factor for algal growth. This has prompted concern about the size of atmospheric N inputs to both the Baltic Sea and the North Sea (Hessen et al., 1993), as well as to poorly buffered lakes where NH_3 deposition is also acidifying (Schuurkes et al., 1986).

Joffre (1988) and Lindfors et al. (1991) have modelled the deposition of NH_3 to sea areas and demonstrate the specific micrometeorology associated with air–sea exchange processes. As with vegetation, the atmospheric resistance for exchange (R_a) depends on surface roughness (parameterized by the roughness length, z_o). However, over water surfaces z_o varies with meteorology and is closely related to windspeed and wave formation. Similarly, the sub-layer resistance R_b is different over water surfaces, and is again dependent on windspeed and surface roughness. Formulation for each of these quantities has been provided by Lindfors et al. (1991) though this is semi-empirical and is subject to considerable uncertainty, particularly in the transition from smooth to rough surfaces. Air–sea exchange is also dependent on atmospheric stability which introduces a strong seasonality into deposition rates. In spring and summer the air temperature is larger than the water temperature resulting in stable atmospheric conditions and much reduced transport compared with autumn and winter. By assuming that both the concentration of NH_4^+ in sea water and the air-liquid interface resistance are negligible, Lindfors et al. (1991) estimated an average deposition velocity of 8 mm s^{-1} for the Baltic Sea. There are few experimental results with which to confirm these model estimates, though they are supported by limited laboratory measurements of Dollard and McKay (1993) and Duyzer et al. (1993), who showed that rates of uptake are limited by aerodynamic resistances (R_a, R_b) with negligible transfer resistance at the surface. However, these experiments were conducted with very large NH_3 concentrations of

20–40 $\mu g\, m^{-3}$, so that it is possible that these rates of uptake would not occur in typical ambient conditions.

While Lindfors et al. (1991) provide a detailed meteorological treatment, their assumption of negligible sea-water NH_4^+ concentrations is expected to be a significant source of error. In many situations sea-water NH_4^+ may limit NH_3 deposition rates and even allow NH_3 emission. The direction of NH_3 exchange over water surfaces is dependent on the air concentration of NH_3 and the gaseous concentration in equilibrium with aqueous NH_4^+. This is similar to the exchange over croplands, so that this equilibrium air concentration might be referred to as the "compensation point" for the water surface. The compensation point may be calculated using published values of the Henry equilibrium (H_{NH_3}, Dasgupta and Dong, 1986) and from the dissociation constant of NH_4^+ in water ($K_{NH_4^+}$, Bates and Pinching, 1950), where temperature (T) is in Kelvin and the NH_3 partial pressure is in atmospheres:

$$H_{NH_3} = \frac{[NH_3 \cdot H_2O]}{[NH_3]_{air}} = 56.0 \exp\left(4092 \times \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \text{mol}\, l^{-1}\, \text{atm}^{-1}. \quad (2)$$

$$K_{NH_4^+} = \frac{[NH_3 \cdot H_2O][H^+]}{[NH_4^+]} = 5.67 \times 10^{-10} \times \exp\left(-6286 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \text{mol}\, l^{-1}. \quad (3)$$

It should be noted that while such values are currently used in existing calculations, they are strictly appropriate for dilute solutions only. A correction due to the presence of other ions is required for sea water, which amounts to at least 20% (Asman, unpublished results).

The pH dependence of the NH_4^+ equilibrium in water is not important for exchange with the sea which is well buffered to about pH 8.1. However, different values of pH will strongly affect lake compensation points, with most deposition to acidic waters. Because of efficient nitrification of NH_4^+ to NO_3^-, lake surface NH_4^+ concentrations are generally rather small. For example, measurements at Blelham Tarn in the Lake District of northern England gave a pH of 7.1 (Carrick and Sutcliffe, 1982) and surface water NH_4^+ concentration of 6 $\mu g\, l^{-1}$ (Stewart et al., 1982). Assuming a temperature of 10°C, provides a compensation point of 0.005 $\mu g\, NH_3\, m^{-3}$. This is much smaller than typical air concentrations (Table 5) so that such lakes generally represent efficient sinks for NH_3 dry deposition, and formulations such as that of Lindfors et al. (1991) may be used. Exceptions apply for eutrophic lakes where both pH and NH_4^+ may be high. In a shallow German lake near Berlin (Großer Müggelsee) Dudel and Kohl (1992) measured a pH of 8.5 and NH_4^+ of 10–1000 $\mu g\, l^{-1}$. This provides a compensation point of 0.2–20.6 $\mu g\, NH_3\, m^{-3}$ (at 10°C), which suggests that such lakes emit NH_3 for much of the time.

