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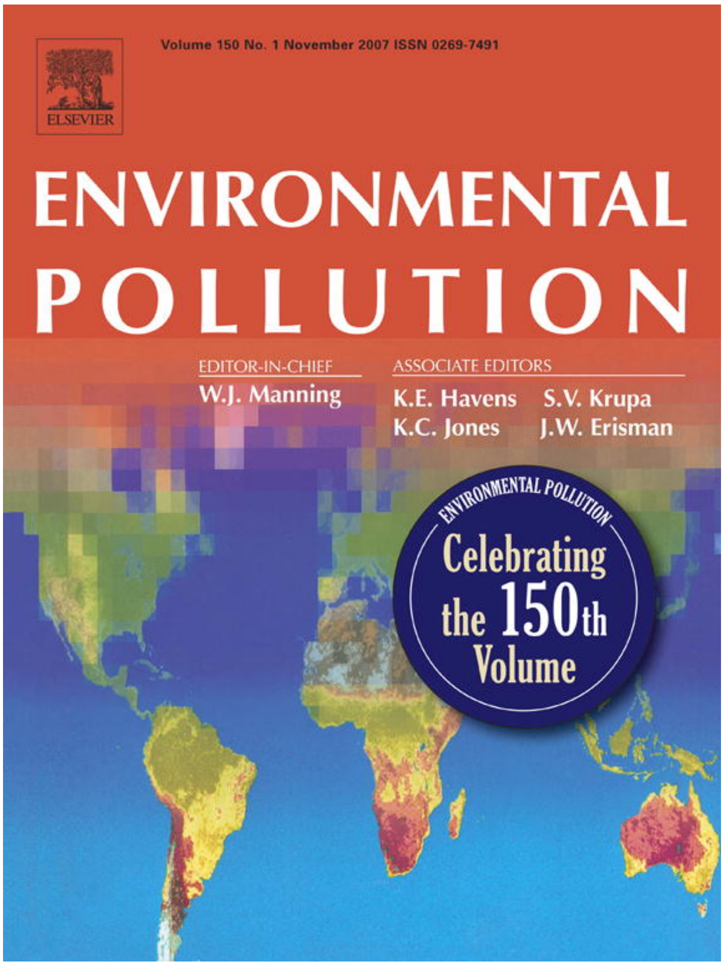
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Review

Reduced nitrogen in ecology and the environment

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Half of industrial ammonia production is eventually lost to the global environment with significant effects.

Abstract

Since the beginning of the 19th century humans have increasingly fixed atmospheric nitrogen as ammonia to be used as fertilizer. The fertilizers are necessary to create amino acids and carbohydrates in plants to feed animals and humans. The efficiency with which the fertilizers eventually reach humans is very small: 5–15%, with much of the remainder lost to the environment. The global industrial production of ammonia amounts to 117 Mton NH_3-N year^{-1} (for 2004). By comparison, we calculate that anthropogenic emissions of NH_3 to the atmosphere over the lifecycle of industrial NH_3 in agriculture are 45.3 Mton NH_3-N year^{-1}, about half the industrial production. Once emitted ammonia has a central role in many environmental issues. We expect an increase in fertilizer use through increasing demands for food and biofuels as population increases. Therefore, management of ammonia or abatement is necessary.

Keywords: Reduced nitrogen; Emission; Nitrogen cycle; Ammonia; Effects; Abatement

1. Introduction

In 1827 the German professor Von Liebig (1827) reported that about 27 kg/ha free fertilizer was obtained by wet deposition from the atmosphere, which was regarded as so much that additional fertilizer was not necessary to grow plants. Since that time a debate was started on the validity of this number and the start of fertilizer and environmental ammonia research was a fact. Von Liebig appeared to be wrong at that time, overestimating the atmospheric deposition as a result of measurement errors. However, in large industrialized parts of the world the current deposition far exceeds this number as the result of increased intensities of agriculture, industrial processes and traffic. The central role of ammonia in environmental problems is now becoming more widely recognized.

Nitrogen, present in amino acids, proteins, and DNA, is necessary for life. While there is an abundance of nitrogen in nature, almost all is in an unreactive form (gaseous nitrogen, N_2) that is not usable by most organisms. In the absence of human intervention, the supply of reactive nitrogen in the environment is not sufficient to sustain the current abundance of human life. Thus humans learned in the early 20th century how to convert gaseous N_2 into forms that could sustain food production. Over 40% of the world's population is here today because of that capability.

There are two major problems with nitrogen: some regions of the world do not have enough reactive nitrogen to sustain human life, resulting in hunger and malnutrition, while other regions have too much nitrogen (mainly due to the burning of fossil fuel and inefficient incorporation of nitrogen into food products) resulting in a large number of major human health and ecological effects (e.g. Vitousek et al., 1997; Mansfield et al., 1998; Langan, 1999; Erisman et al., 1998a,b; Cowling et al., 2001; Galloway et al., 2003). The rate of

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change of the problem is tremendous, probably greater than that for any other major ecological problem. For example, half of the synthetic nitrogen fertilizer ever used on Earth has been used in just the last 15–20 years. Opportunities to reduce these problems are plentiful. A prerequisite to reduce these problems is the development of a sound scientific base on which to begin to discuss policy options.

