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Ammonia and ammonium in the atmosphere: Present knowledge and recommendations for further research

Willem A.H. Asman

National Environmental Research Institute, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Abstract

The atmospheric behaviour of ammonia (NH_3) and ammonium (NH_4^+) including emission, surface exchange and wet deposition, is discussed. Some modelling aspects are also described. Although much more is known about the atmospheric behaviour of NH_3 and NH_4^+ aerosol than ten years ago, many essential aspects are still poorly known.

1. INTRODUCTION

Ammonia (NH_3) and ammonium (NH_4^+) are important atmospheric components, the former being the most abundant alkaline component in the atmosphere. A substantial part of the acid generated in the atmosphere by the oxidation of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) is neutralized by NH_3. As a result NH_4^+ is a major component of atmospheric aerosols and precipitation. NH_3 and NH_4^+ also play important roles in biological cycles. Nitrogen (N) can be a limiting factor for growth in oligotrophic ecosystems. In many ecosystems a substantial part of the N input is caused by the deposition of NH_3 and NH_4^+ from the atmosphere. In some areas these two components dominate the N input. Very high concentrations of NH_3 (annual average of about 75 $\mu g\ m^{-3}$) can cause direct damage to vegetation (van der Eerden, 1982). When NH_3 and NH_4^+ are deposited and enter the soil as NH_4^+, nitrification can occur by Nitrosomas and Nitrobacter leading to the overall reaction (Van Breemen et al., 1982): $NH_4^+ + 2\ O_2 \rightarrow 2\ H^+ + NO_3^- + H_2O$.

As a result, not only is acid formed by the oxidation, but also the acid formed in the atmosphere is no longer neutralized by NH_3. In this way NH_3 and NH_4^+ can cause acidification of the soil which may lead to adverse effects on vegetation. In forest ecosystems high inputs of NH_3 and NH_4^+ lead to the leaching of K^+, Mg^{2+} and Ca^{2+} from the soil, often resulting in increased ratios of NH_4^+ to K^+, Mg^{2+} and/or Al^{3+} to Ca^{2+} in the soil solution (Roelofs et al., 1985). As a result, a net flux of Mg^{2+}, Ca^{2+} and K^+ from the root system to the soil solution occurs. Moreover, coniferous trees can take up NH_4^+ by the needles and compensate for this by excreting K^+ and/or Mg^{2+}. This combination of effects results in K^+ and/or Mg^{2+} deficiencies, severe nitrogen stress and as a consequence premature shedding of needles.

Another effect is that large deposition fluxes of NH_3 and NH_4^+ cause nitrogen-poor species to disappear, because they are no longer able to compete with nitrophilous species. An example of this is found in the lowland heaths in The Netherlands. Bobbink et al. (1992) report that over 35% of the former heathland has now been replaced by grassland. (For an overview of effects see Sutton et al., 1993c). In central Europe about 65-80% of the threatened vascular plants are adapted to low nutrient conditions (Nilsson and Grennfelt, 1988). In this paper the symbol NH_x is used, standing for the sum of NH_3 and NH_4^+.

In large parts of Europe the critical load of nitrogen to ecosystems is exceeded. The critical load is defined by "a quantitative estimate of an exposure to one or more pollutants below which no harmful effects may occur" (Nilsson and Grennfelt, 1988). The critical load for forests and heathlands is 15-20 kg N ha^{-1} $year^{-1}$ and is even lower in some more sensitive regions (Hettelingh et al., 1991). Asman (1994a) presents a detailed review of NH_x. In this paper a short review is given of all processes involved as well as atmospheric transport models. Needs for further research are also discussed.

2. EMISSION

Most of the 4534 ktonne N $year^{-1}$ NH_3 emission in Europe (excl. the former USSR, Figure 1), is caused by agricultural activities (Buijsman et al., 1987; Asman, 1992). The emission from livestock is dominant, but that from the application of fertilizers is also important. The emission of NH_3 in Europe is comparable to that of nitrogen oxides (5094 ktonne N $year^{-1}$ excl. the former USSR; Pacyna et al., 1991). No significant emission to the atmosphere of either NH_4^+ or organic nitrogen components takes place. The NH_3 emission from livestock depends on many factors (Isermann, 1990): the nitrogen content of the food and the relative share of amino acids, the housing and storage system, the farmer's way of working, properties of the manure, fertilizer and the soil, the method of application of manure and fertilizer, the time between spreading and ploughing (for arable land), the duration of the grazing period and meteorological conditions. Information on global NH_3 emissions can be found in Schlesinger (1992). Emission factors for livestock categories representative for The Netherlands are presented are: 19.0, 4.4, 0.2, 10.0 and 1.4 kg N $animal^{-1}$ $year^{-1}$ for respectively cattle, pigs, poultry, horses and sheep (Asman, 1992). The emission factors for fertilizers vary from about 2 to 15% of the nitrogen content, depending on the type. The average emission factor for fertilizers in Europe is about 5% of the nitrogen content (Asman, 1992).

