

## A global budget for atmospheric NH<sub>3</sub>

WILLIAM H. SCHLESINGER & ANNE E. HARTLEY

*Departments of Botany and Geology, Duke University, Durham, N.C. 27706, USA*

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**Abstract.** We provide an assessment of the global sources of NH<sub>3</sub> in the atmosphere, which indicates an annual flux of about 75 Tg of N as NH<sub>3</sub>. The emissions from land are dominated by the release of NH<sub>3</sub> during the hydrolysis of urea from the urine of domestic animals (32 TgN/yr) and by emanations from soils in unmanaged ecosystems (10 TgN/yr) and from fertilized agricultural soils (9 TgN/yr). Emissions from the sea surface may approach 13 TgN/yr. The total annual source of NH<sub>3</sub> is in reasonable agreement with estimates of global NH<sub>4</sub><sup>+</sup> deposition from the atmosphere, the major fate of atmospheric NH<sub>3</sub>. As an alkaline atmospheric species, NH<sub>3</sub> emitted to the atmosphere each year can neutralize only about 32% of the annual production of H<sup>+</sup> in the atmosphere from natural and anthropogenic sources.

### Introduction

Atmospheric ammonia is derived from a variety of sources, of which emanations from decomposing excrement, inadvertent losses during the production and application of fertilizer, and losses from burning biomass are thought to be the most important. Despite its relatively short mean residence time in the atmosphere, about 10 days, NH<sub>3</sub> is the third most abundant nitrogen gas (after N<sub>2</sub> and N<sub>2</sub>O). In the remote marine atmosphere, concentrations average about 0.06 μg/m<sup>3</sup> (Ayers and Gras 1980), whereas downwind of strong point-sources, values of 300 μg/m<sup>3</sup> are not uncommon (e.g. Harper et al. 1983).

Ammonia is the only natural alkaline gas in the atmosphere. It is important in the neutralization of anthropogenic acidity in the atmosphere by reactions such as:



Thus, the major sink for atmospheric NH<sub>3</sub> is conversion to NH<sub>4</sub><sup>+</sup>, which is

deposited in dry particles or as a dissolved ion in precipitation. In many areas, the release of ammonia to the atmosphere has increased in recent years (Asman et al. 1988), and ammonium contributes to excessive atmospheric deposition of nitrogen in areas that are downwind of major sources (Draaijers et al. 1989). Many of these areas show forest decline, perhaps due to nitrogen saturation (Nihlgard 1985; Aber et al. 1989) and increasing soil acidity resulting from nitrification of  $\text{NH}_4$  inputs (Van Breeman et al. 1982; Verstraten et al. 1990).

Despite its importance to biogeochemistry, the atmospheric budget for  $\text{NH}_3$ , particularly estimates of source strength, is poorly constrained. Bowden (1986) estimated total inputs of about 150 TgN/yr (as  $\text{NH}_3$ ), whereas Warneck (1988) suggested only about 1/3 of that value (54 TgN/yr). Although the importance of releases during animal husbandry and fertilizer usage is well known, we know much less about the natural release of  $\text{NH}_3$  from soils. Using a model of soil processes, Dawson (1977) estimated an annual release of 39 TgN/yr from soils in undisturbed ecosystems. Estimates of net release to the atmosphere are complicated by the uptake and assimilation of  $\text{NH}_3$  by living plants (Denmead et al. 1976; Nason et al. 1988; Langford and Fehsenfeld 1992). In this paper, we compile values from the literature and estimate the soil flux of  $\text{NH}_3$  from the world's undisturbed ecosystems. Then, we derive a new global estimate for the total flux of  $\text{NH}_3$  to the atmosphere from all sources.

### Ammonia emissions from soils

When soil solution pH exceeds 7.0,  $\text{NH}_3$  gas is formed by the deprotonization of  $\text{NH}_4^+$ , viz:



This reaction accounts for the loss of significant amounts of ammonium and urea fertilizers applied to agricultural soils, particularly in arid and semi-arid regions where soils are often alkaline (Terman 1979). Little is known about the loss of  $\text{NH}_3$  from non-agricultural soils, in which  $\text{NH}_4^+$  is derived from the mineralization of organic N compounds. We should expect the greatest losses from coarse, dry soils with limited cation exchange capacity and low rates of nitrification (Nelson 1982; Freney et al. 1983; Sahrawat 1989; Fleisher et al. 1987).