The least known part of the nitrogen cycle is the reduced nitrogen form. Reduced nitrogen, such as ammonia, ammonium and amines, is essential in food production, in ecology and also in the environment. Emissions of ammonia to the atmosphere can contribute to particulate matter formation affecting human health, contributing to eutrophication and acidification of aquatic and terrestrial ecosystems after deposition and to nitrous oxide formation, contributing to the greenhouse effect. The scientific basis for reduced nitrogen in ecology and in the environment needs to be strengthened. We here summarize the issues associated with increased ammonia emissions and discuss the need and possibilities for abatement measures.

2. The nitrogen cycle

Nitrogen is an important element – the most abundant constituent of the atmosphere. It is also one of the essential elements for the growth of plants and animals. Reduced nitrogen has a crucial role in ecology and in the environment. It is useful to look at the reactions of elements in the form of a closed cycle. Such a cycle is often termed a biogeochemical cycle because chemistry, biology, and geology all provide important inputs. Cycling of elements is often governed by kinetics and may involve the input of energy, so that chemical equilibrium states are not attained. The ultimate source of energy for driving energetically uphill reactions is the sun. The Earth's surface receives an average radiation input of 100–300 W/m^2/day, depending on latitude. Some of this is captured by photosynthesis, and used to produce high-energy content molecules, such as oxygen.

2.1. Ammonia in the early atmosphere

Before the Earth's crust was formed, we speak of the First Atmosphere, comprising probably entirely of H_2 and He. These gases are relatively rare on Earth compared to other places in the universe and were probably lost to space early in Earth's history because Earth's gravity was not strong enough to hold lighter gases. Once the core differentiated the heavier gases could be retained and the Second Atmosphere was formed mainly by volcanic out gassing. Gases produced were probably similar to those created by modern volcanoes (H_2O, CO_2, SO_2, CO, S_2, Cl_2, N_2, and H_2), NH_3 (ammonia) and CH_4 (methane). No free O_2 existed at this time (not found in volcanic gases). As the Earth cooled, H_2O produced by out gassing could exist as liquid in the Early Archean, allowing oceans to form. Today, the atmosphere is ~21% free oxygen. Produced O_2 levels by breakup of water molecules by ultraviolet were approx. 1–2% current levels. At these levels Ozone (O_3) can form to shield Earth's surface from UV. Photosynthesis combined $CO_2 + H_2O +$ sunlight into the formation of organic compounds and O_2, produced by cyanobacteria, and eventually higher plants – supplied the rest of O_2 to the atmosphere. The amount of O_2 in the atmosphere has increased with time. Chemical building blocks of life could not have been formed in the presence of atmospheric oxygen. Chemical reactions that yield amino acids are inhibited by the presence of very small amounts of oxygen. Oxygen prevents growth of the most primitive living bacteria such as photosynthetic bacteria, methane-producing bacteria, and bacteria that derive energy from fermentation. Since today's most primitive life forms are anaerobic, the first forms of cellular life probably had similar metabolisms. Today these *anaerobic* life forms are restricted to anoxic (low oxygen) habitats such as swamps, ponds, and lagoons.

Whereas the (Second) atmosphere was composed of high concentrations of ammonia, the current atmosphere has a high oxidizing capacity. We learn from the past that volcanic emissions are an important source for ammonia in the atmosphere.

Nowadays the atmosphere contains mostly elemental dinitrogen, along with other trace gases (ammonia, nitric oxide, nitrogen dioxide, and nitrous oxide). Aquatic systems primarily contain soluble forms of nitrogen, such as nitrate and ammonia/ammonium ion, as well as biological nitrogen found in proteins, DNA, RNA, and other compounds that make up living systems. Since lone pairs of electrons on nitrogen are usually basic, ammonia coexists in both the protonated and de-protonated forms near neutral pH. The most important aspect of the environmental nitrogen cycle is the dynamic exchange of species that occurs between the atmosphere and the surface landmasses and oceans. Fig. 1 shows the nitrogen cycle in its most elemental form.

Living systems are essential for maintaining the balance between nitrogen's reduced and oxidized forms. They play an important role in providing reduced nitrogen compounds for the global cycle, by de-nitrification processes (the conversion of nitrate to N_2 and N_2O), biosynthesis (making amino acids, DNA, and RNA), and *nitrogen fixation* (reduction of N_2 to NH_3 by bacteria in root nodules). Nearly all organisms can use ammonia for biosynthesis (*ammonia assimilation*). Ammonia is also a major metabolic end product, as in the bacterial decomposition of dead organisms (*ammonification*). Mammals eliminate ammonia; however, the liver transforms it into the less toxic compound urea before excreting it. Urea, which is prepared industrially at high pressure from the reaction between ammonia and carbon dioxide, is hydrolysed readily in the environment into ammonia and carbon dioxide, which accounts for ammonia emissions from animal feedlots.