The emission per animal in the stable can vary up to a factor 10, even for the same stable type.

If the animals are grazing in the meadows, the manure is not stored, but deposited directly. After deposition it is therefore immediately exposed to loss processes other than volatilization of NH_3 to the atmosphere. These loss processes are: uptake by the grass, wetting by precipitation (leading to dilution and penetration of the soil with diluted manure) and nitrification. The NH_3 emission rate during the grazing period is for this reason less than it would be if the animals were in the stable, including the contribution during storage and subsequent spreading. The total emission from animals therefore depends on the fraction of the time they are in the meadows. This fraction is not known for all European countries. Van der Hoek (National Institute of Public Health and Environmental Protection, RIVM, pers.

comm., 1991) estimates that if the cows in The Netherlands were the stable all year round, the emission factor would be about 59 kg NH_3 animal^{-1} year^{-1}, but if all the cows were in the meadows during half a year the emission would then be 31 kg NH_3 animal^{-1} year^{-1}.

Table 1
NH_3 emission in European countries excluding the former USSR (ktonne N year^{-1}) (Asman 1992).

Category	Emission	%
Cattle	2391	53
Pigs	819	18
Poultry	282	6
Horses	57	1
Sheep	231	5
Fertilizer application	754	17
Total	4534	100

These facts illustrate that emission factors are not constant and that large geographical differences will occur. At the moment, however, insufficient information is available to calculate local emission factors for all areas and/or farm types in Europe. The uncertainty in the annually averaged European NH_3 emissions is at least 30-40%. The fact that geographical distributions of airborne NH_3 and NH_4^+ as well as wet deposition can be reproduced by atmospheric transport models using the current emission inventory, indicates that the current estimate and its geographical distribution is reasonable. It should be noticed here that even if all other conditions were constant, the annually averaged NH_3 emissions would show interannual variations that are caused by variations in meteorological conditions.

The emissions are often not equally distributed. The average emission density in The Netherlands is about 50 kg N ha^{-1} year^{-1}, but the highest emission density on a 5x5 km^2 grid element is over 200 kg N ha^{-1} year^{-1}. For a sparsely populated country like Sweden the emission density is much less (1 kg N ha^{-1} year^{-1}). The emission densities refer to the average emission for the whole territory of a country, i.e. not only agricultural areas. The NH_3 emission in Europe has doubled since 1950 (Asman et al., 1988).

The average NH_3 emission rate is likely to show a large diurnal variation with a peak during the early afternoon (Asman, 1992). This peak can be explained by a peak in turbulence and one in temperature, both favouring evaporation of NH_3. Moreover, many agricultural activities like manure spreading take place mainly during daytime, which also will lead to increased emissions during daytime. But the emission rate for any particular day can be quite different from this average pattern.

The NH_3 emission rate will also show a significant seasonal variation. This seasonal variation is caused by the spreading of manure and fertilizer in spring and autumn and by the practice of keeping cattle in the meadows in summertime in a large part of Europe. A seasonal variation of the NH_3 emission, derived from measurements of NH_4^+ in air and

precipitation, does not show such large variations. This could indicate that additional NH_3 sources exist, which are important during part of the season (Asman, 1992).

Apart from the major sources, minor sources of NH_3 emission are present. Unfortunately, much less is known about these sources. Buijsman et al. (1987) indicate that these emissions are about 10% of those from animal manure and fertilizer. They include emissions from undisturbed land and are not included in Table 1. There are recent indications that evaporation of NH_3 from agricultural crops may also be an important source during part of the season (Schjørring, 1991; Schjørring et al., 1992; see also section 3).