Measurements of NH_3 in marine air (Table 4) generally show much smaller concentrations than

Table 4. *Examples of atmospheric NH_3 concentrations in marine air*

Location	Concentration ($\mu g\, NH_3\, m^{-3}$)	Ref.	Notes
North Sea	0.2–0.6	Erisman et al. (1986)	marine air masses measured at the Netherlands coast (Petten).
North Sea	0.1–0.5	Ottley and Harrison (1991)	cruises in the southern sector.
Kattegat Sea	0.21 (annual mean)	Hovmand and Grundahl (1991)	measured at the island of Anholt between Denmark and Sweden.
Baltic Sea	0.77 (S. Baltic) 0.19 (N and C. Baltic)	Lindfors et al. (1991)	cruise measurements.
S. Pacific Ocean	0.06 (marine air) 0.34 (continental air)	Ayers and Gras (1983)	coastal measurement at C. Grim, Tasmania.
C. Pacific Ocean	0.001	Quinn et al. (1990)	cruise measurements

in continental air (Table 5), so that the sea compensation point must be small (typically < 0.5 $\mu g\, m^{-3}$), allowing a net transfer of atmospheric NH_3 from land to sea areas. This process is expected to result in NH_3 concentration gradients in the marine atmosphere with distance from the coast, since NH_3 is removed by dry deposition and conversion to NH_4^+. An example of such gradients has been estimated by Asman and Runge (1991) and Asman and van Jaarsveld (1992) for Denmark, and this is shown in Fig. 1. If the sea is treated as a perfect sink for NH_3, assuming a zero compensation point, deposition is expected to decline rapidly with distance from the coast, as in Fig. 1. However, the existence of a compensation point may allow NH_3 emission in remote areas. Quinn et al. (1990) measured NH_4^+ in sea water and NH_3 air concentrations in the remote central Pacific Ocean and used these to infer an emission of 0.1–2.9 ng $NH_3\, m^{-2}\, s^{-1}$. Small air concentrations of NH_3 were maintained because of reaction to form NH_4^+ and precipitation scavenging. In remote sea locations air concentrations of NH_4^+ aerosol are generally much larger than gaseous NH_3, so that while these aerosol deposit very slowly they may constitute a larger dry deposition input than NH_3.

There are few published measurements of simultaneous NH_3 air and NH_4^+ sea water concentration in Europe, which provides a major uncertainty for the estimation of marine NH_3 budgets. However, a recent study of Asman et al. (1994) has applied such measurements to provide modelled estimates of the net ammonia air–sea flux in the Southern Bight of the North Sea. Because of larger air concentrations than in the Pacific, the general pattern was of net NH_3 deposition to the sea, though periods also occurred where the sea acted as a source. Overall, net NH_3 deposition to the area of the North Sea below 56° N was estimated to be 3.7 Gg N $year^{-1}$. This is approximately one quarter of an earlier estimate of Ottley and Harrison (1992), which assumed a zero NH_3 compensation point, and shows the importance of obtaining reliable measurements of sea water NH_4^+ concentrations.

Direct micrometeorological measurements of ammonia air–sea exchange are also extremely sparse. In addition to their laboratory experiments, Duyzer et al. (1993) measured several examples of ammonia concentration profiles at a site on the Dutch coast. Whilst these data represent only a few hours of measurements, they showed both emission and deposition fluxes of ammonia consis-

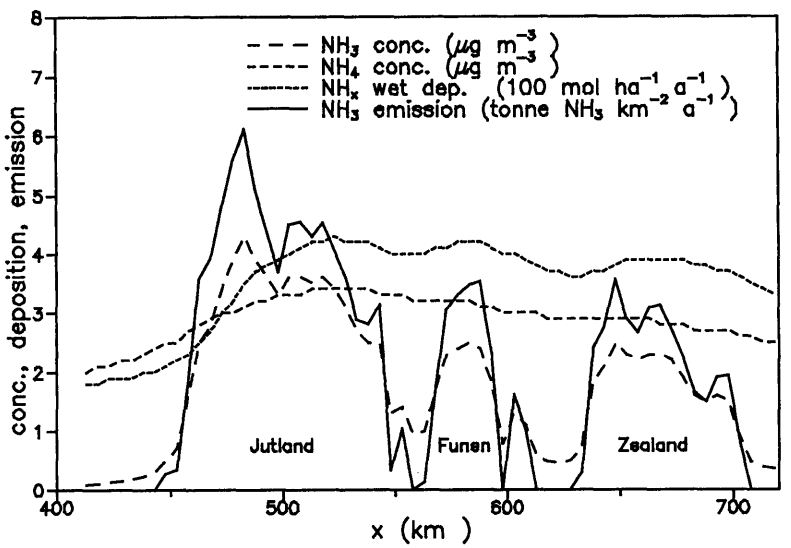

Fig. 1. Modelled annual average emission, concentration and deposition of NH_x over a W–E transect of land and sea areas in Denmark (UTM zone 32 coordinates). Computed using emissions on a $5 \times 5\ km^2$ grid (after Asman and van Jaarsveld, 1992).

tent with a sea water NH_3 compensation point of 1–2 $\mu g\ m^{-3}$. Such micrometeorological gradient measurements may, however, be complicated by spatial variability of sea water NH_4^+ concentrations (probably related to biological activity). This has been shown by measurements in Danish coastal waters and may be reflected in locally variable NH_3 fluxes. For example, sea-water NH_4^+ concentrations may decline with distance from coasts (Asman et al., unpublished data). Coupled to similar gradients in atmospheric NH_3, this clearly complicates the interpretation of flux measurements in coastal areas.