Although reduced nitrogen is preferred for biosynthetic reactions, plants have also learnt to capture the nitrogen they need by *assimilatory nitrate reduction.* This was an evolutionary necessity because nitrate is the dominant soluble form of nitrogen in aerated soils. Formation of reduced nitrogen compounds is energetically uphill. Besides plant use of nitrate, its

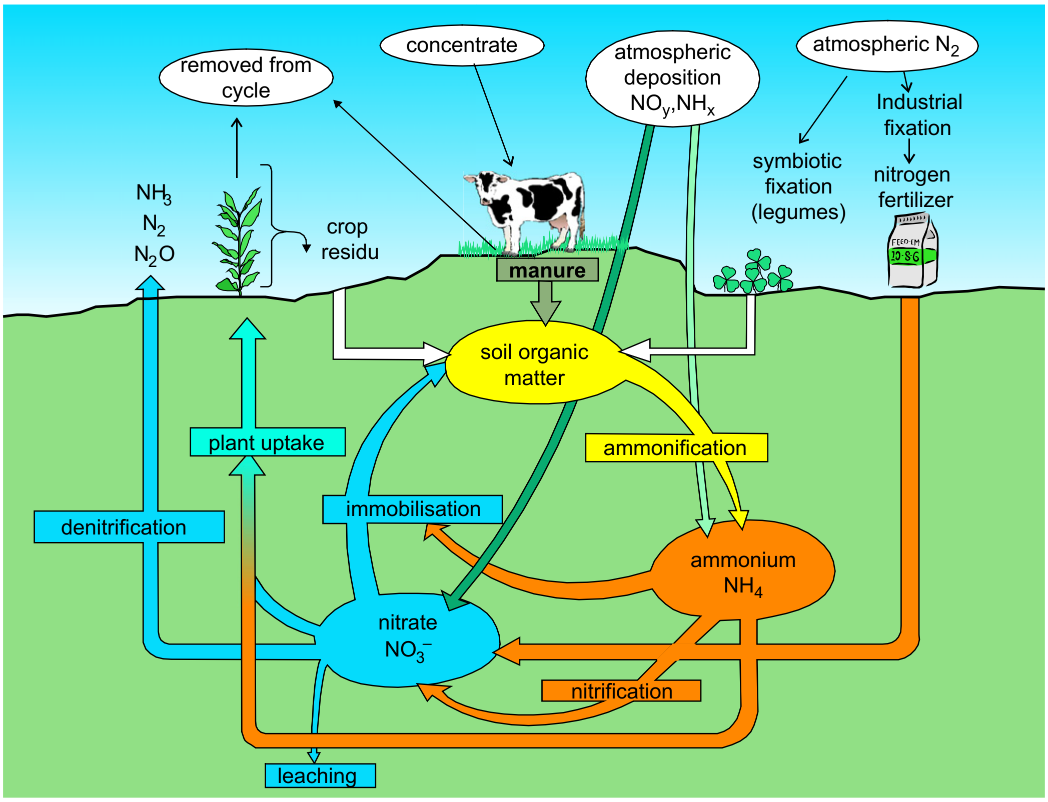

Fig. 1. The most important elements of the nitrogen cycle.

reduction also occurs by bacterial action in oxygen-free soil and sediment environments. For example, nitrogen-fixing bacteria create their own oxygen-free environment in aerated soils by forming nodules on the roots of legumes, such as clover and alfalfa.

3. Human creation of reduced nitrogen

If we go back into history, man has searched ways for centuries to increase the production of food by conserving the nutrients or, in a later stage transporting them from concentrated areas (Guano), creating and adding them (Smil, 2001; Erisman, 2000; Sutton et al., submitted for publication). Since it was discovered that ammonia is the key element for plant growth by Von Liebig (1827), gradually fertilization became more specific and adapted to plant needs. Fritz Haber and Carl Bosch developed the first high pressure industrial process, which fixes nitrogen to ammonia on a large scale in the Haber–Bosch process. The second largest bulk industrial nitrogen feedstock, nitric acid, lies at the other extreme of the redox series. Ammonia is oxidized to produce nitric acid in another reaction, called the Oswald process after its discoverer Wilhelm Oswald. It makes good chemical sense that the principal industrial nitrogen compounds lie at opposite ends of the redox series. With these reagents it is ultimately possible to synthesize any desired intermediate oxidation state of nitrogen.