Measurements of the emission of ammonia from undisturbed soils are given in Table 1. In a few cases, these data were obtained by placing small chambers over the soil, providing a site-specific measurement of flux.



Gravenhorst 1980). Although they avoid the problem of chamber effects, these studies may be affected by agricultural or industrial activities outside of the area of measurement.

The study by Marshall and DeBell (1980) allows some insight to the accuracy of emission estimates using different techniques. These workers compared three different methods for collecting volatilized  $\text{NH}_3$  over a 40-day period after the application of urea fertilizer in a coniferous forest. Their estimates range from 13.1 to 26.0% of the applied nitrogen. Assuming similar variation in unfertilized plots, we can assume that their value in Table 1 is accurate to within a factor of two.

When regional estimates are made using micrometeorological approaches or when measurements are made in low vegetation, the reported flux of ammonia is the net flux, including any losses from attached senescent leaves and uptake by living plants (Whitehead and Lockyer 1987; Whitehead et al. 1988). Studies employing chambers on the soil surface, on the other hand, do not include any effects of the aboveground vegetation. Measurements from undisturbed ecosystems include emissions from the excretions of wild animals that naturally graze these areas, but emissions from domestic animals are given in the next section.

We attempted to assess the accuracy of the estimate for tropical savanna by developing an independent estimate for the 25,000-km<sup>2</sup> Serengeti of Africa based on estimates of animal populations and the emission of  $\text{NH}_3$  from animal excretion each year (Table 2). We used estimates of the emission of  $\text{NH}_3$  from domestic farm animals (Möller and Schieferdecker 1989), adjusted for differences in body mass, to provide per capita emission factors for the major grazing animals of the Serengeti. Considering the uncertainties involved, the resulting value, 0.26 g $\text{NH}_3$ -N/m<sup>2</sup>/yr, is tolerably close to measurements of ammonia volatilization from the soil surface in that system, 0.42 g $\text{NH}_3$ -N/m<sup>2</sup>/yr, by Ruess and McNaughton (1988). The latter value also includes emissions other than those associated with hydrolysis of urea in urine.

Hourly rates of ammonia volatilization range over four orders of magnitude (Table 1), with the highest values found in some grassland ecosystems. Much of this variation may be due to differences in soil temperature and moisture during the period of measurement. For example, 24 hours after wetting a Chihuahuan desert soil, Schlesinger and Peterjohn (1991) found that the rate of ammonia volatilization had increased by a factor of six over previous dry conditions.

Many of the values in Table 1 are derived from midday or summertime measurements, when the rates of volatilization are greatest. Although these values may represent an accurate measurement of flux during the specific period of study, extrapolations of these values to provide annual

Table 2. Emissions of NH<sub>3</sub> from the hydrolysis of ungulate urine in the Serengeti of Africa.

Species	Estimated population	Mean body mass <sup>4</sup> (kg)	Emission factor (kgN/yr)	Total flux (kgN/yr)
Wildebeest	1,150,000 <sup>1</sup>	163	3.6 <sup>5</sup>	4,140,000
Gazelle	625,000 <sup>1,2</sup>	16	0.9 <sup>6</sup>	562,500
Zebra	215,000 <sup>2</sup>	219	5.0 <sup>7</sup>	1,075,000
Buffalo	43,000 <sup>1</sup>	447	9.9 <sup>5</sup>	425,700
Topi	60,000 <sup>3</sup>	108	6.1 <sup>6</sup>	366,000
				6,569,200

Assuming an area of 25,000 km<sup>2</sup> (McNaughton 1985), the average emission for the Serengeti is 0.26 gNH<sub>3</sub>-N/m<sup>2</sup>/yr

<sup>1</sup> Population estimate from Dublin et al. (1990)

<sup>2</sup> Population estimate of Sinclair (1979)

<sup>3</sup> Population estimate of McNaughton (1985)

<sup>4</sup> Body mass from Bell (1971)

