

Final Report

The surface/atmosphere exchange of gaseous ammonia

Special topic in atmospheric chemistry, phase II  
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### Abstract

Micrometeorological measurements of the exchange of gaseous  $\text{NH}_3$  and  $\text{NH}_4^+$  have been made over a wide range of vegetated surfaces. The results are interpreted in terms of processes controlling exchange at the surface, and are coupled with monitored air concentrations also made in this study to estimate the annual exchange of  $\text{NH}_3$  for different vegetated surfaces. Over unfertilised vegetation in the UK dry deposition of  $\text{NH}_3$  is frequently the largest single input of atmospheric N, whereas over ungrazed fertilised agricultural vegetation there is a small net emission of  $\text{NH}_3$  (eg  $< 1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ).

### Original objectives and changes

The project kept closely to the original objectives which were:

- a) To make micrometeorological measurements of the surface/atmosphere exchange of  $\text{NH}_3$  and  $\text{NH}_4^+$  over a range of vegetated surfaces.
- b) To use the results of a) to estimate annual exchange budgets of  $\text{NH}_3$  and  $\text{NH}_4^+$  for different surfaces.

To achieve the second of these objectives monitored air concentrations are required. In reviewing the literature it was noted that there exists a shortage of  $\text{NH}_3$  concentration data, with, for example, the only published data for Scotland being the total  $\text{NH}_x$  ( $\text{NH}_3 + \text{NH}_4$ ) measurements by the European Air Chemistry Network (EACN, Stevenson, 1968). A third objective was therefore set, being:

- c) To monitor concentrations of atmospheric  $\text{NH}_3$  at several sites in S. Scotland. To do this the passive diffusion tube method of Hargreaves and Atkins (1987) was used to provide concentration for up to 18 months.

As a studentship including the production of a Ph.D thesis, the experimental and modelling objectives were complemented by objectives to provide comprehensive reviews on

- a) the literature of the atmospheric ammonia cycle
- b) the micrometeorological theory for estimating surface/atmosphere exchange.

#### Development of methods and techniques

The study required the implementation of existing methods for:

- a) Micrometeorological estimation of surface fluxes by the aerodynamic gradient method (eg Thom, 1975; Garland 1977).
- b) Chemical sampling of  $\text{NH}_3$  and  $\text{NH}_4^+$  using filter pack samplers (Harrison et al, 1986, pers. comm.).
- c) Chemical analysis of  $\text{NH}_4^+$  in solution using continuous flow analysis (Bietz, 1974; Thomas, 1986; pers. comm).

During the course of the study each of the methods were developed and modified. For methods b) and c) this primarily consisted of developing techniques to improve sensitivity and sampling limits. In particular, the preparation of blank (unexposed) filters for  $\text{NH}_3$  sampling was modified to reduce blank values and variability.

In the review of the micrometeorological theory, consideration was given to different methods of stability correction and their usefulness (gradient and integrated profile stability correction) and to approaches to the resistance analogy for describing trace gas transfer. In addition to the usual resistance analogy used in air pollution research, ecophysiological techniques for estimating surface values of temperature and water vapour pressure were applied to estimate surface concentrations of  $\text{NH}_3$ . The relationship between the surface resistance and surface concentration estimates was developed.

Progress achieved in relation to schedule of work

October 1986 - start of project

October 1986 - March 1986

Initial literature survey of  $\text{NH}_3$  surface/atmosphere exchange and micrometeorological theory.

Building and testing of filter pack system and continuous flow analysis for  $\text{NH}_3$ .

March 1987 - November 1987

Initial field measurement campaigns over unfertilized vegetated surfaces using the aerodynamic gradient method.

June 1987

Presentation of initial results to C.C.R.A.C. at Lancaster University.

December 1987 - March 1988

Analysis and consolidation of results.

Initiation of diffusion tube monitoring program.

March 1988 - July 1988

Field measurements over moorland and fertilized grassland.

July 1988 - October 1988

Analysis of data. Development of new computer programs for analysis of aerodynamic gradient method results. Further development of

micrometeorological theory.

November 1988 to February 1989

Development of psychrometry for water vapour flux gradient measurement to provide interpretative data for  $\text{NH}_3$  flux measurements.

Micrometeorological flux measurements over forest, moorland and agricultural grassland. Use of water vapour flux measurement.

January 1989

Presentation of research results to C.C.R.A.C. at the University of Norwich.

March 1989 - May 1989

Analysis of results.

Participation in Great Dun Fell atmospheric nitrogen species experiment.

- a) filter pack measurements of simultaneous gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  concentrations upwind, downwind and at the summit of Great Dun Fell in the presence and absence of cap cloud.
- b) Comparison of  $\text{NH}_3$  diffusion tubes used in this study with those of Harwell Laboratory.

November 1989 - October 1990

Analysis of data and preparation of PhD thesis.

September 1990

Presentation of research results over moorlands at the "International

Conference on Acidic Deposition: Its Nature and Imports", Glasgow.

## Summary of Results and Data

### Profile Measurement

The calculation of surface fluxes of ammonia requires the measurement of windspeed, temperature and ammonia profiles with height above an extensive uniform surface. Figure 1 shows profiles measured over a fertilized agricultural grown field during wet conditions in winter (Bush Estate, February 1989).  $\text{NH}_3$  and  $\text{NH}_4^+$  profiles were measured using the filter pack system and show a high precision of measurement. The decrease in  $\text{NH}_3$  concentration towards the ground shows that  $\text{NH}_3$  deposition was occurring during this run.

Windspeed profiles were measured with sensitive cup anemometers. In this campaign temperature profiles were supplied from the dry bulbs of aspirated psychrometers. The psychrometers provided water vapour flux determinations to supply interpretative data for the  $\text{NH}_3$  exchange measurements.

As expected from theory (eg Sehmel 1980), gaseous  $\text{NH}_3$  was found to exchange much more rapidly than particulate  $\text{NH}_4^+$ . The mean deposition velocity of particulate  $\text{NH}_4^+$  was  $1.9 \pm 2.5 \text{ mm s}^{-1}$  (95% confidence limits). Consequently, the study focussed on the exchange of gaseous  $\text{NH}_3$ .