Ammonia is one of the major gaseous products of global chemical industry, the main use of which is in fertilizer production for food and fibre production. The rates of global ammonia manufacture since 1900 are shown in Fig. 2. After the invention and implementation of the Haber–Bosch process to produce NH_3 from N_2 and hydrogen, the production increased rapidly (Smil, 2001). Overall, 80% of the chemical production of NH_3 is used to produce fertilizer in the forms of ammonium nitrate, urea, calcium nitrate, ammonium bicarbonate and several varieties NPK (mixtures of nitrogen, potassium, and phosphorus). The remainder is used in a wide range of processes, including the production of caprolactam (basis for nylon) and acrylonitril for acryl fibers, for explosives and as a refrigerator replacement for chlorofluorocarbons. Furthermore, for the future use of ammonia in combination with fuel cells as an emission-free transportation fuel is suggested as a serious option (Christensen et al., 2006). The economic value of NH_3 is enormous, both industrially as well as for fertilizers. The investment for farmers in fertilizer is very profitable. An investment of $120 per ha has been estimated to yield a net return of $925, a factor of 7 (Yara, The Fertilizer Handbook). Because of the high-energy requirements of the Haber–Bosch process, the ammonia (and fertilizer) price is strongly coupled to the natural gas and thus the oil price. Fig. 2 shows the NH_3 price since 1970. The average price is about $100/ton NH_3. Annually this yields about 11 billion $. In addition, it is substantial that new ammonia production capacity will come on line in the next 4 years (Gosnell, 2006). This will drive ammonia prices down towards their historic average of about $150/ton NH_3, which will keep the fertilizer price at low levels.

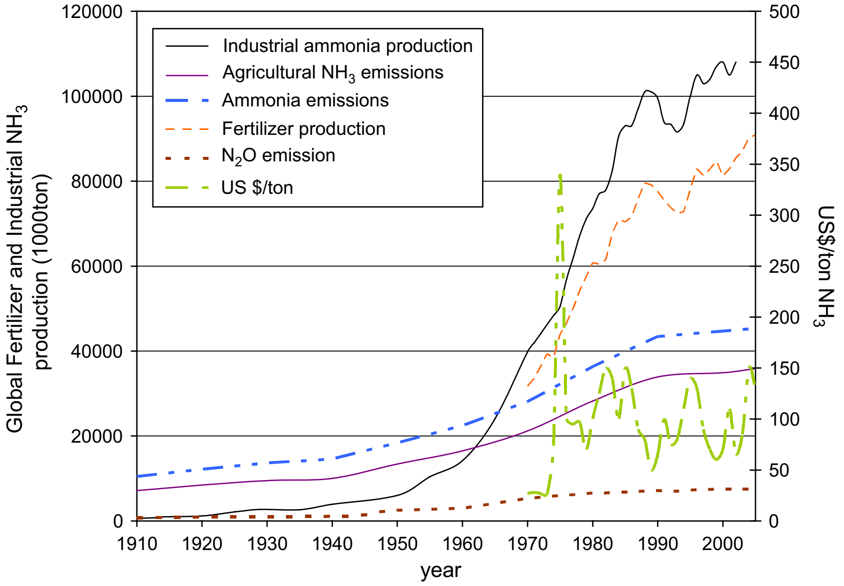

Fig. 2. Global industrial production of NH_3, including the amount which is used for fertilizer production (http://minerals.usgs.gov/index.html) and the NH_3 and N_2O emissions to the atmosphere since 1900 (Olivier et al., 1998); Historical US Gulf Coast NH_3 Prices (Gosnell, 2006).

4. Emissions of ammonia to the atmosphere

It is well-known that ammonia can be emitted into the atmosphere from animal manure and was already demonstrated by Way (1856). These emissions, which are an indirect result of the ammonia fertilizer application in the nitrogen cycle, can be large in areas with intensive livestock breeding. In nitrogen poor areas crop production might benefit from the ammonia emissions, however, in other areas, where the optimum nitrogen is exceeded, the emissions might directly or indirectly lead to environmental impacts. Ammonia is a key gas in atmospheric chemistry, air–surface exchange processes and environmental effects. Direct losses of ammonia during industrial production are relatively small because of the stringent safety regulations and the economic value of ammonia. Fertilizers are also optimized for crop production and losses should be minimized when applied in the field. The best performance is for ammonium nitrate fertilizer, with typical NH_3 losses after field application of 1–2%. However, some fertilizers are less efficient, with NH_3 emissions from ammonium sulphate being typically 5–15%, while those from urea are typically 10–20% (EEA, 2002). Nevertheless, environmental losses are unavoidable even where fertilizers with low NH_3 emissions are used, because the nitrogen use efficiency (NUE) is much less than 100%, which means that within the cascade nitrogen losses will occur (Galloway et al., 2003). The first 100 kg/ha of fertilizer N is three times as effective for crop growth as the second hundred (Socolow, 1999). The world average fertilizer use in 2001 was 90 kg/ha of agricultural land, ranging from 0.2 (Congo) to 562 kg/ha in Ireland (Earth Trends Data Tables), with a strong difference between excess areas and areas where there is shortage. Only about 10–30% of the nitrogen is used in end products (Smil, 2001), the rest is returned to the atmosphere as N_2 or lost to the environment. The efficiency with which the fertilizers eventually reach humans is therefore very small: 14% for vegetarians and only 4% for omnivores (Smil, 2001, 2002).