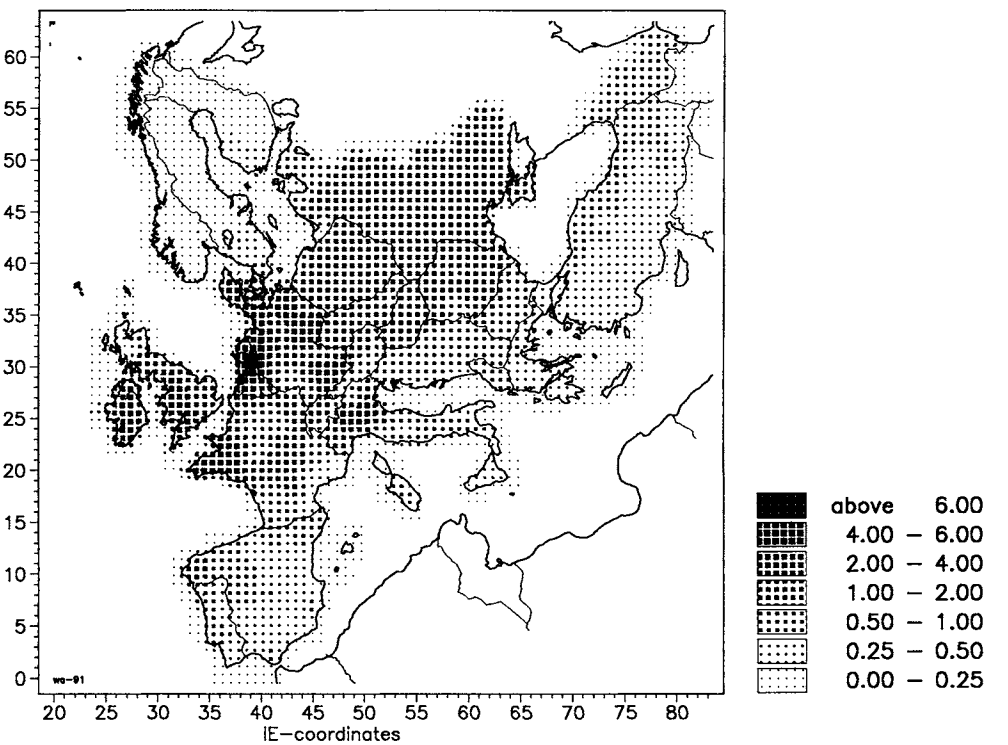

Figure 1. Emission density NH_3 emission on IE grid (75x75 km^2) in Europe without Russia (tonne NH_3 km^{-2} $year^{-1}$). (Reprinted from Asman and van der Hoek, submitted to Atmospheric Environment, 1994. Copyright 1994, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK).

There are also indications that under certain circumstances the sea can act as a source of NH_3 (Quinn, et al. 1988 a,b; Quinn et al., 1990; Asman et al., 1994a). The influence of emissions over the sea is not unimportant for land areas in those parts of Europe that have very low emission densities. Information on emission sources in cities is almost non-existent. Cass et al. (1982) give a list of possible NH_3 sources for California, which could also be very useful

for regions in other parts of the world and Lee et al. (1992) investigated emission from sewage treatment plants in the UK. In general, it can be concluded that there is a lack of knowledge on the geographical distribution of factors that influence the emissions, on emissions from vegetation, emissions over the sea and in cities, on diurnal and seasonal variations in the emission rate, and on what is called "minor sources", which may be very important in more remote areas, such as north Sweden. Moreover, emission inventories with a high spatial resolution (e.g. 5x5 km^{-2}) are needed, at least for areas where dry deposition of NH_3 is relatively important (for areas with a high or medium emission density, see section 6).

3. SURFACE EXCHANGE

An extensive overview of the surface exchange of NH_x from a biological point of view is given by Sutton (1993a,c). By surface exchange is meant here the exchange attributed to atmospheric turbulence. This includes both dry deposition to the surface as well as emission from the surface, but not wet deposition, which is treated in the next section. In contrast to wet deposition, dry deposition is very difficult to measure (Fowler and Duyzer, 1989; Davidson and Wu, 1990). This means that dry deposition is usually not monitored continuously. It is mostly computed from continuously monitored concentrations and meteorological parameters and dry deposition velocities or surface resistances measured by micrometeorological methods during short field campaigns.

The exchange velocity v_e is a measure of the exchange caused by turbulence. The simplest model to describe the surface exchange is the "big leaf model". In this model the transport from an arbitrary point in the atmosphere (reference height) to the surface takes place in three subsequent steps. The first step occurs in the turbulent layer from the reference height to a laminar boundary layer very close (~ 1 mm) to the surface. The second step is through the laminar boundary layer to the surface. The third step is the uptake by the surface. These steps can be represented by the resistances to transport. If emission occurs, the order of the resistances to be overcome is opposite to the one for deposition. The exchange velocity v_e can be expressed as:

$$v_e = \frac{1}{r_a + r_b + r_c} \qquad (1)$$

where: v_e is the exchange velocity (m s^{-1}), r_a is the aerodynamic resistance (s m^{-1}), r_b is the laminar boundary layer resistance (s m^{-1}) and r_c is the surface resistance (s m^{-1})

The "big leaf model" is a simple, but quite useful model. It is, however, possible to make more complicated models, e.g. by splitting resistances into those for transport into different vegetation surfaces. But then all these resistances have to be known. They usually are not because it difficult to infer them from measurements. Under the same meteorological conditions, the aerodynamic resistance is the same for all gases and in fact also for aerosols. Only for aerosols with radii > 5 μm does the additional contribution of gravitational settling become significant. The transport through the laminar boundary layer takes place for gases by molecular diffusion. This is a rather efficient process. Transport of particles is caused by

several processes, none of which are efficient for those with radii < 5 μm. The large difference in exchange/deposition velocity between NH_3 and particulate NH_4^+ is caused mainly by the difference in laminar boundary layer resistance. The surface resistance for uptake of NH_3 by the surface is often low for water-containing media. This is caused by the high solubility of NH_3 in water. The surface resistance for uptake/release of NH_3 is negligible for manure, freshwater and seawater. NH_3 is absorbed well by plants by transport through the stomata (Hutchinson et al., 1972; van Hove et al., 1987). The surface resistance of plants is, however, also low at night, indicating that absorption occurs on other plant surfaces as well (Sutton et al., 1992a). For vegetation r_c will be of the order of 0-100 s m^{-1}. In atmospheric transport models a value of 30 s m^{-1} is often used.