<sup>5</sup> Emission factor scaled from domestic cattle (see Table 4)

<sup>6</sup> Emission factor scaled from domestic sheep (see Table 4)

<sup>7</sup> Emission factor scaled from domestic horse (see Table 4)

estimates of loss are well in excess of realistic estimates of soil nitrogen mineralization, which ranges from 3.0 to 10.0 gN/m<sup>2</sup>/yr in most terrestrial ecosystems (Bowden 1986). Because losses of NH<sub>3</sub> during fertilizer applications typically average about 20% of the amount applied, we believe that it is unrealistic to expect losses from natural ecosystems to exceed 20% of the annual net mineralization of soil nitrogen. Thus, an upper limit for the annual mean rate of ammonia volatilization is about 230 μgN/m<sup>2</sup>/hr, and in most cases this rate appears likely to lie between 1 and 100 μgN/m<sup>2</sup>/hr (0.0088 and 0.88 gN/m<sup>2</sup>/yr).

### A global estimate for NH<sub>3</sub> emission from natural soils

To develop a global estimate of NH<sub>3</sub> flux from natural soils, we assigned a range of emission values to major biomes and multiplied these by estimates of the world land area in each biome (Table 3). Tropical rainforests, boreal forests, and tundra were assumed to have no efflux, since the soils in these ecosystems are normally wet and very acidic. We also assumed no flux from extreme deserts such as the Sahara. The values for temperate forest were applied to the world area of woodland and shrubland. The resulting global flux estimate ranges from 6 to 45 × 10<sup>12</sup> gN/yr lost as

Table 3. Emissions of NH<sub>3</sub> from the soils of natural ecosystems.

Ecosystem type	Area <sup>1</sup> (10 <sup>12</sup> m <sup>2</sup> )	Estimated rate of volatilization <sup>2</sup> (gNH <sub>3</sub> -N/m <sup>2</sup> /yr)		Total annual volatilization (TgN/yr)	
		Low	High	Low	High
Temperate forest	12	0.1	1.0	1.2	12
Woodland & shrubland	8.5	0.1	1.0	0.85	8.5
Tropical savanna	15	0.25	0.75	3.75	11.25
Temperate grassland	9	0.01	1.00	0.09	9
Desert scrub	18	0.01	0.25	0.18	4.50
				6.1	45.3

<sup>1</sup> From Whittaker and Likens (1973)

<sup>2</sup> Derived by annualizing values from Table 1

NH<sub>3</sub>. This range is large and poorly constrained. The low alternative is somewhat smaller than the recent estimate of Warneck (1988) for emission from soils (15 TgN/yr), and it is 8% of the value that we derive here for the total annual global emission of NH<sub>3</sub>. The high alternative, which cannot be dismissed by the available field data, is close to the estimate of 39 TgN/yr derived in the theoretical model presented by Dawson (1977).

Our assumptions yield a conservative estimate of global flux, for some acid soils of tropical and boreal forests show ammonia volatilization (Blasco and Cornfield 1966, Overrein 1968). However, we suggest that a reasonable value for the natural emission from soils is 10 TgN/yr. As we will show later, significantly higher estimates, in conjunction with well constrained estimates of the flux from other sources, would yield a total global source of atmospheric NH<sub>3</sub> that is incompatible with estimates of the major global sink — atmospheric deposition of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>.

### Emission from biomass burning

A substantial amount of the nitrogen in plant tissue is lost as various nitrogen gases, including NH<sub>3</sub>, during combustion (Lobert et al. 1990). Based on measurements of forest fires in Amazonia, Andreae et al. (1988) estimated a global flux of 3.3 TgN/yr to the atmosphere as particulate NH<sub>4</sub><sup>+</sup>, indicating that an estimate including gaseous NH<sub>3</sub> would be even greater than this value. The global flux of NH<sub>3</sub> from biomass burning can

be assessed from estimates of the amount of biomass consumed by fire each year and the average emission of  $\text{NH}_3$  per unit of biomass burned.