6. Co-deposition of NH_3 and SO_2

Much recent attention has been given to the possibility of enhanced dry deposition of NH_3 and SO_2 in the presence of both gases. This interaction, referred to as "co-deposition", was suggested as an explanation of measured forest throughfall fluxes where NH_4^+ and SO_4^{2-} were found in equivalent quantities (e.g., Van Breemen et al., 1982). It was hypothesized that acid-base neutralization by each of the gases provides an efficient sink for dry deposition on the leaf surfaces. While the term co-deposition is usually used to refer to simultaneous effects of SO_2 on NH_3 deposition and vice versa, one-way effects have also been suggested. For example, Brimblecombe (1978) suggested the presence of NH_3 in crop canopies as one of a number of possibilities to explain SO_2 deposition fluxes larger than could be accommodated by dissolution into pure dew. Further laboratory work has examined the NH_3–SO_2 interaction. In a wind tunnel study of deposition to water surfaces, Adema et al. (1986) found the presence of both NH_3 and SO_2 together allowed efficient deposition, whereas deposition of each gas singly was soon saturated by pH limitation to solubility. Van Hove et al. (1989) used controlled chamber measurements to examine deposition to leaf surfaces at different relative humidities. They observed enhanced leaf surface adsorption both at larger relative humidities and in the presence of both gases together. However, this adsorption was small compared with stomatal uptake, and was completely saturated in 5 to 10 h. The limited effect observed in their study may have been a consequence of the requirement to use large air concentrations not typical of field conditions (55–100 $\mu g\ NH_3\ m^{-3}$, 53–84 $\mu g\ SO_2\ m^{-3}$). It is therefore possible that these effects may be more important at smaller ambient concentrations. Even larger concentrations (1–100 ppm) were applied by Benner et al. (1992) who examined the reactions of SO_2, NH_3 and water vapour in laboratory reaction chambers. Though not representative of atmospheric concentrations, these authors found enhanced adsorption and formation of sulphate on reaction vessel walls at increased humidities (60 versus 5% RH) in the presence of both SO_2 and NH_3.

Simultaneous micrometeorological measurements of NH_3 and SO_2 fluxes have only been made recently. Nevertheless, results suggest that the co-deposition interaction is not simple. In particular, the suggestion of equivalent deposition of both gases (Van Breemen et al., 1982) may be challenged, since for much of the time NH_3 emission occurs. For example, Fowler et al. (1992) examined exchange over a previously grazed pasture with air concentrations of 2–6 $\mu g\ NH_3\ m^{-3}$ and 1–3 $\mu g\ SO_2\ m^{-3}$. During dry conditions, showing large NH_3 emission (100 ng $NH_3\ m^{-2}\ s^{-1}$) and surface concentrations (7 $\mu g\ NH_3\ m^{-3}$), rapid SO_2 deposition was observed with R_c close to zero. Following an increase in surface humidity and subsequent dewfall, NH_3 deposition occurred with reduced NH_3 surface concentrations, and this was accompanied by an increased R_c for SO_2 ($>200\ s\ m^{-1}$).

Further extensive micrometeorological results of Erisman and Wyers (1993) challenge simple interpretations of the co-deposition interaction. They support the hypothesis that the deposition enhancement for each gas depends on the relative air concentrations of NH_3 and SO_2 (Sutton, 1990). For example, in the presence of large concentrations of SO_2 they found enhanced NH_3 deposition, though this interaction was most significant in wet and high humidity conditions. They also noted that SO_2 and NH_3 were frequently not deposited in equivalent quantities (2 mol NH_3: 1 mol SO_2), but found enhanced NH_3 deposition with a mean ratio of 5.2 mol NH_3: 1 mol SO_2.