The surface resistance for NH_4^+, which is associated with particles with radii < 2 μm, is assumed to be zero, i.e. the surface is assumed to be a perfect sink. Due to the low diffusivity of the particles, transport through the stomata is negligible and they will be deposited mainly on the outer parts.

The average exchange velocity of NH_3 will be about 20 mm s^{-1} for moorland and grassland (Duyzer et al., 1987; Sutton et al., 1992a,b; Erisman and Wyers, 1994), about 30-40 mm s^{-1} for forest (Duyzer et al., 1992; Wyers et al., 1992; Andersen et al., 1993) and about 8 mm s^{-1} for (sea)water (Lindfors et al. 1991; Asman et al., 1994b). These differences in exchange velocity are caused mainly by differences in roughness for momentum between these surfaces.

The exchange/dry deposition velocity of particles is very difficult to measure, because it is usually rather low. In atmospheric transport models a dry deposition velocity of about 1 mm s^{-1} is used for particulate NH_4^+. Duyzer et al (1987) found a value of 1.8 mm s^{-1} for heather/purple moor grassland. Höfken et al (1983) derived indirectly a dry deposition velocity of 5-15 mm s^{-1} for a forest, which is rather high. Experiments (Larsen et al., 1994) have shown that seaspray does not enhance the dry deposition of particles, as has been suggested by Williams (1982). This means that the dry deposition velocity of particulate NH_4^+ at sea is less than 1 mm s^{-1}.

The flux to the surface is given by:

$$F = -v_e (c_a - c_s^*) \qquad (2)$$

where:

- F = Flux of the component (mol m^{-2} s^{-1}). In this case the flux is by definition negative when material leaves the atmosphere.
- c_a = The concentration of the component in the atmosphere at reference height (mol m^{-3}).
- c_s^* = The theoretical concentration of the component in air (mol m^{-3}), which would be in equilibrium with the concentration in the surface. For NH_3 c_s^* can be important. For particulate NH_4^+ this is not the case, because particles are not re-emitted and c_s^* can therefore be set to 0 in the equation. c_s^* is called "compensation point" and is for NH_4^+ a function of the pH, temperature, NH_4^+ concentration and ionic strength of the surface (Asman et al., 1994a).

The flux can be split up in the deposition flux $F_d = -v_e c_a$ and emission flux $F_e = v_e c_s^*$. The direction of the flux depends entirely on the concentration difference $(c_a - c_s^*)$.

The dry deposition velocity v_d (m s^{-1}) is defined as:

$$v_d \equiv F/c_a \quad (3)$$

In this equation v_d and c_a refer to the same reference height. By comparing (3) with (2) it can be seen that $v_d = v_e (1 - c_s^*/c_a)$ and that $v_d \approx v_e$ when $c_s^* \ll c_a$. It is common practice to measure F and c_a and to derive v_d from it. Then the surface resistance is often computed by estimating r_a and r_b from meteorological measurements and subtracting $r_a + r_b$ from $1/v_d$ (r_c' derived from measurements is equal to $1/v_d - r_a - r_b$). The computation of v_d is correct, but r_c' is equal only to r_c if $c^*_s = 0$. If $r_c = 0$, but $c^*_s \neq 0$, then r_c' would actually exceed 0. In practice though, this will pose problems only when $c^*_s/c_a > 0.2$; in other words, a value of r_c', which is significantly larger than 0 could not only indicate that the surface resistance is larger than 0, but also that the component could be present in the surface.

NH_3 is present in many surfaces. In manure or recently fertilized soil large concentrations occur and c_s^* will be much larger than c_a, resulting in a net emission. Also in the sea c_s^* is not zero and can sometimes be larger than c_a (Quinn et al., 1988a,b; Quinn et al., 1990; Asman et al., 1994a). In agricultural crops there NH_3 is also present in the surface (see Farquhar et al., 1983 and Schjørring, 1991 for a review) and emission can occur. NH_3 is an important intermediate in the photorespiratory N cycle, in the conversion of nitrate to amino acids, and in the breakdown of proteins. The compensation point may vary considerably during the life cycle of plants. It seems to be especially high during senescence (Harper et al., 1987; Parton et al., 1988; O'Deen, 1989; Morgan and Parton, 1989). High concentrations can also occur during grainfilling and after anthesis. Compensation points of 1-5 μg NH_3 m^{-3} in air are not uncommon for agricultural crops in northwestern Europe (Schjørring, 1991). Semi-natural ecosystems often show very low compensation points (0.01 μg NH_3 m^{-3} in air; Sutton et al., 1992a,b) Langford and Fehsenfeld (1992) found a somewhat higher compensation point of 0.1 μg NH_3 m^{-3} in air in a forest in Colorado. Quinn et al. (1990) found a surface concentration ranging from 0.05 - 0.36 μg NH_3 m^{-3} (average 0.17) for sea-water in the North Pacific. Asman et al. (1994a) found an average surface concentration for the North Sea of about 0.27 μg NH_3 m^{-3}. The compensation point in manure or intensively grazed pastures is often so high, that the airborne concentration has no influence on the flux.