Estimates of  $\text{CO}_2$  released from biomass burning range from 2 to  $6 \times 10^{15}$  gC/yr (Wong 1978; Seiler and Crutzen 1980), with nearly 80% of the release occurring in the tropics (Crutzen and Andreae 1990). In gases collected from 5 forest fires throughout North America, Hegg et al. (1990) measured an emission of  $1.81 \pm 0.87$  g $\text{NH}_3$ /kgC consumed, assuming that the average biomass contained 49.7% carbon. Their measurements yield a global flux of 3 to 9 TgN/yr as  $\text{NH}_3$  from biomass burning. In a laboratory study, Lobert et al. (1990) found that about 4% of the nitrogen in biomass was released as  $\text{NH}_3$  during combustion. Assuming that the mean C/N ratio in vegetation is about 150 (Vitousek et al. 1988), we calculate that 0.5 to 1.6 TgN/yr is released as  $\text{NH}_3$  during biomass burning. We recognize that the C/N ratio of foliage and small branches, which represent a large portion of the biomass consumed by fire, is often as low as 50. Thus the global emissions calculated from this approach may be as high as 5 TgN/yr. As in the case of emissions from soils, the uncertainty of estimated emissions from biomass burning extends over an order of magnitude, but an estimate of about 5 Tg/yr appears to be a reasonable value (Andreae 1991). Even the maximum estimate of 9 TgN/yr is only 12% of the total annual global flux (cf. Hegg et al. 1990).

### **Emissions from domestic animals**

Emissions from domestic animals are calculated from estimates of the worldwide population of domestic animals and measurements of the annual volatilization of  $\text{NH}_3$  from the production of urine and feces by each individual. Losses of  $\text{NH}_3$  from urine typically average 20% of the nitrogen content of urine deposited on grassland (Whitehead and Bristow 1990).

As for the recent global inventory of methane emissions (Lerner et al. 1988), estimates of the worldwide population of animals were derived from the FAO Production Yearbook of 1989 (Table 4). Estimates of the annual emission per individual were derived from surprisingly convergent values given by ApSimon et al. (1987) and Buijsman et al. (1987), who segregate the emissions during periods of active grazing from emissions derived from the disposal of wastes that accumulate when animals are housed indoors. In the UK, cattle typically spend 50% of the year indoors (Kruse et al. 1989) and about 50% of the emission of  $\text{NH}_3$  is derived from the subsequent spreading of barnyard wastes (Buijsman et al. 1987). Thus, the animal emissions factors derived from the European farms are prob-

Table 4. Global emissions of N in NH<sub>3</sub> derived from domestic animals.

Animal category	World population estimate <sup>1</sup>	Emissions per individual <sup>2</sup> (kgN/yr)	Total NH <sub>3</sub> emission (TgN/yr)
Cattle	1,281,472,000	15.5	19.86
Water buffalo	140,028,000	15.5 <sup>3</sup>	2.17
Sheep	1,175,524,000	2.4	2.82
Goats	526,440,000	2.4 <sup>4</sup>	1.26
Camels	19,072,000	2.4 <sup>4</sup>	0.05
Pigs	846,174,000	2.35	1.99
Horses, mules & asses	118,386,000	15.0	1.78
Poultry	11,335,000,000	0.21	2.38
			32.31

<sup>1</sup> From FAO (1989a)

<sup>2</sup> From ApSimon et al. (1987) and Buijsman et al. (1987)

<sup>3</sup> Assumes cattle emission factor

<sup>4</sup> Assumes sheep emission factor

ably applicable to areas of the world where livestock are at pasture during the entire year. The resulting estimate of global emissions from this source is 32 TgNH<sub>3</sub>-N/yr (Table 4).

Roughly 2/3 of this total is derived from cattle, so uncertainties in the emission factor for cattle are critical to the accuracy of the global estimate. Based on the range of emissions factors for cattle compiled by Möller and Schiefferdecker (1989), the contribution of cattle could be as high as 22.1 kgN/yr per animal, and the global emission from domestic animals would be about 37 TgN/yr. Thus, the uncertainty in this component of the global estimate is as much as 30%.