By contrast to these studies, recent measurements by Sutton et al. (1993a) suggest that in some situations over agricultural croplands "co-emission" may be a more appropriate term, as large concentrations of SO_2 may promote NH_3

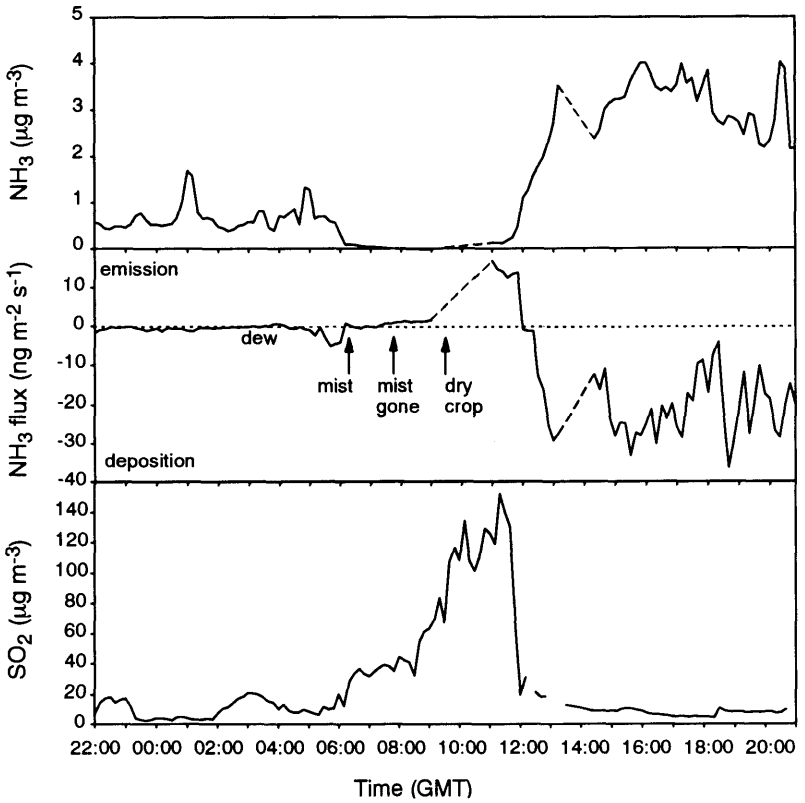

Fig. 2. Measurements of NH_3 (2 m), SO_2 (1 m) and NH_3 flux over a wheat canopy in C. England. Data are 10 minute means. Results for 19 May 1992; canopy 0.6 m tall (Sutton et al. 1993a). NH_3 measured using a continuous wet annular denuder described by Wyers et al. (1992a); SO_2 measured using a pulsed fluoresence monitor (Thermo Electron, Warrington, UK).

emission rather than enhancing deposition. Fig. 2 shows the time course of SO_2 and NH_3 concentrations for a day alongside the NH_3 flux over a wheat crop. It is possible from these measurements to examine the effect of SO_2 on the NH_3 flux, since very large SO_2 concentrations were experienced for several hours. Rather than SO_2 enhancing the NH_3 deposition rate, measurements during this period suggest NH_3 emission! It seems likely that reaction with SO_2 or associated acidic aerosol in the atmosphere depleted NH_3 concentrations, which dropped to near zero. Because of the existence of the compensation point over croplands (here about 1 μg NH_3 m^{-3}), NH_3 emission occurred during this period. With a subsequent reduction in SO_2, air concentrations of NH_3 were able to increase above the compensation point allowing NH_3 deposition. A possible criticism of these data is that there may be some storage error associated with the NH_3 flux due to rapidly changing air concentrations. However, for these gradient measurements made close to the ground (<2 m), the errors are trivial compared with the magnitude of the flux, with storage fluxes of typically 0–2 ng m^{-2} s^{-1} for this period (Sutton et al., 1993a). It is also possible that some of the NH_3 emission was due to evaporation of dew, though only small fluxes occurred during this period, with the largest fluxes from the dry canopy.

Each of these micrometeorological studies emphasize the complexity of the co-deposition interaction, with the degree of enhancement depending on environmental conditions (surface wetness, surface humidity), relative air concentra-

tions and ecosystem type. The last example of exchange NH_3 and SO_2 over a wheat field in particular demonstrates that the relative rates of atmospheric and leaf surface reaction may also be relevant. For co-deposition to be important, leaf surface neutralization must occur at rates similar to turbulent transfer. By contrast, reaction of the gases in the atmosphere need only occur slowly in order to deplete concentrations and therefore favour NH_3 emission.

7. Further uncertainties

A further uncertainty concerning NH_3 exchange is the possibility of reaction with acid gases or dissociation of aerosols on time-scales similar to turbulent exchange. Equilibria exist in the atmosphere between NH_3 and the acid gases HNO_3 and HCl, which react to form aerosol NH_4NO_3 and NH_4Cl. Emission of NH_3 may perturb this equilibria favouring aerosol production. Conversely, depletion of NH_3 associated with dry deposition may allow aerosol dissociation. If adjustment of the equilibrium is rapid (<2 min) vertical gradients in the first few metres (e.g., 0–2 m) above the ground will reflect reaction as well as exchange with the surface. This provides a potential restriction on micrometeorological measurements, as well as the possibility for altered exchange rates (e.g., Pandis and Seinfield, 1990).