Most of the NH_3 emission originates from low-level sources (ground-level, stables), which results in rather high concentrations close to the earth's surface. The concentration decreases rapidly with distance due to atmospheric mixing. The flux to the earth's surface close to the source is often high. In this way more than 20% of the NH_3 emission can be dry deposited within a few kilometres from the source (Asman and van Jaarsveld, 1992). This situation differs from that for SO_2, which originates mostly from high-level sources for which dry deposition cannot take place until atmospheric turbulence has mixed the emissions down to the surface - this takes a considerable distance to achieve.

A reasonable estimate of the exchange velocity of NH_3 can be found by assuming a surface roughness for momentum of 0.3 m and a surface resistance of 30 s m^{-1}. This would give a dry deposition velocity of 22 mm s^{-1} for a windspeed of 5 m s^{-1} and a surface concentration of 0. This would lead to a removal rate due to dry deposition of about 7% h^{-1} if the NH_3 is homogeneously mixed over a 1000 m high mixing layer. Under the same conditions, assuming a laminar boundary layer resistance of 600 s m^{-1} a removal rate of 0.6% h^{-1} can be found for NH_4^+.

It would be a good idea to model the surface exchange of NH_3 from the exchange velocity and a surface concentration. In this way both emission and dry deposition could be modelled. This is, however, possible only if the surface concentration were known.

The past ten years has given us much information on the exchange velocity of NH_3 on land. More information is needed on the exchange velocity at sea, the surface concentrations of NH_3 (vegetation, sea) and its temporal variation, and on the dry deposition velocity of particulate NH_4^+.

4. WET DEPOSITION

Components can be removed by different wet deposition processes. There exist removal processes within clouds (in-cloud scavenging) and removal processes below the cloud base (below-cloud scavenging), where components are removed by falling raindrops and snowflakes. Cloud- and precipitation water are usually acidic. Consequently, most of the NH_3 taken up by the drops reacts with H^+ to form NH_4^+. It is therefore possible to distinguish between the contribution of NH_3 and particulate NH_4^+ only if models are used. NH_3 is a highly soluble gas. Cloud droplets are so small (about 10 μm) that they take up NH_3 rapidly. Almost all NH_3 is found in the cloud droplets after the few seconds it takes to achieve equilibrium with NH_3 in the surrounding air. The NH_3 concentration in the interstitial air has then become very low. NH_4^+-containing aerosol acts as condensation nucleus, i.e. that water vapour condenses onto aerosols when the air becomes saturated with water vapour. In this way almost all NH_4^+ in clouds will become part of cloud droplets. NH_3 and NH_4^+ are transferred rapidly to the cloud droplets, but this does not necessarily lead to their removal from the atmosphere. The removal of NH_x from the atmosphere by in-cloud scavenging is therefore more determined by the dynamical and physical processes that result in precipitation formation. Raindrops of typically a radius 500 μm and are much larger than cloud drops. The time they need to fall from the cloud base to the surface is relatively short (a few minutes). Raindrops are so large that the transport of airborne NH_3 to the drops is not fast enough for equilibrium with the surrounding air to be reached before they strike the surface. Consequently they will take up NH_3 after collection, unless contact with the surrounding air is avoided. For this reason the NH_4^+ concentration in precipitation in agricultural areas is often too high. This is caused by uptake (dry deposition) of NH_3 to the wetted funnel of bulk collectors, which are not closed during dry periods. NH_4^+-containing aerosol is not captured very well by falling raindrops. Usually not enough information is known to model dynamical and physical processes in clouds in atmospheric transport models. Moreover, if such information were available it would often take too much cpu-time to perform the necessary calculations. For these reasons scavenging is often modelled by using so called "scavenging coefficients".

The change in airborne concentration due to scavenging is then described by:

$$c_a = c_{a,0}\, e^{-\lambda t} \qquad (4)$$

where $c_{a,0}$ is the concentration in the air at the onset of the precipitation (mol m^{-3}), λ is the scavenging coefficient (s^{-1}) and t=time (s).

Scavenging coefficients are used to describe the effect of in- and below-cloud scavenging separately, or sometimes an overall scavenging coefficient is used to describe the effect of both processes together. Scavenging coefficients apply to gases as well as aerosols.

A general function for the scavenging coefficient is:

$$\lambda = a I^{b} \quad (5)$$

where I is the precipitation rate (mm h^{-1}). The scavenging coefficient increases with precipitation rate. For the cloud volume (in-cloud scavenging) a is about $4x10^{-4}$ and b about 0.64 for both NH_3 and NH_4^+. For the below-cloud volume (below-cloud scavenging) a is about $9.9x10^{-5}$ and b about 0.62 for NH_3 (Asman, 1994b). The below-cloud scavenging coefficient of particulate NH_4^+ is not well known, but is less than 10^{-5} s^{-1} (Pruppacher and Klett, 1978).