### Emissions from fertilizer application

Applications of ammonia, ammonium-based, and urea fertilizers to cultivated and pastured lands can result in significant losses of volatile NH<sub>3</sub>. Much of the early literature for upland soils was reviewed by Terman (1979), Nelson (1982) and Fenn and Hossner (1985). Generally, losses are greatest with ammonia, urea, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> applications, and slight with NH<sub>4</sub>NO<sub>3</sub>. Losses are reduced when fertilizers are placed below the soil surface and the soil is wet. Losses from forest fertilization are often somewhat lower than those from cultivated and pastured land, especially



when the nitrogen is applied in inorganic forms. A compilation of recent studies suggests that at least 20% of urea-N and 10% of  $(\text{NH}_4)_2\text{SO}_4$ -N are lost in a short period after application to upland soils (Table 5). These losses include the losses from the leaves of crop plants (Schjøerring 1991). Field studies of emission following the use of  $(\text{NH}_4)_2\text{SO}_4$  are relatively few (Table 5), but the losses reported are similar to those found in laboratory studies (e.g. Gasser 1964; Meyer et al. 1961; Fenn and Kissel 1973) and in mass-balance studies in the field (Nõmmik 1966). Similar losses of  $\text{NH}_3$  are seen when fertilizers are applied to rice paddies (Fillery et al. 1984; Freney et al. 1990; De Datta et al. 1991).

The FAO Yearbook for Fertilizer indicates that worldwide production of nitrogen fertilizer was 85.2 Tg in 1988–1989, of which 79.4 Tg was available for agricultural use. Forty-four countries, representing 71% of worldwide production, report data for urea, indicating that 40% of the global production of nitrogen fertilizer, or 34.1 Tg/yr, is in this form. Similarly, we estimate that  $\text{NH}_4\text{NO}_3$  accounts for 24% (20.4 TgN/yr) of world production and  $(\text{NH}_4)_2\text{SO}_4$  accounts for 5.5% (4.7 TgN/yr). Most of the remainder is listed as unspecified nitrogen fertilizer, which may also include a portion in these forms.

Our estimate for the global emission of  $\text{NH}_3$  from fertilizer (Table 6) is based on the breakdown of fertilizers given by the FAO statistics and estimated emissions from major types, derived from Table 5. Emissions from urea dominate the global total of 8.5 TgN/yr. Our emission factor for urea (20%) is higher than that used in some recent regional assessments (Buijsman et al. 1987, Whitehead and Raistrick 1990), but it appears conservative based on many of the data in Table 5. Our estimate of total emission from fertilizers is about 10% of the annual fertilizer production — somewhat larger than that included in other assessments of atmospheric  $\text{NH}_3$  balance (Warneck 1988). Losses of  $\text{NH}_3$  from fertilizers applied to the 10% of the Earth's surface in intensive agriculture rival the natural emissions from the 90% of the land surface in other use.

### **Ammonia volatilization from the sea**

Low concentrations of  $\text{NH}_3$  in the remote marine atmosphere led Quinn et al. (1987) to postulate gaseous losses of  $\text{NH}_3$  from the sea surface following Henry's law for the distribution of soluble gases between the solution and gaseous phase. Subsequent measurements in a wide area of the Pacific Ocean suggested a flux of  $7 \mu\text{mol}/\text{m}^2/\text{day}$  (Quinn et al. 1990) and  $10 \mu\text{mol}/\text{m}^2/\text{day}$  (Quinn et al. 1988) from pelagic and near-shore environments, respectively. A flux of  $7 \mu\text{mol}/\text{m}^2/\text{day}$  is equiva-

Table 5. Some field estimates of  $\text{NH}_3$  volatilization following fertilization of agricultural fields, pastures, and forests.