There are several studies that provide an overview of ammonia emissions to the environment, such as Buijsman et al. (1987), Erisman (2000), EEA (2002), and Battye et al. (2003). The global NH_3 emission is estimated to be 53.7 Tg N of which 10.7 Tg is of natural origin about 65% is from agriculture and 16% is natural (Table 1). The data from different sources in Table 1 reflect the variation in estimates. Currently volcanic emissions are not included in the emission inventories and might contribute to the global balance. Other natural emissions come from large colonies of seals or penguins. These emissions are not relevant on a global scale, but might contribute locally to nitrogen enrichment and

Table 1
Global atmospheric sources of ammonia (Asman et al., 1998; Bouwman et al., 1997)

Source	Ammonia emission (10^6 ton N year^{-1})	%
Dairy cattle	4.3	8
Non-dairy cattle	8.6	16
Buffaloes	1.2	2
Pigs	3.4	6
Poultry	1.9	4
Sheep/goats	1.5	3
Other animals	0.7	1
Subtotal domestic animals	*21.6*	*40*
Fertilizers	9.0	17
Agricultural crops	3.6	7
Biomass burning	4.1	8
Seas	8.2	15
Other sources	7.2	13
Total	53.7	100

because they are isolated hotspots, and are ideal to study the ammonia emissions and transport. Most important sources are animal excreta (21.6 Tg N), fertilizer use (9 Tg N), and biomass burning (5.9 Tg N). Other sources include biomass burning, coal burning, cars equipped with a three-way catalyst, pets, household application of ammonia, vegetation, industry (Erisman, 2000). Although these sources only comprise a minor part of the emissions, they might be relevant locally. This holds for the urban emissions of cars, pets and industries, affecting the local chemical climate and forming ammonium aerosols (e.g. Ansari and Pandis, 1998). The main agricultural sources are also given in Table 1. Animal husbandry is the most important source. The emissions result from housing systems and application of manure in the field. Especially in systems where there is a high protein diet for the animals the emissions are high. The driving forces for emissions of reduced forms of nitrogen are the protein uptake of animals, housing systems, the ammonium content in manure, climate (wind, precipitation, and relative humidity) and soil properties. We are currently able to model the emissions on an annual basis, provided the agricultural data are available (Dämmgen and Hutchings, in press). Inventories of agricultural emissions are becoming available for different areas of Europe and North America. The spatial scale needs to be refined in order to meet the requirements of dispersion models to assess the transport and deposition. Furthermore, the temporal variation in emission factors can be very large both from day to day as well as during the seasons. When using emission inventories the temporal variation needs to be addressed separately (Hellsten et al., submitted for publication). There is still a big gap in the Nitrogen balance at different scales. Much farm-level research has shown that the gap between input and output of N can be up to 40% (Oenema et al., 2007). This is called the Enigma of the Nitrogen balance by Allison (1955). It is suspected that denitrification is the most important process that can explain the gap, even though organic nitrogen, emissions of amines and ammonia emissions, might play a role. It demonstrates that the ammonia emissions are uncertain and there is a need to estimate the emissions as the result of a Nitrogen balance model (Dämmgen and Hutchings, in press).

During the last 30 years a strong increase in fertilizer use and in livestock breeding in China, South Korea, India, and Eastern and Central parts of the USA has resulted in increased ammonia emissions. The emissions are mainly concentrated in the Northern Hemisphere (e.g. Dentener and Crutzen, 1994). Even within these areas there is a large variation in the spatial distribution of the emissions. Locally, the emission of ammonia can be much higher, e.g. in the Netherlands the emission is on the average 30 kg/ha, similar to that estimated for the Eastern part of North Carolina (Cowling et al., 1998). Fig. 2 shows the trend in global emission estimates based on statistics and emission factors. The data up to 1995 stem from Olivier et al. (1998), Asman et al. (1998), and Bouwman et al. (1997) (see also http://www.mnp.nl/edgar/model/v32ft2000edgar/). The FAO scenarios on global agricultural activities (http://www.fao.org/docrep/W5146E/w5146e00.htm#Contents) were taken to translate the trend up to 1995 into data for 2005. The agricultural ammonia emission becomes a smaller part of the fertilizer use in time. A non-linear relationship is expected, but with a gradual increase because of intensification and decreasing efficiency. Fig. 2 shows that by combining different statistical data from different sources questions can be raised about the inconsistency of the results. The data suggest that until 1965 ammonia emissions were higher than the industrial ammonia production and the ratio reduced to almost 50% in 2005. This reflects the uncertainty in the ammonia emissions, but also the uncertainty in the cascade of nitrogen that starts with the fertilizer application. Ammonia emissions are based on animal numbers, excretion factors and emission factors. The emission factors are constant in time and the linear relation between animal numbers therefore determines the trend in ammonia emissions. One might expect that the emission factors increase with higher inputs of nitrogen as fertilizer, because the nitrogen use efficiency decreases with higher inputs. Furthermore, there is a retention in the emissions related to fertilizer application, because the reactive nitrogen first takes part in the cascade on farm-level (see Fig. 1) and then cascades through the environment, where source and sink terms are highly variable in time and space. This leaves the amount of reactive nitrogen that is eventually lost to the environment as the result of fertilizer highly uncertain. This means that the emission factors in the past are either overestimated, or current emissions are underestimated.