Below-cloud scavenging occurs in the lowest few hundred metres of the atmosphere (the average cloud base height during precipitation in northwestern Europe is about 300-400 m), whereas in-cloud scavenging takes place in a much larger volume. Below-cloud scavenging is less efficient than in-cloud scavenging, both for NH_3 and NH_4^+ aerosol. Despite the much larger concentration of NH_3 near the surface in areas where net-emission is occurring (Erisman et al., 1988), in-cloud scavenging contributes the largest fraction to the NH_4^+ concentration in precipitation. Computations for Denmark show that the contributions of the different processes to the NH_4^+ concentration in precipitation is: in-cloud scavenging of NH_3 15%, in-cloud scavenging of NH_4^+ 77%, below-cloud scavenging of NH_3 6% and below-cloud scavenging of NH_4^+ 2% (Asman and Jensen, 1993).

During precipitation periods NH_3 and NH_4^+ are removed very efficiently (on the order of 75% h^{-1}) from the atmosphere, much more so than the removal due to dry deposition. But as precipitation occurs only 5-10% of the time in northwestern Europe, the total amount of NH_x wet deposited is not necessarily larger than the total amount dry deposited. Maps with the annual wet deposition of NH_x in Europe are presented in Buijsman and Erisman (1988) and Schaug et al. (1993).

The wet removal of NH_x in statistical transport models can be modelled well if information is known on precipitation statistics (length of dry and wet periods). In other transport models it is necessary to know the same type of information, i.e. the fraction of the area that is exposed to precipitation if the whole area is supposed to be wet when precipitation is collected in one sampler. Usually only part of an air mass is exposed to precipitation. In this part NH_x will be removed almost entirely after one hour of exposure. The concentration in the dry part will not change much and can be transported to other areas. More information on this type of precipitation statistics is needed.

5. REACTION

In northwestern Europe most NH_3 reacts with acid aerosols that contain sulphuric acid (H_2SO_4). This reaction has been investigated in the laboratory (Robbins and Cadle, 1958; Baldwin and Golden, 1979; Huntzicker et al., 1980; McMurry et al., 1983). The reaction proceeds rapidly at high relative humidity and will take only a few seconds. The reaction rate is limited by the rate at which NH_3 diffuses to the acidic particle. At low relative

humidity the reaction is slower because only 10-40% of the collisions of NH_3 with a particle lead to a reaction (Huntzicker et al. 1980; McMurry et al., 1983). The reaction proceeds faster when the particles involved are small, because the diffusion is then faster. The pseudo-first-order reaction rate decreases with the degree of neutralization of the particle. Moreover, the reactions by which H_2SO_4-containing aerosols are formed could also limit the uptake of NH_3 if all of the acid is already neutralized. Not enough is known at present about these possibilities to quantify the reaction rate that actually takes place. A minor part of NH_3 reacts with gaseous nitric acid (HNO_3) and gaseous hydrochloric, acid (HCl) to form particulate NH_4NO_3 or NH_4Cl, which is part of the aerosols that contain other components (Stelson et al., 1979; Stelson and Seinfeld, 1982a,b,c; Pio and Harrison, 1987; Allen et al., 1989). Unlike the reaction with H_2SO_4-containing aerosol, which is a one-way reaction, these reactions can occur in both directions:

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3 \qquad \text{and} \qquad NH_3 + HCl \rightleftharpoons NH_4Cl \tag{6}$$

The fact that these reactions are in equilibrium means that if the concentration of one or two of the gaseous components becomes very low the component in aerosol form will dissociate. NH_3 can also react with OH, O and $O(^1D)$. Levine et al. (1980) found that the reaction with OH was most important. When adopting a constant and relatively high OH-concentration of $4x10^6$ molecules cm^{-3} (Logan et al., 1981) a pseudo-first-order reaction rate of $5.4x10^{-7}$ s^{-1} for NH_3 is found. This value is much lower than the pseudo-first-order rate for the reaction with H_2SO_4-containing aerosol, HNO_3 and HCl (see below). These reactions are therefore usually neglected in regional transport models.

It is also possible to estimate the reaction rates from field measurements, but it is then necessary to make several assumptions, which may not always be valid. Lenhard and Gravenhorst (1980), Erisman et al. (1988) and Harrison and Kitto (1992) measured a pseudo-first order reaction rate of NH_3 between 10^{-4} and 10^{-6} s^{-1}. The reaction rate can also be estimated by changing the rate in atmospheric transport models until the best agreement is obtained with measured concentrations of NH_3 and NH_4^+ in air and NH_4 in precipitation. Asman and Janssen (1987) found in this way a pseudo-first-order reaction rate of $8x10^{-5}$ s^{-1}. A value of this order gives good results even for annual average concentrations on a global scale according to Dentener and Crutzen (1993), who include all relevant processes in a more sophisticated way. This reaction rate is about 30% h^{-1}, which is much greater than the oxidation rates of sulphur dioxide (SO_2; of the order 1% h^{-1}) or nitrogen dioxide (NO_2; of the order 4% h^{-1}). It should be noted that the rate derived in this way is an annual average value. The rate may well show diurnal and seasonal variations which may depend on the local meteorological and chemical conditions. As a consequence, even the annual average reaction rate may show geographical variations.