Soil type	Fertilizer application (kgN/ha)	Percentage loss rate	Interval of observation (days)	Reference
<b>UREA APPLICATION</b>				
<i>Cultivated land</i>				
Mollisol	120	4–9	10–16	McInnes et al. (1986)
Entisol	120	17		
Mollisol	168	30	3–5	Keller & Mengel (1986)
Alfisol	168	11	3–5	
Mollisol				
Row-cropped	200	7–30	12–20	Beyrouty et al. (1988)
No-till	200	31–35		
Ultisol	100	14–46	7	Hargrove et al. (1987)
Aridisol	40–120	9–23	20	Aggarwal et al. (1987)
Mollisol	448	13	14	Harding et al. (1963)
<i>Pasture and grassland</i>				
Alfisol	200	30	8	Lightner et al. (1990)
Inceptisol	100	28	6	Black et al. (1985)
Ultisol	100	35–43	15	Reynolds & Wolf (1988)
Spodosol	112	21–29	7	Volk (1959, 1961)
Vertisol	336	7–10	12	Kissel et al. (1977)
<i>Forest</i>				
Spodosol	220	22–26	40	Marshall & DeBell (1980)
Spodosol	200	0.7–14	45	Nason et al. (1988)
Spodosol	224	30	1	Camire & Bernier (1981)
Spodosol	200	20–22	28	Nõmmik (1973)
Spodosol	100	4	7	Volk (1970)
Spodosol	500	3.5	48	Overrein (1968)
Alfisol	200	4–13	30	Craig & Wollum (1982)
<b><math>\text{NH}_4\text{NO}_3</math> APPLICATION</b>				
<i>Cultivated land</i>				
Mollisol	168	3.7	3–5	Keller & Mengel (1986)
Alfisol	168	1.5	3–5	
Mollisol	448	1.3	14	Harding et al. (1963)
<i>Pasture and grassland</i>				
Spodosol	112	0.3	7	Volk (1959, 1961)
Vertisol	336*	2.2–2.9	12	Kissel et al. (1977)
<i>Forest</i>				
Alfisol	200	0	30	Craig & Wollum (1982)
Spodosol	224	0.3	1	Camire & Bernier (1981)

Table 5 (Continued)

Soil type	Fertilizer application (kgN/ha)	Percentage loss rate	Interval of observation (days)	Reference
<i>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> APPLICATION</i>				
<i>Cultivated land</i>				
Mollisol	448	7.8	14	Harding et al. (1963)
<i>Pastureland</i>				
Vertisol	33–280	50	4	Hargrove et al. (1977)
Vertisol	33–280	27–39	4	Kissel et al. (1977)
Spodosol	112	0.4–19	7	Volk (1961)
<i>Forest</i>				
Spodosol	224	0	1	Camire & Bernier (1981)

\* Applied as Ca(NO<sub>3</sub>)<sub>2</sub>

Table 6. Global emissions from production and use of nitrogen fertilizers and industrial chemicals.

Form	Global production <sup>1</sup> (TgN/yr)	Emission factor <sup>2</sup>	Global emissions (TgN/yr)
Urea	34.1	0.20	6.8
NH <sub>4</sub> NO <sub>3</sub>	20.4	0.025	0.5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4.7	0.10	0.5
Other fertilizer	20.2	0.03	0.6
Total fertilizer	79.4		8.40
Other industrial production	5.8	0.01	0.06
Total production	85.2		8.46

<sup>1</sup> FAO (1989b)

<sup>2</sup> Derived from Table 5, as described in the text.

lent to  $4.1 \mu\text{mol}/\text{m}^2/\text{day}$ , which is in the range of values found for undisturbed soils (Table 1). Assuming this flux estimate is appropriate for the global surface area of the sea ( $361 \times 10^{12} \text{ m}^2$ ), the global flux from the sea is as much as 13 TgN/yr. Marine  $\text{NH}_3$  has a short atmospheric lifetime (Quinn et al. 1990). The global flux from the sea is nearly equal to a recent independent estimate of 16 TgN/yr for the deposition of  $\text{NH}_3/\text{NH}_4^+$  on the sea surface (Duce et al. 1991).

### Other sources of atmospheric ammonia

Other sources of atmospheric ammonia appear to contribute  $<10\%$  to the annual budget in the atmosphere (Table 7). We derived the value for human excrement using the approach of Warneck (1988), assuming that the current human population has now reached 5 billion. All recent assessments conclude that emissions from coal combustion and automobiles are small, and we have adopted the values of Warneck (1988).

### A global budget for atmospheric $\text{NH}_3$

Our 'best' estimate for total global emission of  $\text{NH}_3$  is 75 TgN/yr. Emissions from fertilized agriculture and domestic animals account for over half the total, reflecting the level of direct human impact on the global ammonia budget of the atmosphere. Estimates of the potential range of  $\text{NH}_3$  emission extend from 50 to 128 TgN/yr (Table 7). However, with the exception of the emission from undisturbed soils, most of the estimates of individual sources are fairly well constrained.