The results of the  $\text{NH}_3$  exchange measurements show a clear distinction between measurements made over unfertilised vegetation and fertilised agricultural vegetation. These different surface types are therefore separated in the following sections.

### Natural and unfertilized vegetation

Over natural and unfertilized vegetation a consistent pattern of rapid deposition was seen with generally near zero surface resistance ( $r_c$ ). Some

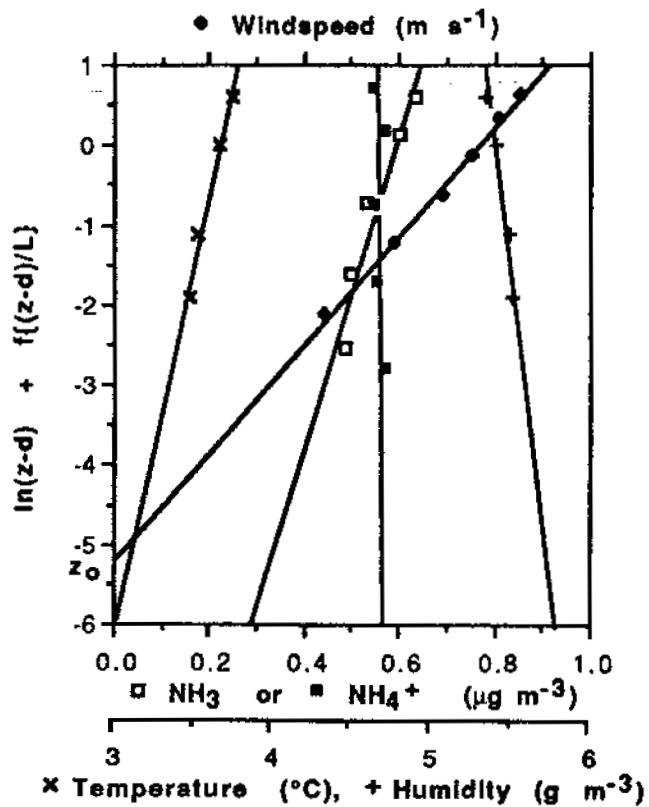


Figure 1. Example profiles measured at Bush, February 1989. Temperature and water vapour profiles measured by aspirated psychrometry. Data are for Run 6 except  $\text{NH}_4^+$  which is for Runs 1-6 combined. For height axis,  $z$  is in meters;  $f\{(z-d)/L\}$  accounts for stability correction.



exceptions to this pattern were seen. In dry conditions a small  $r_c$  ( $< 50 \text{ s m}^{-1}$ ) was sometimes recorded, while over a surface with exposed calcareous soil (recently harrowed) the mean  $r_c$  was  $125 \text{ s m}^{-1}$ . Limited measurements were made over forest vegetation and while subject to large uncertainty (because of the small gradients measurable over forests) the results are consistent with the rapid deposition observed at other unfertilised sites. A summary of the data collected over natural and unfertilised vegetation is given in Tables 1 and 2.

#### Fertilised agricultural vegetation

Over fertilised agricultural vegetation a bi-directional pattern of exchange was observed. In wet and cool conditions deposition occurred, whereas in warm and dry conditions emission occurred. Emission fluxes of up to  $24 \text{ ng m}^{-1} \text{ s}^{-1}$  were recorded. In wet conditions in summer  $r_c$  was variable ( $0\text{-}130 \text{ s m}^{-1}$ ), while wintertime measurements showed rapid deposition to wet surfaces ( $r_c < 30 \text{ s m}^{-1}$ ). During a period of light frost an increased  $r_c$  of up to  $80 \text{ s m}^{-1}$  was observed. The wintertime measurements provided a series of precise flux determinations, and these are given in Figure 2 as an example of the detailed presentation of results given for the other sites by Sutton (1990). Table 3 summarises the flux measurements over fertilised agricultural vegetation. It should be noted that all of the measurements represent background exchange and were made at least six weeks after application of nitrogen fertilisers.

#### Monitoring of atmospheric ammonia

Passive diffusion tube samplers were used to monitor atmospheric  $\text{NH}_3$  concentrations at several sites in S. Scotland. (Table 4). A summary of the concentrations recorded are given in Table 5. The highest concentrations were, as expected, measured at a farmyard site, whereas the lowest concentrations were recorded at a hill site in a forest clearing. Extensive monitoring was made at four background sites (not near local sources) and the air concentrations given as seasonal means are shown in Figure 3. At each of the sites the highest concentrations were recorded

site, month/year (surface type)	no of runs	$u\{1\text{ m}\}$ ( $\text{m s}^{-1}$ )	$T\{z_0\}$ ( $^{\circ}\text{C}$ )	$r_{a+b}$ ( $1\text{ m}\}$ * ( $\text{s m}^{-1}$ )	$\chi\{1\text{ m}\}$ ( $\mu\text{g m}^{-3}$ )	Deposition flux $\text{NH}_3$ ( $\text{ng m}^{-2}\text{s}^{-1}$ )	$V_d\{1\text{ m}\}$ ( $\text{mm s}^{-1}$ )	$r_c \dagger$ ( $\text{s m}^{-1}$ )	$\chi\{z_0\}$ ( $\mu\text{g m}^{-3}$ )
Huntingdon 8/1987 (neutral grassland)	9	2.5	(18)	58.2	2.00	33.9	16.3	3.1	-0.14
Harwell 3/1988 (calcareous grass'd)	6	3.3	8	63.5	1.77	14.3	5.3	125	1.01
Great Dun Fell (all) ( <i>Eriophorum</i> moor)	12	3.9	(7)	45.0	0.67	17.3	19.6	5.9	0.01
Fala Moor 11/1987 ( <i>Eriophorum</i> moor)	7	1.7	5	65.6	0.23	5.04	21.5	-19.1	-0.06
Fala Moor 5/1988 (mixed spp moor)	8	5.2	13	23.2	0.64	23.5	30.3	7.1	0.07
Wether Law 2/1989 ( <i>Calluna</i> moor)	8	7.0	-0	19.0	0.08	1.71	27.7	17.1	0.05

Table 1. Mean values for  $\text{NH}_3$  exchange measurement campaigns over natural and unfertilized surfaces. Values are arithmetic means of runs (unweighted) apart from where noted: \* reciprocal mean, from arithmetic mean of  $V_m$ ; † difference of mean  $r_{a+b}$  and mean  $r_t$  (reciprocal of arithmetic mean  $V_d$ ). Positive fluxes imply deposition of  $\text{NH}_3$ . Values in brackets are means of available data.