The dry deposition velocity of NH_3 is large compared to that of particulate NH_4^+. A high reaction rate, such as has been found, favours particulate NH_4^+ over NH_3. As a consequence, the dry deposition velocity of NH_x as a whole is lower than if the reaction rate were lower. The lower dry deposition velocity of NH_4^+ promotes also long-range transport of NH_x.

It is rather unsatisfactory that no more information is known on the reaction rate of NH_3. More information on the reaction mechanisms and the temporal and spatial variability of the reaction rate is needed.

6. MODELLING

A historical overview of the modelling of NH_x is given by Asman (1994a). Most of the NH_3 is emitted from a large number of scattered low-level sources (ground-level, stables). As a consequence the NH_3 concentration shows an extremely high spatial variability. Thousands of stations are needed to get a reliable average concentration for a country. This of course is not possible and that is why models are urgently needed in this case. But a good spatial resolution in a model can be achieved only if there is an emission inventory with a high spatial resolution is available. The results of a model can then be verified with measurements at a limited number of stations in areas with different emission densities (Asman and van Jaarsveld, 1992).

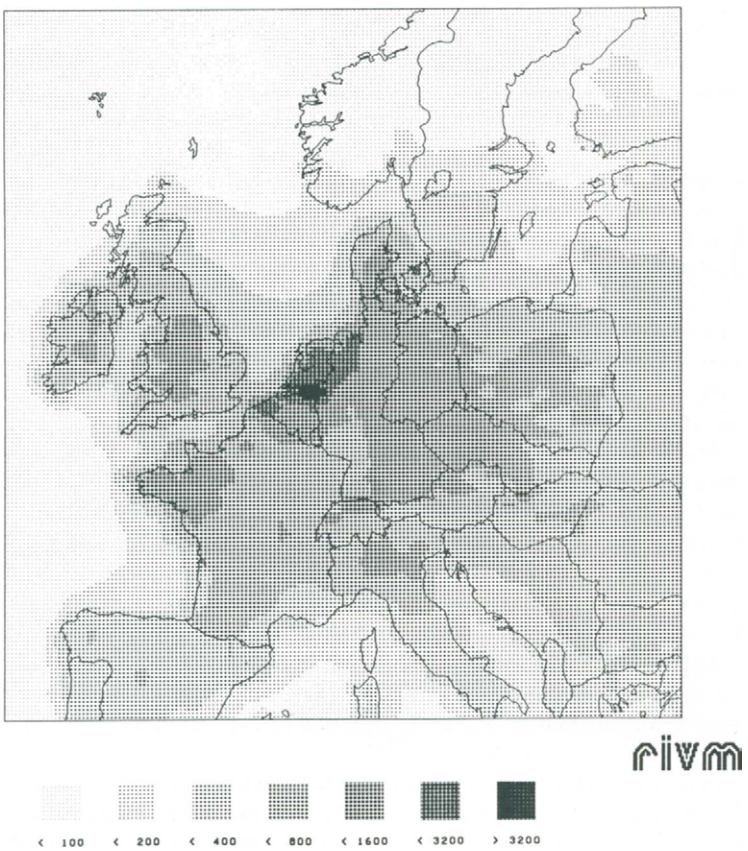

Figure 2. Modelled total deposition of NH_x in Europe (mol ha^{-1} $year^{-1}$); 1000 mol ha^{-1} a^{-1} = 14 kg N ha^{-1} $year^{-1}$. (Reprinted from Asman and van Jaarsveld, 1992. Copyright 1992, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK).

Models are also needed to calculate import/export balances for areas. The reaction product NH_4^+-containing aerosol is transported over long distances. This results in concentrations in air and precipitation (the contribution of NH_4^+-containing aerosol to precipitation is larger than that of NH_3) which do not show a high spatial variability. This means that a good impression of the concentration field can be obtained from measurements. Normally atmospheric transport models are developed either for short ranges (< 10 km) or for long ranges (500 - 2000 km). A transport model for NH_x should be capable of both, at least if realistic NH_3 concentrations and dry depositions are needed. The average value of the dry deposition of NH_3 in a grid element in a model (e.g. a 150x150 km^{-2} area in the EMEP model) is not incorrect. It is, however, not representative of the deposition of a nature area that covers only part of the grid element. Some attempts have been made to correct the EMEP model outputs for differences in deposition to ecosystems within the 150x150 km^2 grid element used (Hettelingh et al., 1991). This is done by redistributing the deposition within the grid element in such a way that the total deposition to the whole grid element does not change. In this way mass is conserved (see also discussions in Sutton et al., 1993b), but due to the local character of NH_3, this approach is unlikely to give correct results near important emission areas, i.e. those areas where dry deposition of NH_3 is larger than wet deposition of NH_x.