Huebert et al. (1988) have provided evidence for these reactions having effects on HNO_3 gradients in the presence of very large NH_3 fluxes, however there is more debate about their importance at lower background concentrations (Harrison et al., 1989; Sutton et al., 1993d). In addition, while the small vapour pressure of ammonium sulphate aerosol prevents dissociation, emission of NH_3 may also be associated with rapid reaction with acid sulphate aerosol. For example, this could modify the emission fluxes of NH_3 from the wheat field discussed in the previous section (Fig. 2) providing a restriction to the interpretation of these data. At present further field measurements and application of chemical models are required to investigate these possibilities before account can be taken in long term deposition budgets.

Estimation of NH_3 exchange over semi-natural ecosystems may also be complicated by the existence of feed-backs limiting dry deposition (Sutton et al., 1992b). It was suggested earlier that the contrast in NH_3 exchange between croplands and semi-natural ecosystems is a response to the large N inputs received by croplands. It is possible, therefore, that intense long-term deposition of N species (both NH_x and NO_y) in polluted regions may alter the biology of semi-natural ecosystems resulting in an increased tendency to NH_3 emission. In this respect, both the studies in Table 3 which showed periods of emission, were made over heathlands in heavily NH_3 polluted areas of the Netherlands. Emission occurred during very dry, low humidity conditions, though the net flux was still toward deposition.

Finally the issue of complex terrain provides a limitation to estimating deposition fluxes to ecosystems. Current application of resistances and deposition velocities is one-dimensional and does not take account of the effects of horizontal inhomogeneity, such as forest edges, small strips of woodland and local sources. These effects are expected to be particularly important for gaseous NH_3 deposition to semi-natural ecosystems, both because of the predominance of ground level agricultural emissions, and because deposition is largely controlled by R_a and R_b, which are altered at boundaries in vegetation roughness.

8. Air concentrations of ammonia

Information on air concentrations of NH_3 is useful both for modelling deposition inputs using the inferential technique and for assessing the results of long range transport models (see below). Measurement of NH_3 with the sensitivity required for atmospheric monitoring is labour intensive, so measurements have only been made at a few sites, and examples are given in Table 5. The data show large regional differences as well as large local variability. This is emphasized by the results of Allen et al. (1988) who measured NH_3 at 19 sites in an area of S. E. England (Fig. 3). While most of their sites show concentrations in the range 2–4 $\mu g\ NH_3\ m^{-3}$, two sites, in livestock breeding areas, gave 20–30 $\mu g\ m^{-3}$. The general level of background concentrations can be reasonably predicted by large scale models. For example, Asman and van Jaarsveld (1992) estimate a concentration of 1–2 $\mu g\ NH_3\ m^{-3}$ for this area.

However, the small scale variability shown in

Table 5. *Examples of NH_3 concentrations and variability at European sites*

Location	Mean conc. NH_3 ($\mu g\ m^{-3}$)	Range of monthly means	Reference and method
S. Sweden, Ekeröd, (agricultural area)	0.29	0.03–0.68	Ferm (1983). Single-bore denuder.
spring, summer	0.23, 0.54		
autumn, winter	0.33, 0.05		
S. E. England, Essex			Allen et al. (1988).
mean 12 mid-range sites:	2.60	0.6–5.0	Filter pack.
mean 2 livestock farms:	24.3	3–66	
roof-top, rural area:	1.36	0.1–29.4 (daily means)	
S. Scotland. (agric. area)	1.14		Sutton (1990).
spring, summer	1.34, 1.62	0.05–3.13	Passive diffusion tubes.
autumn, winter	0.85, 0.77		
(forest area)	0.44		
spring, summer	0.53, 0.65	0.00–1.76	
autumn, winter	0.19, 0.38		
Netherlands. (agric. areas)			Erisman et al. (1986).
Bilthoven:			Single-bore denuder.
spring, summer	2.8, 3.9	1.5–5.4	
autumn, winter	3.2, 2.5		
Houtakker:			
spring, summer	19.4, 14.6	3.5–33.7	
autumn, winter	15.5, 14.6		
C. Netherlands. (forests in agricultural region)			Vermetten et al. (1990). Oxidation and analysis as NO_x.
Speuld:			30 m height.
spring, summer	5.5, 6.7	1.8–8.8	
autumn, winter	5.0, 4.5		
Kootwijk:			
spring, summer	7.9, 8.2	3.4–12.0	
autumn, winter	6.2, 5.4		
Denmark (forest areas):			Hovmand et al. (1993).
Frederiksborg (Zealand)	0.29	0.05–0.98	Filter pack. (Data for 1992;
Ulborg (Jutland) (agricultural areas)	0.55	0.15–1.04	ranges are unpublished results).
Keldsnor	1.05	0.18–1.97	
Tange	1.58	0.77–3.70	