5. Atmospheric transport and atmosphere–biosphere exchange

Recently several papers giving overviews of the atmosphere–biosphere interactions have been published (e.g. Krupa, 2003; Erisman et al., 2005a,b; Sutton et al., submitted for publication, 2007; Bleeker et al., 2007). Here only the most important issues are discussed. The relevance for reduced nitrogen in the atmosphere is:

- it provides the only atmospheric base, neutralizing toxic acids;
- it forms particulate matter (ammonium nitrate and sulphates), which has a relevance in human health reduction and plays a role in climate cooling; and
- it provides a means to transport reactive nitrogen to other areas.

Reduced nitrogen is very reactive in the different environments and therefore its lifetime is limited. However, when converted into ammonium the atmospheric lifetime could be extended up to 1 week. There are some environments, however, that make that ammonia can exist. Pratt (2006) measured high ammonia concentrations in caves. Within caves the air stream is limited and no dilution takes place. In some caves bats' droppings emit ammonia and also goats' and/or sheep dung emits ammonia and measured concentrations range from 2 to 2000 ppm (Pratt, 2006). The animals and other organisms living in the caves are gradually adapted to the high concentrations (Pratt, 2006). There is evidence that other animals and even humans will not expose themselves to these concentrations.

Bleeker et al. (2007) provide next to country-specific case studies, also an overview of the European situation with respect to the link between emissions of NH_3 and the modelled and measured concentration/deposition of reduced nitrogen. Responses in ambient concentration and deposition to change in NH_3 emission are seasonally well understood. Where substantial reductions have been made the benefits are clear at the decreased scale in aerosol and precipitation composition. Short-term changes in emissions are not well quantified, nor in the emissions, nor in the responses in concentrations and deposition. The long-term measurements for reduced nitrogen follow the emission trend. The extended data sets made it clear that following emission trends by means of measurements can only adequately be done when long-term measurements are available. Current measurements make it possible to evaluate policy progress on ammonia emission abatement. This is especially true for the situation in Denmark and the Netherlands, where the NH_3 ammonia reduction is followed by the monitoring results from the national monitoring networks. However, this is only possible since both these networks were designed to follow the expected changes in emissions, based on extensive pre-studies used for developing the measuring networks. The UK also performed such a pre-study for developing their national monitoring network. Clear trends from this network could not be found, but this is mainly due to only small changes in emission levels. Another case in the UK, where it was possible to detect changing emissions in measured concentrations of NH_3, was related to a study following an event of Foot and Mouth Disease in different regions in the UK (Sutton et al., 2004). Also here a modelling pre-study was used for designing the layout of the measurement network, in order to effectively detect the expected emission changes within different regions. In previous years the instrumentation (i.e. models and monitoring equipment) to evaluate the link between ammonia emission and the concentration and/or deposition of reduced nitrogen has improved, making an explanation for the so-called ‘ammonia gap’ possible (Erisman et al., 1998a,b; Erisman and Monteny, 1998; Van Jaarsveld et al., 2000). Originally the ammonia gap existed in two parts: (i) an absolute difference between measurements and concentrations based on modelling; and (ii) a difference in trend between measurements and modelled data. There have been several studies done focussing on explaining these two gaps (see Bleeker et al., 2007). There is no difference between the measured and modelled trend. By extending the monitoring period, improving the emission estimates and taking the meteorological conditions into account this is solved (Van Jaarsveld et al., 2000). However, the absolute systematic difference is still in the order of 30%. The explanation of the difference can be by two factors, probably contributing both: (i) underestimation of certain emissions; and (ii) parameterisation (overestimating) of the dry deposition in agricultural areas. Apart from the Netherlands and Denmark, where emissions decreased by about 30%, in most countries where monitoring takes place the concentrations did not change much (UK and Switzerland). In these countries the emission reductions were only very limited. However, no systematic gap such as in the Netherlands is signalled (UK, Denmark, and Switzerland). For the whole of Europe it is questionable if the decrease in emissions that took place in the early nineties as the result of the poor economics in the Eastern part of Europe can be detected. This is troubled by the fact that at the same time the SO_2 emissions strongly decreased affecting the lifetime and transport distance of ammonia. Models and input data are still inadequate to show these changes.

Interactions between SO_2, NO_X and NH_X have created a change in the main form of NH_X from $(NH_4)_2SO_4$ to NH_4NO_3. Increases in ambient NH_3 and NH_4 in ppt in remote areas of Europe require quantitative explanation and more detailed measurements to demonstrate the cause (Fowler et al., 2005). The EMEP monitoring sites that have been in place are not aimed to detect ammonia from agriculture and therefore the signal is not detectable. Furthermore, for the new EMEP monitoring strategy there is lack of implementation especially in Eastern Europe. It is therefore concluded that the evaluation of the absolute emissions in Europe and the changes therein is difficult because of lack of monitoring data covering the whole of Europe.