Chemical species	no of runs	$u\{1\text{ m}\}$ ( $\text{m s}^{-1}$ )	$T\{z_0\}$ ( $^{\circ}\text{C}$ )	$r_{a+b}$ ( $1\text{ m}\}$ * ( $\text{NH}_3$ )	$V_m\{1\text{ m}\}$ ( $\text{NH}_3$ ) ( $\text{mm s}^{-1}$ )	$\chi\{1\text{ m}\}$ ( $\mu\text{g m}^{-3}$ )	Deposition Flux ( $\text{ng m}^{-2}\text{s}^{-1}$ )	$V_d\{1\text{ m}\}$ ( $\text{mm s}^{-1}$ )	$r_c \dagger$ ( $\text{s m}^{-1}$ )	$\frac{V_d(\chi)}{V_m(\text{NH}_3)}$
$\text{NH}_3$	4	3.3	(6)	9.7	103	0.20	11.0	65.9	5.5	0.64
$\text{NH}_4^+$	5	3.5	(6)	10.0	100	1.14	9.7	16.6	—	0.17

Table 2. Mean values for  $\text{NH}_3$  and  $\text{NH}_4^+$  exchange measurement over coniferous forest at Dunslair Heights, Peebles. Equivalent  $V_m(\text{NH}_3)$  given for  $\text{NH}_4^+$  data to compare rates by  $V_d/V_m$ .

site, campaign	no of runs	$u(1\text{ m})$ ( $\text{m s}^{-1}$ )	$T(z_0')$ ( $^{\circ}\text{C}$ )	$r_{a+b}$ ( $1\text{ m}$ ) * ( $\text{s m}^{-1}$ )	$\chi(1\text{ m})$ ( $\mu\text{g m}^{-3}$ )	Deposition Flux $\text{NH}_3$ † ( $\text{ng m}^{-2} \text{s}^{-1}$ )	$V_d(1\text{ m})$ ( $\text{mm s}^{-1}$ )	$r_c$ † ( $\text{s m}^{-1}$ )	$\chi(z_0')$ ( $\mu\text{g m}^{-3}$ )	$\chi(z_0'')$ ( $\mu\text{g m}^{-3}$ )
Bush 6/1988 (cut forage grass)	17	1.47	14.0	58.8 <i>min.: 0.00</i> <i>max.: 0.96</i>	0.21 <i>0.00</i> <i>0.96</i>	-7.7 <i>-22.2</i> <i>1.3</i>	<i>emis.</i> <i>emis.</i> <i>12.8</i>	<i>emis.</i> <i>-15</i> <i>emis.</i>	0.59 <i>-0.02</i> <i>1.82</i>	3.1 <i>-0.9</i> <i>7.3</i>
Bush 2/1989 (cut forage grass)	6	6.08	0.6	56.0 <i>min.: 0.54</i> <i>max.: 3.14</i>	1.29 <i>0.54</i> <i>3.14</i>	14.5 <i>5.1</i> <i>35.1</i>	12.3 <i>6.5</i> <i>20.6</i>	25 <i>-7.5</i> <i>80</i>	0.19 <i>-0.26</i> <i>0.42</i>	— — —
Stenton 6/1989 (barley) ‡	9	1.70	12.7	48.8 <i>min.: 0.47</i> <i>max.: 1.30</i>	0.99 <i>0.47</i> <i>1.30</i>	-6.3 <i>-23.9</i> <i>4.7</i>	<i>emis.</i> <i>emis.</i> <i>5.3</i>	<i>emis.</i> <i>121</i> <i>emis.</i>	1.24 <i>0.57</i> <i>1.69</i>	2.3 <i>0.6</i> <i>7.4</i>
Stenton 6/1989 (wheat) §	4	—	16.1	—	1.51	—	—	—	—	—

Table 3. Summary of  $\text{NH}_3$  exchange and environmental conditions for measurements over fertilized agricultural surfaces. Values in standard type are arithmetic means of runs (unweighted) apart from where noted. Minimum and maximum values during measurement periods are given in italics. Notes: \* reciprocal mean from arithmetic mean of  $V_m$ ; † difference of mean  $r_{a+b}$  and mean  $r_t$  (mean  $r_t = 1/\text{mean } V_d$ ); ‡ negative fluxes imply  $\text{NH}_3$  emission; † Values calculated using stability corrections from psychrometer temperature values; § within-canopy profiles only, reference height 1.1 m above ground level.