Models can also be used to compute the import or export of NH_x to or from countries. It is almost impossible to infer such transboundary fluxes from measurement data. They can also be used to estimate the contribution of in- and below-cloud scavenging of NH_3 and NH_4^+ aerosol to the wet deposition of NH_x. This cannot be derived from measurements. Moreover, models can be used to estimate historical or future depositions by using emissions representative for these periods. In this case one should check that the emissions of other components like SO_2, NO_x and hydrocarbons have not changed so much that the reaction rate of NH_3 to particulate NH_4^+ is altered considerably (Asman et al., 1988). Most models are able to reproduce measured concentrations and depositions reasonably well, except for NH_3, which can be handled by only a few models and then not even very well.

Figure 2 shows the total NH_x deposition in Europe (sum of wet and dry deposition of NH_3 and NH_4^+). Model results show that in northwestern Europe 44% of the emitted NH_3 is dry deposited as NH_3, 6% is wet deposited as the contribution of NH_3 to the wet deposition of NH_x, 14% is dry deposited as NH_4^+ aerosol and 36% is wet deposited as the contribution of NH_4^+ aerosol to the wet deposition of NH_x (Asman and van Jaarsveld, 1992).

There is a need for atmospheric transport models for NH_x that have a spatial resolution that is sufficient to calculate realistic NH_3 concentrations. Such models should also be able to take into account that the dry deposition velocity differs from one surface to another, as otherwise e.g. no realistic dry deposition of NH_3 to forests can be calculated.

7. CONCLUSIONS

The most important conclusion which can be drawn from the information presented here is that deposition of NH_x takes place mainly in two forms, namely dry deposition of NH_3 close to the source and wet deposition of NH_x at larger distances from the source contributed by the NH_4^+ aerosol. This indicates that the possibility exists of reducing the deposition of NH_x to nature areas close to those with a high NH_3 emission density. This can be done to

some extent by selectively reducing NH_3 emissions close to these areas. This strategy does not work at long distances from important source areas, however. In these areas deposition of NH_x can be reduced only by cutting down all the emissions in a much larger area. A policy to reduce the deposition of NH_x should also take into account the contribution of NO_x and its reaction products to the total nitrogen deposition, as well as protection of other parts of the environment (soil, ground water) from emissions when atmospheric emissions are reduced. There exist good technical possibilities for reducing NH_3 emissions. A reduction can be obtained by altering the factors which lead to high emissions:

a. Reducing the nitrogen content of the animal food in such a way that optimal nutrition is obtained for the stage of development of the animal under consideration. Nowadays the same food is often used for animals of almost all ages.
b. Adding some amino acids to the animal food for non-ruminants (pigs etc.), so that no overdoses of other amino acids are needed.
c. Prescribing housing and storage systems which give the lowest losses. There exist considerable differences in the emission rate per animal for different housing and storage systems.
d. Ploughing the manure under as soon as possible after spreading or injecting the manure in the ground in the case of grassland.
f. Spreading of manure and application of fertilizers under meteorological conditions (low temperatures, just prior to the onset of precipitation) which favour low emissions.

Apart from these measures, emissions of NH_3 can be reduced by taking more technical measures, such as biofiltring of the air coming from stables. These measures are more expensive, however. But it is most important that the nitrogen cycle for a country, region or farm be as balanced as possible. This means a sharply reduced import of nitrogen-containing animal food, limitations to the number of animals ha^{-1} and in general, eliminating waste of such a precious element as nitrogen, leading to fine-tuning of the nitrogen supply to match the nitrogen demand of the crops.

The conversion of nitrogen from manure and fertilizers into plant products is rather efficient (70±10%; Isermann, 1993). This efficiency can be increased by the adding of amino acids to the food, as mentioned earlier. The fact that humans in western Europe eat (animal) protein far in excess of their requirements than they need, leads also to a high production of animal proteins with all the ill consequences for the environment. Reduction of the share of animal proteins in the human diet could therefore also have beneficial environmental consequences. Although much more is known about the atmospheric behaviour of NH_x than 10 years ago, far from all essential information is known. Good progress has been made on the exchange velocity of NH_3 and also on the development of methods for continuously measuring NH_3. No models are, however, presently available that give good results for dry deposition of NH_3 to forests. Further information is needed on:

a. Geographical differences in emission factors.
b. Diurnal and seasonal variation in the NH_3 emission.
c. Emission inventories for some countries with a high or medium emission density are needed.
d. Emissions from plants and cities and other "minor sources".
e. Exchange velocity of NH_3 at sea.
f. Surface concentration of NH_3 for vegetation and seawater and its temporal variation.

g. The dry deposition velocity of particulate NH_4^+.
h. Precipitation statistics needed in atmospheric transport models.
i. The reaction of NH_3 to NH_4^+: mechanisms, rate and its temporal and spatial variation.

Moreover, atmospheric transport models for NH_x should be developed that have a spatial resolution that is sufficient to calculate realistic NH_3 concentrations and the possibility of having different dry deposition velocities for different surfaces.

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