The role of cuticular resistances in NH_3 fluxes to semi-natural vegetation has been shown to be the most important in regulating the deposition flux (Sutton et al., submitted for publication, 2007). This resistance determines which NH_3 concentration and which responses have key implications and more work is necessary. Dry deposition of NH_3 close to major sources contributes typically 4–10% of the total emissions within 500 m of the source, in North America and in Europe. There are differences in aerosol neutralization in Europe and North America leading to different appreciations of the role of NH_3 in atmospheric chemistry. In Europe sulphate is mostly neutralized by ammonia and nitrate equilibrium changes, influencing the transport distance of ammonium. In North America aerosol is generally not neutralized. The neutralization factor of aerosol and precipitation might be a good indicator for the relevance and emissions of NH_3.

Within the quantification of the atmosphere–biosphere interactions of ammonia models have been developed these past years. The uncertainty in these models is dominated by the cuticle (and water layer) uptake and release of ammonia and the apoplast concentrations regulating the exchange between the atmosphere and stomata (Nemitz et al., 2000).

Previous concept of the oceans everywhere being a source of ammonia to the atmosphere is probably wrong. Measurements have shown that low latitude (warm) waters can be regarded as sources, whereas high latitude (cold) waters as sinks. This is explained by strong temperature dependence of the Henry's Law constant for ammonia and leads to a significant reduction in the global marine flux of ammonia to the atmosphere. Uncertainty in the size and sign of the spatial distribution of the air–sea flux of ammonia is mainly due to the poorly defined concentration driving force (difference between normalized air and water concentrations). There are few reliable measurements. This situation is in urgent need of attention if we are to understand the role that ammonia from the oceans plays in particle formation and in controlling the pH of rain and particles in the remote marine atmosphere.

Methylamines are stronger bases than ammonia and so, although their fluxes across the air—sea interface are only a few percent of those for ammonia, they can constitute 10—20% of the atmospheric basicity in offshore marine environments. There is, however, little research on methylamines and it is advised to foster more research in this area.

6. Effects

Even though the environmental consequences of fertilizers are well recognized when it comes to nitrate pollution in groundwater (e.g. Van Grinsven et al., 2006), eutrophication of coastal waters and resulting hypoxia (e.g. Rabalais and Turner, 2001) and the N_2O emissions contributing to climate change (e.g. Mosier et al., 1998), the effects of NH_3 emissions are less well recognized and often relegated to consideration as a ‘‘local problem’’ in highly intensive livestock breeding areas such as the Netherlands, Italy, parts of Germany and Denmark. However, during the last 30 years a strong increase in fertilizer use and in livestock breeding in China, South Korea, India, and Eastern and Central parts of the USA has resulted in increased emissions.

Van Breemen et al. (1982) showed how atmospheric ammonia deposition contributes to soil acidification in natural areas where the deposition was up to 120 kg N/ha. Ammonia deposition has a direct relation to eutrophication of surface waters and natural areas, threatening biodiversity (Phoenix et al., 2006). The combination of acidification and eutrophication leads to base cation leaching from the soil and an imbalance in nutrient status (N-excess; De Vries et al., submitted for publication). Furthermore, through nitrification in the soil, soil acidification occurs and nitrate is leached leading to groundwater pollution. During the process of nitrification NO and N_2O can be formed. The fertilization of the system with ammonia leads to changes in the carbon sequestration affecting climate change (e.g. Nadelhoffer et al., 1999). Direct exposure of humans or vegetation to high levels of NH_3 can lead to toxification and serious effects. The ‘burning’ of vegetation has been observed near to intensive livestock breeding farms (e.g. Erisman, 2000). It has been demonstrated in the lab that plants can grow solemnly on atmospheric NH_3. Root uptake of NO_3 is lowered during these exposures. Very high exposure of atmospheric NH_3 can be dealt with by the plant until toxicity is reached. There are no indications of toxicity at long-term exposure with low to moderate concentrations of NH_3 (Castro et al., in press). NH_4 is relevant in the exposure of humans through its contribution to particulate matter concentrations (e.g. Ansari and Pandis, 1998; Aneja et al., 2006), which also contribute to the cooling through the (in)direct aerosol effect (Liao et al., 2004). Finally, deposition of NH_3 and NH_4^+ particles can lead to acidification damaging the cultural heritage and can contribute to reduced visibility at scenic vistas and airports. One ammonia molecule does not cause one specific effect, but can lead to a cascade of effects (Galloway et al., 2003; Erisman et al., 2005a,b).