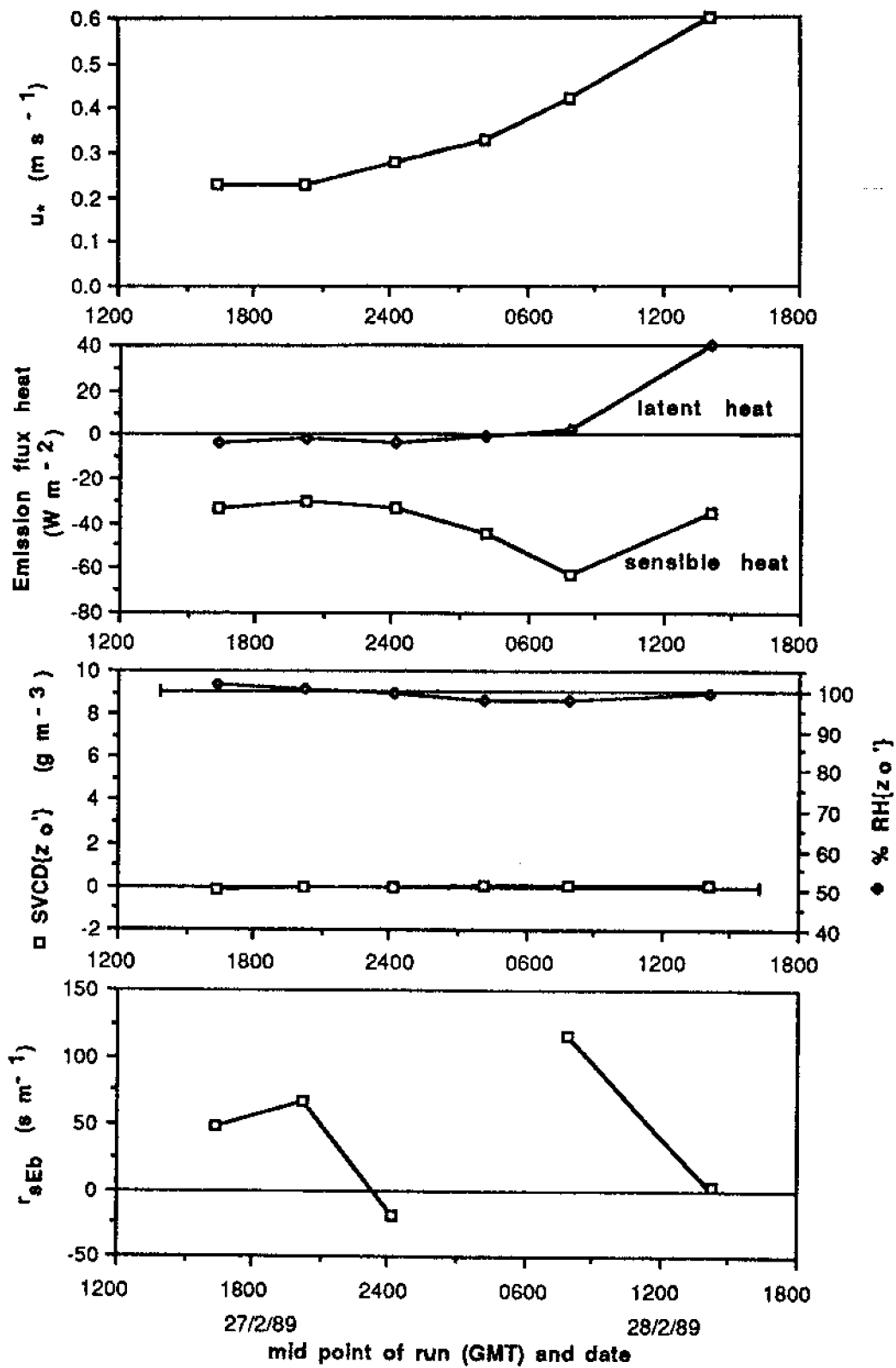


Figure 2a. Course of ammonia exchange and environmental conditions measured over fertilized cut grassland at Bush, February 1989. Notes: positive heat fluxes denote emission; SVCD = saturated vapour concentration deficit; RH = relative humidity. Figure continued overleaf.

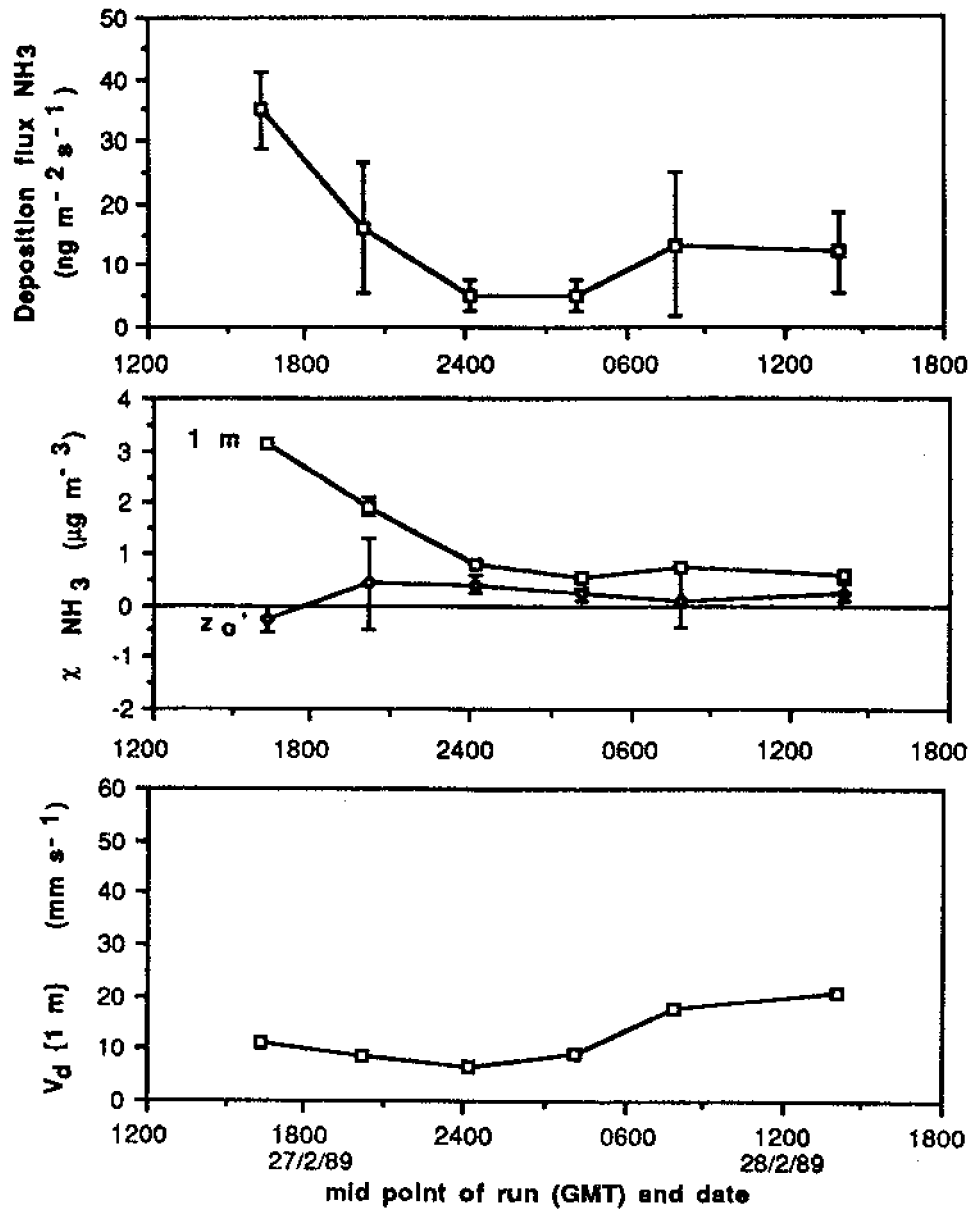


Figure 2b. Course of ammonia exchange and environmental conditions measured over fertilized cut grassland at Bush, February 1989. Note: positive fluxes of NH<sub>3</sub> denote deposition. Error bars (not given for V<sub>d</sub>) are 95% confidence limits. Figure continued overleaf.