Annual denitrification appears to return over 150 TgN/yr from land to the atmosphere, mostly as  $\text{N}_2$  (Bowden 1986; Schlesinger 1991). The flux of  $\text{NH}_3$  (75 TgN/yr) appears to be the next largest transfer from the biosphere to the atmosphere in the global nitrogen cycle. It exceeds the flux of other trace biogenic nitrogen gases, such as the natural flux of  $\text{N}_2\text{O}$  and NO from soils [(ca. 6 and 20 TgN/yr, respectively) Davidson 1991]. Of course, unlike  $\text{N}_2$ , the emissions of  $\text{NH}_3$  and NO from land remain as forms of 'fixed' nitrogen that may return to cycle in the biosphere on a relatively short time scale.

The ammonium content in Greenland ice cores provides a historical record of variations in atmospheric emissions during the last several centuries (Spencer et al. 1991). High concentrations of  $\text{NH}_4^+$  are found in layers of ice that show independent evidence of forest fires. If other

Table 7. A budget for atmospheric NH<sub>3</sub>.

Inputs:	'Best' estimate (TgN/yr)	Potential range
Domestic animals (Table 4)	32	24–40
Sea surface (text)	13	8–18
Undisturbed soils (Table 3)	10	6–45
Fertilizers (Table 6)	9	5–10
Biomass burning (text)	5	1–9
Human excrement* (Warneck 1988)	4	
Coal combustion* (Warneck 1988)	2	
Automobiles* (Warneck 1988)	0.2	
TOTAL INPUTS	75	50–128
Outputs:		
Wet deposition on land (Warneck 1988)	30	
Dry deposition on land (Warneck 1988)	10	
Wet deposition on sea surface (Duce et al. 1991)	16	
Reaction with OH radical (Warneck 1988)	1	
TOTAL OUTPUTS	57	

\* incremented to represent current human and automobile populations.

sources of NH<sub>3</sub> have relatively constant values, annual variations in the atmospheric budget of NH<sub>3</sub> could be due to variations in biomass burning, despite our suggestion that fires contribute only 7% to the average annual flux of NH<sub>3</sub> to the atmosphere (Table 7).

A 19-year record of precipitation chemistry in the eastern United States suggests that the deposition of NH<sub>4</sub><sup>+</sup> has declined 34% from 1963 to 1982 (Likens et al. 1984). This trend is surprising given the increasing use of urea fertilizer and the increasing practice of no-till agriculture, in which urea is spread directly on the soil surface often producing large emissions (Beyrouy et al. 1988; Raczkoswki and Kissel 1989). Greater emissions from fertilized agriculture may be masked by decreasing emissions from other sources that contribute to the ammonia budget of North America. Decreasing deposition of NH<sub>4</sub><sup>+</sup> may also be caused by an increasing regional emission of SO<sub>2</sub> during the same interval, as the reaction of NH<sub>3</sub>

with  $\text{H}_2\text{SO}_4$  to produce  $(\text{NH}_4)_2\text{SO}_4$  aerosols appears to increase the mean residence time and the potential for long-range transport of  $\text{NH}_3/\text{NH}_4^+$  in the atmosphere (Allen et al. 1988; Hedin et al. 1990). In light of the recent lower levels of  $\text{SO}_2$  emission in eastern North America, an inadvertent test of this hypothesis is currently underway.

### Processes that remove $\text{NH}_3$ from the atmosphere

Several attempts have been made to estimate the global atmospheric deposition of  $\text{NH}_4^+$  in rainfall and dry fallout. The deposition calculated by Berner and Berner (1987), 23 TgN/yr, is probably too low, because it can not account for the fate of the better-known sources in Table 7. Their value may underestimate deposition on land by underestimating the dry deposition of  $\text{NH}_3$  and  $\text{NH}_4^+$  on plant surfaces. In a forest of eastern Tennessee, Lindberg et al. (1986) found that 33% of the annual input of  $\text{NH}_4^+$  from the atmosphere was deposited or absorbed as  $\text{NH}_3$  on plant surfaces. Such high rates of dry deposition have also been recorded in other areas (Tjepkema et al. 1981; Heil et al. 1988; Langford and Fehsenfeld 1992).