Biodiversity decreases when nitrogen increases as has been shown in the literature (e.g. Dise and Stevens, 2005; Klimek et al., 2007; Goulding et al., 1998; Bobbink, 2004; Stevens et al., 2004) and illustrated in Fig. 3. More recently data have become available showing that reduced nitrogen inputs are more effective in decreasing biodiversity than is oxidized nitrogen (Haddad et al., 2000; Pitcairn et al., 2003; Paulissen et al., 2004; NEGTAP, 2001). Reduced nitrogen is more readily available, stimulating growth. Furthermore, increased levels of ammonium can be toxic to plants (e.g. Castro et al., in press). Sub-arctic vegetation is very sensitive to a high nitrogen load. Reduced N is much more harmful for (semi)natural vegetation

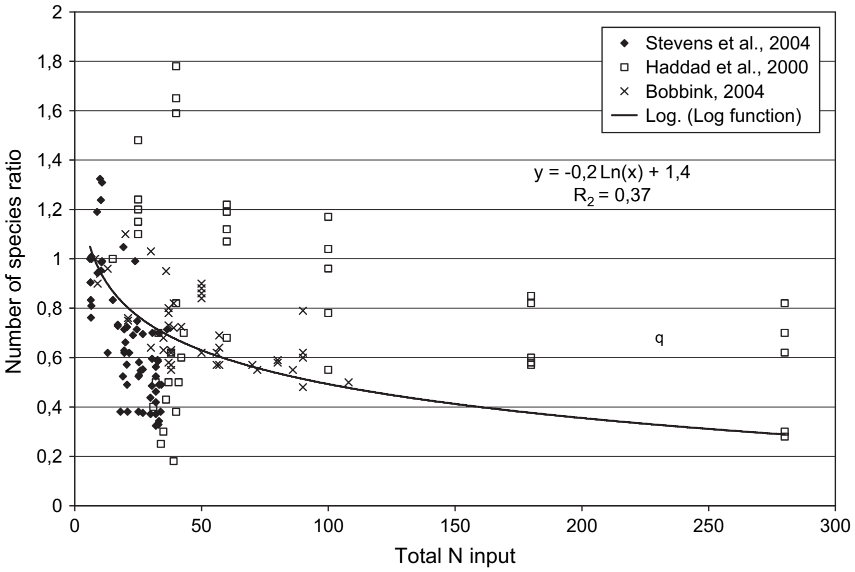

Fig. 3. Number of species in terrestrial systems decreasing with increasing nitrogen input (kg/ha). Shown is the ratio of the number of species at increased levels compared to those at low level N. Data sources: Dise and Stevens (2005), Goulding et al. (1998), Bobbink (2004), Stevens et al. (2004), and Haddad et al. (2000).

compared to oxidized N, not only in abiotic heath lands, grasslands and soft-water lakes but also in ecosystems which are not sensitive to acidification like mires, fens and coastal waters (De Vries et al., submitted for publication). There are also observations of severe effects of reduced N on vascular plants and lichens in the Mediterranean region. Bog species are during relatively short-term exposure much more sensitive to NH_3 compared to NH_4. It is known that harmful effect of NH_4 occurs after long-term exposure, after saturation of the bog with N.

However, this does not imply that oxidized N is less important, because further in the cascade the original form of reactive nitrogen is not important (Erisman et al., 2005a,b).

Another reason for an increasing concern is the successful policy to reduce sulfur emissions, which has not led to a similar decrease in deposition of sulfur in remote (sensitive) areas of Europe. This is caused by the change in the ratio of SO_2 and NH_3 emissions, which has been the case these past years in Europe and USA. NH_3 emission increased or remained fairly constant and SO_2 decreased affecting aerosol formation and gas deposition inducing important non-linearity's in sulfur and oxidized nitrogen emission–deposition relationships and changing deposition patterns (Fowler et al., 2005).

These effects, and uncertainties associated with these effects, all emphasize the need for more complete scientific understanding of both the beneficial and detrimental effects and the intended and unintended consequences of continuously increasing circulation of ammonia in commerce and in the atmosphere and the biosphere of the Earth. The agricultural area used for food production is not expected to increase to a large degree, in contrast to the world population which will increase for the next few decades, and the per-capita resource consumption which will increase for decades to come requiring more food and energy (including biomass). Biomass will have a large contribution to the world energy production. About 70% of the targets of 20% greenhouse gas emission reduction and a 20% share of sustainable energy in 2020 in Europe will be from biomass. Furthermore, 10% of the biofuels in the EU and in the US will have to be of biological origin. In order to enhance the necessary food and biomass production the productivity of land must increase by intensifying production, changing to more productive crops and by increased application of fertilizers. Because of the strong link between food production and NH_3 emissions, it is expected that NH_3 emissions will increase in coming years in several areas of the world.

7. Conclusions

Currently the ammonia wasted to the atmosphere is about half of the global industrial production of ammonia. The estimates of global, regional and local ammonia emissions have high uncertainties which increase with the smaller scale. Emission factors depend on the type of source, climate and environmental conditions, and farmer management. The emission factors probably changed over time because of increased nitrogen fertilization rates. There is a need for a new thorough updating of the N cycle of at least the anthropogenic part, improving data on fluxes, reservoirs and also on uncertainties. This should be done for regions and globally.

Effects of ammonia to the environment are clearly visible and widespread. Ammonia has therefore become a continental issue, which needs international agreements on abatement. Because of the cascade of reduced nitrogen through the agricultural system and the environment an integral approach is needed, focussed on the reduction of reactive nitrogen formation and/or on the reduction of concentrating nitrogen in intensive agricultural areas.

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