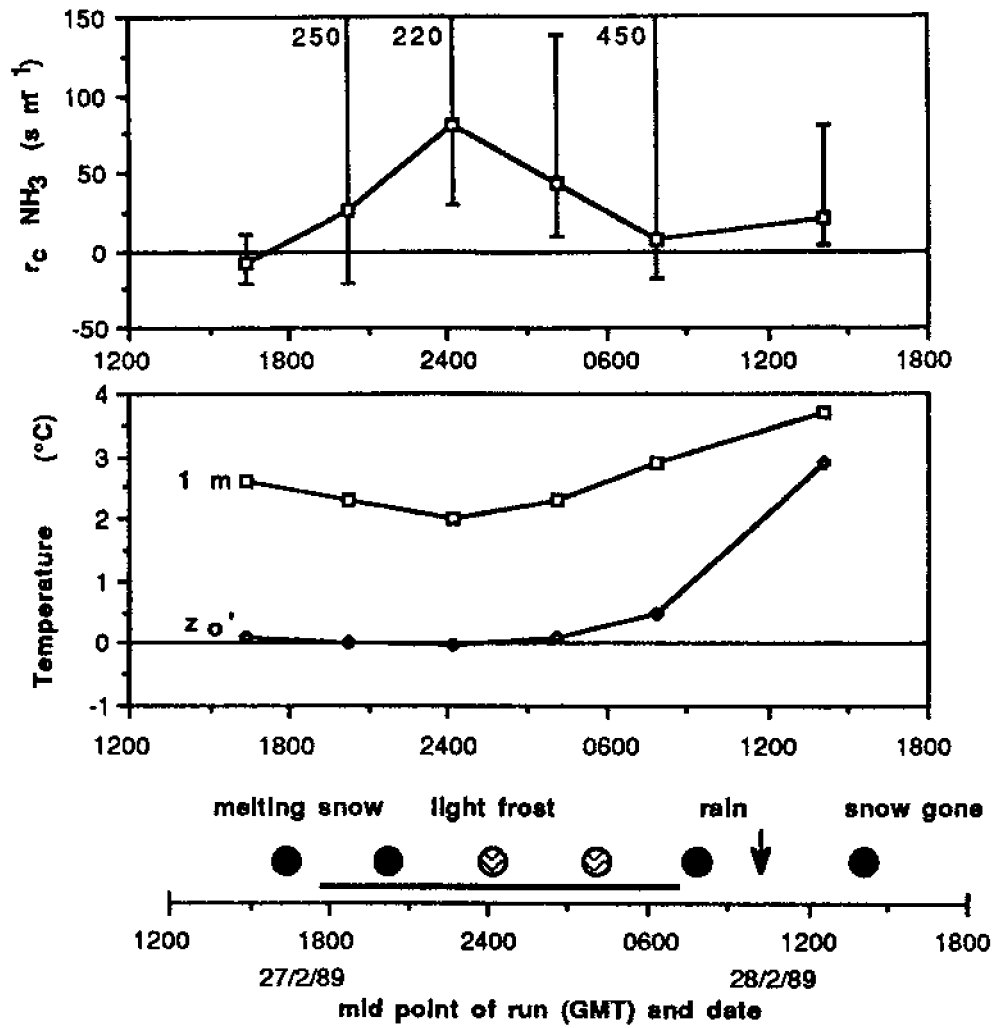


Figure 2c. Course of ammonia exchange and environmental conditions measured over fertilized cut grassland at Bush, February 1989. Error bars for  $r_c$  are 95% confidence limits. Surface conditions were assessed visually; black circles denote a wet surface and hatched circles a frozen surface. The horizontal bar denotes night-time.

Site Name	Site description	Dates	NGR
Bush Estate	Monitoring in S. Scotland Lay field in agricultural area, Penicuik, Midlothian.	1/1988- 6/1989	NT247639
Dunslair Heights (top site)	Clearing at top of hill (600 m AMSL) in Glentress Forest (conifer plantation), Peebles, Borders.	2/1988- 6/1989	NT288405
Glentress Forest (bottom site)	Clearing on exposed ridge, S. of Dunslair Heights (300 m AMSL) in Glentress Forest, Peebles, Borders.	2/1988- 6/1989	NT289405
Fala Moor	Open moorland (300 m AMSL) managed for low density sheep and grouse. Remote site 2 km N. of Brothershiels Farm. Nearest road 2 km S.E. Heriot, Midlothian.	1/1988- 6/1989	NT423578
Brothershiels Farm	By trees in Farm yard. Silage and cattle nearby in yard. Silage smell continual. Nearest road 2 km S.W. Heriot, Midlothian.	12/1988- 6/1989	NT420560
Edinburgh roadside	Main road kerbside. (3.5 m up on lamp post ) Old College, South Bridge, Edinburgh.	3/1989- 6/1989	NT260734
Edinburgh roof top	Roof of University Geography department. 200 m east of main road site. Edinburgh.	2/1989- 6/1989	NT262734
Indoors I.T.E.	Indoor site in laboratory work place. No air conditioning, openable windows. Bush Estate, Penicuik, Midlothian.	12/1988- 6/1989	NT246638
Devilla Forest	Other sites Measurements within and above Scots Pine ( <i>Pinus sylvestris</i> ) canopy. 4 reference levels. Kincardine, Fife, C. Scotland.	6/1989- 10/1989	NS959893
Great Dun Fell	Measurements at 4/5 sites in approximate NE-SW trajectory over hill. Wharley Croft (200 m AMSL) N. Pennines, Cumbria Fellside (550 m AMSL) and Durham, England. GDF summit (847m AMSL) Tyne Head (550 m AMSL)	4/1989	NY698246 NY704295 NY710322 NY753350

Table 4. Sites used for monitoring ammonia by diffusion tubes. Notes: NGR, national grid reference; AMSL, above mean sea level.