Fig. 3 provides an uncertainty which is difficult to include in regional models. The existence of horizontal air concentration gradients has been examined on a local scale at the boundary of a heathland nature reserve and an ammonia source area (agricultural land) by Asman et al. (1989). Large gradients were found for the first 1–2 km from the source area, though at a greater distance NH_3 concentrations were more representative of a larger area. By contrast to NH_3, NH_4^+ aerosol is not emitted directly, being a reaction product of NH_3, so that its spatial distribution is much more uniform. For the same sites in Fig. 3, Allen et al. (1988) found the mean NH_4^+ concentration to be 4.04 $\mu g\ m^{-3}$, with a co-efficient of variation ($\sigma_{n-1}/\bar{x}$), between areas of 18%.

9. Approaches to mapping ammonia dry deposition

The two main approaches that have been used to describe regional dry deposition are the inferential technique and atmospheric transport models.

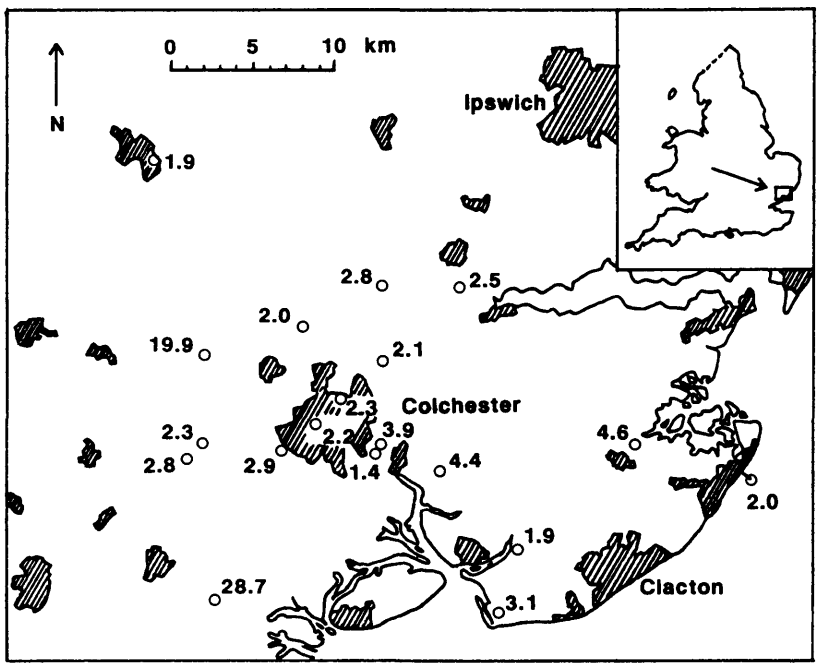

Fig. 3. NH_3 concentrations in an area of S. E. England. Means from 8 months monitoring ($\mu g\ NH_3\ m^{-3}$). Overall mean 4.9 $\mu g\ m^{-3}$, coefficient of variation 140%. Data taken from Allen et al. (1988).

These approaches are necessary because actual measurement of fluxes, such as by micrometeorological methods, is extremely labour intensive, and allows measurements at only a few sites for limited periods. An alternative approach is to map dry deposition based on forest throughfall measurements (Lövblad et al., 1992). However, while this technique may be useful for examining sulphur deposition, interactions of deposited N with plant canopies limit its use for estimating NH_3 and NH_4^+ deposition (Lövblad and Erisman, 1993).

9.1. Inferential technique

The simplest way to model long term dry deposition is to couple monitored air concentrations to representative deposition velocities. This approach is often termed the inferential technique, and may vary from a simple constant value of V_d, to calculation of time series of V_d from information on R_a, R_b, and R_c (e.g., Hicks et al., 1985). It may be used to estimate deposition to specific sites or applied with mapped concentration fields to estimate regional dry deposition patterns. General application of this method for ammonia is limited both by lack of air concentration information and by the bi-directional nature of NH_3 fluxes. As discussed above, NH_3 is only monitored at a few sites and spatially very variable, which prevents accurate regional mapping. Because of temporal variation in air concentrations and meteorological conditions it is also desirable to have time resolved V_d, such as every 1–3 h. However, again lack of NH_3 air concentration data limit this.