Warneck (1988) estimates the global atmospheric deposition of  $\text{NH}_4^+$  as 48 TgN/yr. If his estimate for the deposition on the ocean surface is revised upward to 16 TgN/yr based on the recent, comprehensive treatment by Duce et al. (1991), the global atmospheric deposition is 56 TgN/yr (Table 7). Reactions of  $\text{NH}_3$  with OH radical in the atmosphere make a small additional contribution (1 TgN/yr) to the annual global loss of  $\text{NH}_3$  from the atmosphere (Warneck 1988). Thus, our estimate of global  $\text{NH}_3$  emission (75 TgN/yr) is somewhat higher than our best estimate of the global sink (57 TgN/yr) (Table 7).

The lower bound of the potential range of the estimated global emission (50 to 128 TgN/yr) overlaps with the estimated global sink, which speaks strongly for a conservative estimate of the emission from undisturbed soils — the component with the most poorly constrained contribution to the global flux. Any upward revision in the estimated global sink of atmospheric  $\text{NH}_3$ , perhaps as a result of better estimates of dry deposition on land, would be more compatible with our current estimate of the global source strength of atmospheric  $\text{NH}_3$ . Further refinements of the atmospheric budget of  $\text{NH}_3$  are needed, but in any case, the excess of  $\text{NH}_4^+$  deposition over  $\text{NH}_3$  emission noted in earlier assessments of the global nitrogen cycle (Söderlund and Svensson 1976; Lemon and Van Houtte 1980) has largely been reconciled.

Our estimate of total  $\text{NH}_3$  emission to the atmosphere allows a calculation of the maximum potential neutralization of natural and anthropogenic acidity in rainfall. An emission of  $75 \times 10^{12}$  gN/yr as  $\text{NH}_3$  can consume  $5.4 \times 10^{12}$  moles of  $\text{H}^+$ , by reactions such as that in equation 1. The neutralization will be lower to the extent that plants and soils directly absorb  $\text{NH}_3$ .

A variety of reactions produce  $\text{H}^+$  in rainfall. If all precipitation were in chemical equilibrium with atmospheric  $\text{CO}_2$ , producing a rainfall pH of 5.6, the total deposition of  $\text{H}^+$  on the Earth's surface would be  $1.24 \times 10^{12}$  moles/yr. The production of NO by lightning [ $20 \times 10^{12}$  gN/yr (Levine et al. 1984)] and by soil microbes [ $20 \times 10^{12}$  gN/yr (Davidson 1991)], and its removal in rainfall as  $\text{HNO}_3$  potentially contributes an additional  $2.9 \times 10^{12}$  moles/yr of  $\text{H}^+$  to rainfall. Similarly, volcanic emanations of  $\text{SO}_2$  that form  $\text{H}_2\text{SO}_4$  in rainfall contribute  $1.3 \times 10^{12}$  moles  $\text{H}^+$ /yr, and the oxidation of biogenic S gases could produce  $4.1 \times 10^{12}$  moles  $\text{H}^+$ /yr (Schlesinger 1991). Although free acidity from carbonic acid may be reduced in the presence of strong acids and NO and  $\text{SO}_2$  may be removed by processes other than rainfall, the total potential acidity from natural sources is about  $9.5 \times 10^{12}$  moles  $\text{H}^+$ /yr.

Anthropogenic sources of acidity add about  $7.4 \times 10^{12}$  moles/yr of  $\text{H}^+$  to the atmosphere (Schlesinger 1991), nearly equalling the natural sources. Thus, the  $\text{NH}_3$ -derived neutralization of atmospheric acidity, even acidity derived from natural sources, is incomplete, amounting to only  $5.4 \times 10^{12}$  moles/yr or 32% of total atmospheric acidity.  $\text{NH}_3$  may be an important source of alkalinity in precipitation in some regions affected by air pollution, but the subsequent atmospheric deposition of  $\text{NH}_4^+$  is potentially acidifying to soils as a result of the generation of  $\text{H}^+$  during nitrification.

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