Site Name	Seasonal mean concentrations of NH <sub>3</sub> (µg m <sup>-3</sup> )				
	Spring Mar., Apr., May	Summer Jun., Jul., Aug.	Autumn Sep., Oct., Nov.	Winter Dec., Jan., Feb.	Annual Mean *
Bush Estate	1.34 (6)	1.62 (6)	0.85 (4)	0.77 (6)	1.14
Dunslair Heights (600 m)	0.53 (6)	0.65 (6)	0.19 (4)	0.38 (4)	0.44
Glentress Forest (300 m)	0.68 (6)	0.95 (5)	0.32 (4)	0.37 (5)	0.58
Fala Moor	0.69 (6)	0.74 (5) 2.50 (6) †	0.19 (4)	0.59 (5)	0.55
Brothershiels Farm	11.2 (2)	—	—	3.68 (4)	—
Edinburgh roadside	3.41 (2)	—	—	—	—
Edinburgh roof top	3.02 (2)	—	—	0.84 (1)	—
Indoors (ITE)	7.34 (2)	—	—	7.46 (4)	—

Table 5. Seasonal arithmetic mean concentrations of atmospheric ammonia from diffusion tube monitoring in S. Scotland. Values in brackets are the number of runs from which each mean is calculated. \* Mean of seasonal values. † This value is doubtful and results from the inclusion of one probably contaminated outlying run (run 8) of 10.5 µg m<sup>-3</sup>.

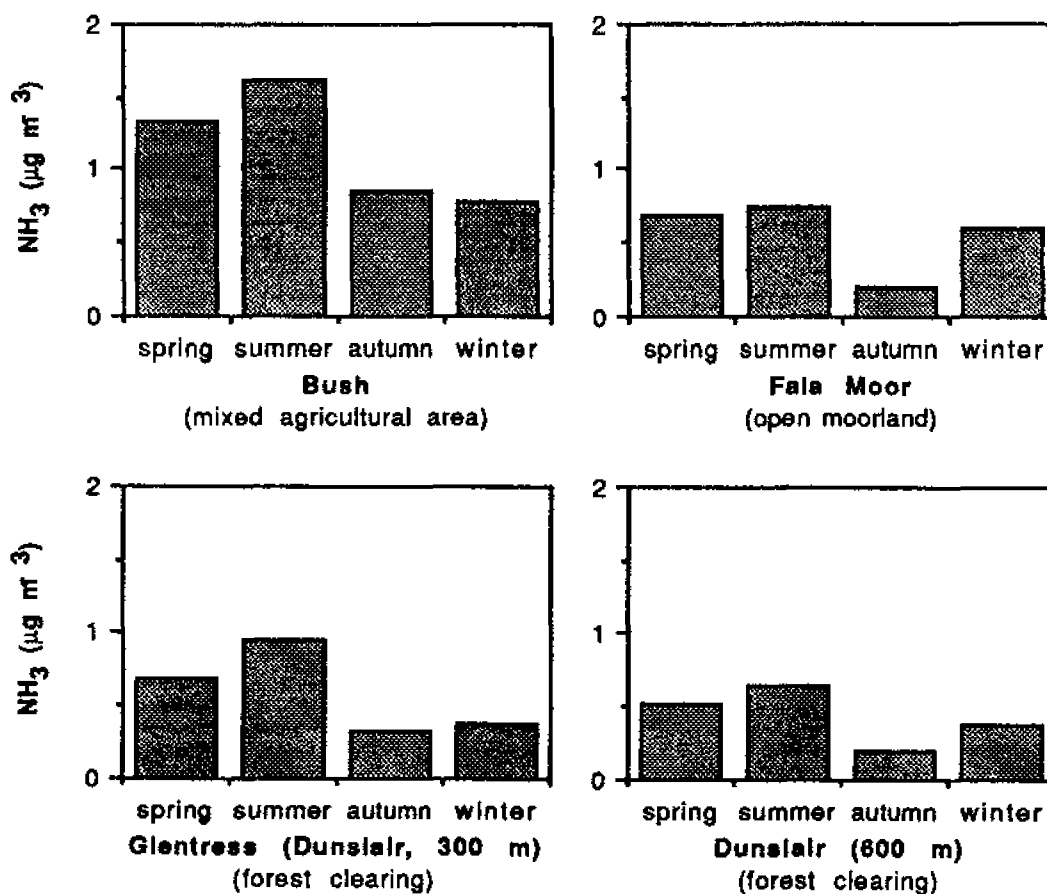


Figure 3. Bar charts of seasonal atmospheric NH<sub>3</sub> concentrations at four background rural sites in S. Scotland. Data from Table 5.



in the spring and summer and the lowest concentrations in the autumn and winter.

The results were compared with concentrations reported by RGAR (1990) which were made using similar diffusion tube techniques. The results of RGAR (1990) predict larger air concentrations in S. Scotland than reported here. Results of a field comparison and other data in the literature suggest the data of RGAR (1990) may overestimate concentrations by at least a factor of 2.

#### Interpretation of results and conclusions

The surface exchange results observed over the different vegetation types in different environmental conditions were considered in relation to each other and the literature of  $\text{NH}_3$  exchange measured by micrometeorological, controlled chamber and throughfall/stemflow methods.

It was concluded that the exchange of  $\text{NH}_3$  between the atmosphere is the net result of exchange with plant tissues through stomata and with the soil (bidirectional) and with uptake by leaf surfaces. It is probable that it is the higher nitrogen status of fertilised ecosystems which results in net emission frequently occurring from these surfaces.