An advantage of the inferential technique is that it may be applied to estimate deposition to different ecosystems. Hence the problems of estimating deposition to semi-natural ecosystems and agricultural lands may be separated. Most interest concerns estimates to semi-natural ecosystems and forests. Over these surfaces the inferential technique may be applied by using typical values of R_c (Table 3). Other factors, such as co-deposition, are difficult to treat explicitly at present because of the uncertainty involved. However, the co-deposition effect may be included implicitly, as the presence of SO_2 may explain the rapid rates of NH_3 deposition observed. The presence of bi-directional exchange

of NH_3 over agricultural lands limits the use of the deposition velocity approach, and the factors controlling the compensation point are so complex as to prevent its inclusion in modelling. In particular, knowledge of the net annual exchange over agricultural croplands is at present so uncertain, that emission in the range 0–10 kg N ha^{-1} yr^{-1} is the current best estimate (Table 2). This variation is expected to include effects of climate as well as crop N dynamics, so that emission is largest in warmer and more continental regions. The compensation point is more straight forward to estimate over lakes and seas, so that, coupled with air concentrations and appropriate resistances, sound estimates of exchange should be possible.

9.2. *Long-range transport models*

Long range transport models for NH_3 consider the entire atmospheric cycle of NH_3 and NH_4^+, including emission, diffusion, reaction and deposition, so that a mass consistent budget is maintained. The complexity of each of these interacting processes necessarily means that the description of dry deposition is simpler than is possible in the inferential technique. However, the main aim of these models is to describe the regional, country to country, transport and deposition of pollutants.

In the first atmospheric transport models for NH_x (e.g., Asman and Janssen, 1987) constant values of V_d were used of 8 mm s^{-1} for NH_3 and 1 mm s^{-1} for NH_4^+. In newer models (e.g., TREND, Asman and van Jaarsveld, 1992; EMEP, Iversen et al., 1991; Sandnes and Styve, 1992) a diurnal variation in V_d is included, and in the EMEP model some dependence on the underlying surface. In the EMEP model V_d for NH_3 over land surfaces is set to 10 mm s^{-1} for daytime and 2.5 mm s^{-1} for night, while V_d NH_4^+ is set to a constant 1 mm s^{-1}. Over sea surfaces a latitude and seasonal dependence is used to calculate V_d with a maximum of 8 mm s^{-1}. In the TREND model only diurnal variation is treated, which takes into account differences in atmospheric stability and mixing (Monin-Obukhov length, friction velocity). R_c for NH_3 is set at 30 s m^{-1}, resulting in an average V_d of 12.2 mm s^{-1}. This value of R_c was chosen to reflect the average for all land surfaces including rapid deposition to unfertilized lands and emission from agricultural areas. For NH_4^+, an apparent R_c of 600 s m^{-1} was adopted giving an effective V_d of 1.4 mm s^{-1}.

While such models provide a useful description of ammonia budgets, estimation of dry deposition is nevertheless restricted by the mapping resolution used. For example, the EMEP model provides estimates on a 150×150 km^2 grid, though in the TREND model variable resolution emission inputs are possible, even down to point sources where emissions data are available. Only where a very detailed emissions grid (e.g., 5×5 km^2) is available can reasonable agreement be obtained between measured and modelled NH_3 concentrations, although much larger grids are sufficient for NH_4^+ aerosol. The use of regionally averaged V_d, however, provides a limitation to examining NH_3 dry deposition inputs to specific ecosystems. Some uncertainty may also result from the averaging of input variables in each grid to calculate average deposition. In this case the computed single point average dry deposition may be different to the actual area average for the grid. Unless there is little variation within the grid, very detailed emission information is again required to obtain good agreement (Asman and van Jaarsveld, 1992). For large parts of Europe the smallest emission grid is 75×75 km^2, so that more detailed emission estimates (e.g., 5×5 km^2) are required before the resolution of predicted deposition can be improved. A further limitation of these models is that regional differences in actual V_d for NH_3 are expected as a result of regional variation in land-use. For example, rapid deposition to the moorlands of northern Scotland may be contrasted with a very limited dry deposition in agricultural regions, such as the Netherlands. This effect may result in regional bias in these models, with, for example, dry deposition being underestimated in Scotland and over-estimated in the Netherlands.

9.3. *Model concentration and inferential technique combination*

An approach that has been suggested to provide increased spatial resolution in mapped deposition estimates is to combine the smoothed air concentration output from long range transport models (typically 50 to 150 km grid square) with calculated local deposition velocities (e.g., 5 km grid squares) to infer local dry deposition (e.g., Lövblad and Erisman, 1993). By using ecosystem specific surface roughness (z_o) and R_c it is possible to provide a detailed deposition field. The advan-

tage of this method is that it avoids the need for intensive monitoring which is not available for NH_3. However, the results will appear better than they really are, as local variability in emissions and air concentrations are not treated. In addition, the mass consistency built into transport models is not maintained. While this might not seem a requirement for applying deposition velocities, this results in a spatial bias in deposition. For example, in regions representing efficient NH_3 sinks, air concentrations are depleted, so that dry deposition is less. In this combination approach, the increased local V_d to such areas is combined with an non-depleted air concentration so that deposition is over-estimated.