The understanding of surface exchange developed, and reported in full by Sutton (1990) was used to estimate annual budgets of  $\text{NH}_3$  exchange for different surfaces. The results of these calculations are summarised in tables 6, 7 and 8. For short natural and unfertilised vegetation the calculations are straightforward, assuming  $r_c = 0$ . Depending on air concentration estimates at different sites,  $\text{NH}_3$  deposition at the sites considered varies between 3-10  $\text{kg N ha}^{-1} \text{ year}^{-1}$ . Deposition to forests is more uncertain, largely as a result of the different methods to calculate the boundary layer resistance ( $r_b$ ). The method of Wesely and Hicks (1977) is preferred, but requires rescaling of monitored  $\text{NH}_3$  air concentrations for effects of near surface depletion (Table 7). For the background sites

site type	location	$r_c$ (m)	$u$ (10 m) (m s <sup>-1</sup> )	ref. height (m)	$V_d$ <sup>b</sup> (mm s <sup>-1</sup> )	$\chi$ NH <sub>3</sub> ( $\mu\text{g m}^{-3}$ )	Deposition flux NH <sub>3</sub> -N <sup>b</sup> (kg ha <sup>-1</sup> year <sup>-1</sup> )
Moorland S. Scotland, upland	Fala Moor, Midlothian <sup>a</sup>	0.03	4.2 <sup>d</sup>	1.5	20.4	0.55 <sup>f</sup>	2.9
N. Scotland, remote	Lerwick, Shetland	0.03	7.1 <sup>a</sup>	1.5	33.0	$\approx 0.4$ <sup>h</sup>	3.4
Unfertilized meadow S. England, lowland	SSSI, Huntingdon <sup>a</sup>	0.02	3.6 <sup>d</sup>	2.5	16.0	$\approx 2.6$ <sup>g</sup>	10
Forest S. Scotland, upland	Glentress forest (300 m) <sup>a</sup>	0.5	3.3 <sup>e</sup>	1.5	34 (61)	0.58 <sup>f</sup>	5.1 (9.2)
	Glentress forest (600 m) <sup>a</sup>	0.3	5.3 <sup>e</sup>	1.5	48 (81)	0.44 <sup>f</sup>	5.4 (9.3)
C. Scotland, lowland	Glencorse wood, Bush <sup>a</sup>	1.0	3.9 <sup>d</sup>	1.5	46 (120)	1.1 <sup>f</sup>	13 (34)
E. England, lowland	Thetford forest, Norfolk	1.0	3.9 <sup>d</sup>	2.5	42 (99)	$\approx 2.6$ <sup>g</sup>	29 (67)
Agricultural crop C. Scotland, lowland Bush <sup>a</sup>	Calculations for when grass wet (see Table 7.5) winter ( $r_c = 0$ s m <sup>-1</sup> )	0.02	3.9 <sup>d</sup>	1.5	17.2	0.77 <sup>f</sup>	—
	spring ( $r_c = 50$ s m <sup>-1</sup> )	0.04	3.3 <sup>d</sup>	1.5	9.3	1.3 <sup>f</sup>	—
	summer ( $r_c = 100$ s m <sup>-1</sup> )	0.06	3.3 <sup>d</sup>	1.5	6.6	1.6 <sup>f</sup>	—
	autumn ( $r_c = 50$ s m <sup>-1</sup> )	0.02	4.4 <sup>d</sup>	1.5	9.8	0.85 <sup>f</sup>	—

Table 6. Ammonia surface exchange budgets for a range of U.K. natural and unfertilized vegetated surfaces. Calculations referenced at the height of NH<sub>3</sub> monitoring. Wet surface calculations for an agricultural crop at Bush are also given for inclusion in Table 8 below.

Notes: a, For further site details see Sutton (1990); b, For natural surfaces the deposition velocity is calculated assuming  $r_c = 0$ . In accordance with results for the wet agricultural crop surface, in Winter  $r_c = 0$  and in Summer  $r_c = 100$  s m<sup>-1</sup>; for Spring and Autumn  $r_c = 50$  s m<sup>-1</sup>.  $r_b$  is calculated according to Garland (1977). For forest sites, the method of Wesely and Hicks (1977) gives better estimates (values in brackets), but these need to be corrected for surface depletion (see Table 7).

Windspeed data sources: c, transformed from  $u$  (2 m) data for 1988–89 (Crossley, 1990, unpublished results); d, From the MORECS database (see Ball *et al.*, 1983); e, From Chandler and Gregory (1976).

Concentration data sources: f, From Chapter 6 diffusion tube data; g, Estimated from Allen *et al.* (1988); h, Estimated from EACN total NH<sub>x</sub> data (see Table 1.5, Sutton, 1990), assuming  $1/3$  NH<sub>x</sub> = NH<sub>3</sub>.

site	$V_d$ (10 m) (mm s <sup>-1</sup> )	$\chi$ (10 m) ( $\mu\text{g m}^{-3}$ )	Deposition flux NH <sub>3</sub> -N (kg ha <sup>-1</sup> year <sup>-1</sup> )
Glentress forest (300 m)	25, 38	0.77	5.0, 7.5
Glentress forest (600 m)	33, 47	0.58	5.0, 7.1
Glencorse wood, Bush	35, 67	1.45	13, 25
Thetford forest	35, 67	3.15	29, 55

Table 7. Ammonia deposition budgets for example forests in the U.K. calculated using at 10 m reference height above the surface. The deposition velocity,  $V_d$ , is calculated as  $1/(r_a\{10\text{ m}\} + r_b)$ . Concentrations are rescaled for surface depletion assuming monitoring is made over short unfertilized vegetation where  $r_c = 0$ . To a good approximation  $\chi\{10\text{ m}\} = 1.32 \chi\{1.5\text{ m}\} = 1.21 \chi\{2.5\text{ m}\}$  (see Appendix 8, Sutton, 1990).