9.4. Incorporation of land-use specific deposition velocities into long range transport models

A further way to improve estimates of deposition from long range transport models is to include a more detailed dependence of V_d on the land-use within grids. By incorporating this information directly in transport models, mass consistency is maintained and regional bias from use of constant V_d minimized. For example, inclusion of land-use on a 50×50 km grid would account for the above noted difference in $V_{d\,NH_3}$ between Scotland and the Netherlands. This approach might use V_d for unfertilized land calculated from an R_c of 5–30 s m^{-1}. The loss of NH_3 from grazed fields and crop fertilization is already treated as an emission term in models, while at other periods there is probably an approximate balance between emission and deposition over croplands. A zero V_d may therefore be appropriate for these surfaces. The ability to include these effects depends on the model concept, though for this purpose a nested grid model, allowing increased resolution in areas of interest and V_d to vary between grids, would be most suitable (e.g., ACDEP model, Asman et al., personal communication). In many models it will also be possible to include seasonal as well as diurnal variation in V_d.

In atmospheric transport models consisting of one vertical layer (e.g., Asman and Janssen, 1987; EMEP model) it is assumed that NH_3 emissions are instantaneously diluted over the whole mixing layer. In practice, emission plumes are diluted slowly, so that there is enhanced dry deposition near sources. Such models correct for this effect by including a "local deposition" term, which is added to the dry deposition within the grid square where emission occurs. For a V_d of 8 mm s^{-1} this fraction (α) was 24% of the emission (Janssen and Asman, 1988). However, α is expected to be much larger when the surface is very rough and dry deposition efficient, such as with forest. In this case, α may be up to 60% of the emitted NH_3. By contrast, α is much reduced over agricultural lands where there is little net dry deposition. It is clear that where models allow V_d to vary between grid elements, different values of α should also be calculated.

10. Conclusions

Measurements of ammonia exchange between the ground and the atmosphere show that this gas is both emitted from and deposited to land surfaces. Exchange is closely related to ecosystem N status and cycling, with grazed and fertilized ecosystems showing both emission and deposition, but semi-natural unfertilized ecosystems generally showing rapid deposition. Over agricultural croplands net emission occurs, typically 0–10 kg N ha^{-1} $year^{-1}$, while over intensively grazed pastures estimated emissions are in the range 1–40 kg N ha^{-1} $year^{-1}$. For each, the largest losses are associated with heavy N fertilization rates and warm climates. Over semi-natural ecosystems and forests, the deposition process may be described using deposition velocities (V_d) and canopy resistances (R_c). Typical values of R_c are in the range 5–30 s m^{-1}, though larger R_c may occur in very dry conditions, or when the ground is frozen. Other factors affecting NH_3 exchange rates include interactions with acid gases and feed-backs limiting deposition to semi-natural ecosystems, though the quantitative importance of these effects is uncertain. Over sea and lake surfaces both NH_3 emission and deposition are expected, though there is a shortage of measurements to quantify this at present.

A compensation point exists for NH_3 exchange, which is the air concentration in equilibrium with plant tissues (or sea/lake surface) NH_4^+. It would be attractive to incorporate this into the resistance approach, however, variability between ecosystems and with environmental conditions make such an approach extremely complex. Existing long term modelling of NH_3 exchange has used

the inferential technique and long range transport models. In the former, deposition is inferred from monitored air concentrations and calculated V_d. This has the advantage that it may be applied to specific ecosystems for comparison with ecological effects (e.g., critical loads), but is severely restricted by the lack of NH_3 monitoring data available. Long range transport models describe the whole cycle of atmospheric NH_x including emission, dispersion, transformation and deposition. The mass consistency of such an approach enables estimates of regional patterns of deposition to be made for both wet deposition and dry deposition of NH_3 and NH_4^+. Where large grid average emissions (e.g., $150 \times 150\ km^2$) are used, deposition estimates have little connection with local scale concentrations and deposition. However, use of local emission inputs (e.g., $5 \times 5\ km^2$) provides a reasonable correlation with actual air concentrations. Such models, are nevertheless, often implemented to use the same V_d for all land areas, though diurnal variation is incorporated in some models. This restricts the relevance of modelled dry deposition inputs to specific ecosystems, since exchange is known to vary with ecosystem type.

A possible improvement in modelling NH_3 dry deposition is to combine the concentration field output from transport models with local V_d estimated for specific ecosystems. However, the untreated local variability in air concentrations may be masked by application of variable V_d. In addition, lack of mass consistency is expected to bias estimated deposition in different areas, limiting the utility of this method. An alternative approach is to include land-use information within long range transport models and allow V_d to vary according to the land-use in grids. The ability to include this effect depends on the model concept, though this approach has the advantage that mass consistency is maintained and regional bias in deposition minimized.

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