Where paired values are given in the table, the first is calculated using the Garland (1977) formulation of  $r_b$  and the second using the Wesely and Hicks (1977) formulation. The latter method is considered to give better estimates of  $r_b$  over forest surfaces.

season	mean $T$ (°C)	mean flux $\text{NH}_3$ dry conditions ( $\text{ng m}^{-2} \text{s}^{-1}$ ) <sup>a</sup>	mean flux $\text{NH}_3$ wet conditions ( $\text{ng m}^{-2} \text{s}^{-1}$ ) <sup>b</sup>	mean flux $\text{NH}_3$ frozen conditions ( $\text{ng m}^{-2} \text{s}^{-1}$ ) <sup>c</sup>	% time surface: dry, wet, frozen <sup>d</sup>	mean seasonal flux $\text{NH}_3$ ( $\text{ng m}^{-2} \text{s}^{-1}$ ) <sup>e</sup>
Winter	4	—	13.2	4.9	0, 88, 12	12.2
Spring	8	-5	12.1	8.3	34, 61, 5	6.1
Summer	15	-15	10.6	—	60, 40, 0	-4.8
Autumn	10	-5	8.3	5.6	33, 61, 6	3.7
Annual background flux ( $\text{ng NH}_3 \text{m}^{-2} \text{s}^{-1}$ ):						4.3
Annual background flux ( $\text{kg NH}_3\text{-N ha}^{-1} \text{year}^{-1}$ ):						1.1
Additional emission following fertilization with $\text{NH}_4\text{NO}_3$ ( $\text{kg NH}_3\text{-N ha}^{-1}$ ):						-1.2
Additional emission during senescence/hay drying ( $\text{kg NH}_3\text{-N ha}^{-1}$ ):						-0.3
Overall annual flux ( $\text{kg NH}_3\text{-N ha}^{-1} \text{year}^{-1}$ ):						-0.4

Table 8. Example exchange budget of  $\text{NH}_3$  for a fertilized grass crop at Bush. Positive fluxes denote deposition. The main body of the table considers background exchange processes occurring throughout the year. Estimates of the increased emission following fertilizer application and during plant senescence/hay drying are included at the base of the table.

Notes: a, Typical values for the temperatures from the data collected at Bush 6/1988 and Stenton 6/1989; b, Calculated from Table 6; c, Calculated similarly to wet surface data but assuming  $r_c = 100 \text{ s m}^{-1}$ ; d, Data from 3 hourly values of state of ground at Edinburgh airport for 1989; e, Sum of % components: wet, dry or frozen.

considered,  $\text{NH}_3$  deposition to forests varies between 5 and 55 kg N ha<sup>-1</sup> year<sup>-1</sup>.

The results are compared with other components of N deposition by Sutton (1990) and it is concluded that dry deposition of  $\text{NH}_3$  is frequently the largest single component of atmospheric N deposition.

Conversely, a budget accounting for the bi-directional exchange over agricultural cut grassland gave an annual net emission of < 1 kg N ha<sup>-1</sup> year<sup>-1</sup> (Table 8).

A full summary of the findings of this study (Sutton 1990) is appended to this report along with the published and manuscript versions of Sutton *et al* (1989, 1991).

## AREAS REQUIRING FURTHER STUDY

More information is required on:

- The extent of increased  $r_c$  for unfertilized surfaces in very dry conditions (low humidity) or in the presence of high atmospheric  $\text{NH}_3$  concentrations. The effect of acid gases ( $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ) on this response and the chemical mechanism of deposition.
- The confirmation of increased  $r_c$  over unfertilized vegetation surfaces with exposed calcareous soil.
- The size of  $r_c$  for different temperatures in frozen conditions.
- The relative importance of surface wetness/dryness (free water and humidity) and temperature in controlling the bi-directional exchange over fertilized crop surfaces.
- The relative size of soil and plant compensation points for fertilized agricultural and unfertilized natural ecosystems, and the response to different fertilizer application rates.
- The magnitude of  $\text{NH}_3$  emission following fertilizer application to agricultural surfaces, from cut vegetation left in the field, and during senescence for both annual and perennial plant species.
- The concentration of  $\text{NH}_3$  in the atmosphere.
- The validity of passive diffusion tube measurements of  $\text{NH}_3$  concentrations.
- The extent of non-conservation of  $\text{NH}_3$  fluxes for different exchange situations.
- The magnitude of  $r_b$  over forests.
- The effect of  $\text{CO}_2$  on reducing  $\text{NH}_3$  solubility in water (separate from pH effects).

## RECOMMENDED CRITERIA FOR FUTURE MEASUREMENTS OF $\text{NH}_3$ SURFACE/ATMOSPHERE EXCHANGE

Further studies of the exchange of  $\text{NH}_3$  over vegetated surfaces should:

- define the vegetation, soil type and management, especially the use or absence of fertilizers.
- measure  $\text{NH}_3$  and  $\text{NH}_4^+$  separately so as to identify the exchange processes of each. This allows resistance and surface concentration analyses to be made.
- measure environmental variables during exchange measurements, particularly surface temperature, wetness and humidity.
- include both day and night-time measurements.
- where possible identify the source of any  $\text{NH}_3$  emission.

## PUBLICATIONS LIST

- Sutton M.A., Fowler D. and Moncrieff J.B. (1989) Measurement of atmospheric ammonia and the assessment of its exchange with vegetated surfaces. In: *Changing composition of the troposphere* (WMO technical conference, Sofia, 23–27 October 1989). Special Environmental Report No. 17 (WMO - No. 724), pp 154–157. World Meteorological Organization, Geneva, Switzerland.
- Sutton M.A. (1990) The surface/atmosphere exchange of ammonia. Ph.D. thesis, University of Edinburgh, UK.
- Sutton M.A., Moncrieff J.B. and Fowler D. (1991a) Deposition of atmospheric ammonia to moorlands. *Environ. Pollut.* (Submitted).
- Sutton M.A., Fowler D. and Moncrieff J.B. (1991b) Exchange of atmospheric ammonia with vegetated surfaces: unfertilized vegetation. (In preparation).
- Sutton M.A., Fowler D., Storeton-West R.L. and Moncrieff J.B. (1991c) Exchange of atmospheric ammonia with vegetated surfaces: fertilized vegetation. (In preparation).
- Sutton M.A. and Fowler D. (1991) Monitoring of atmospheric ammonia using passive diffusion tube samplers. (In preparation).

## REFERENCES

- Allen A.G., Harrison R.M., Wake M.T. (1988) A meso-scale study of the behaviour of atmospheric ammonia and ammonium. *Atmos. Environ.* **22**, 1347–1353.
- Ball D.F., Radford G.L. and Williams W.M. (1983) A land characteristic data bank for Great Britain. Bangor Occasional Paper No. 13. Institute of Terrestrial Ecology, Bangor Research Station, Penrhos Road, Bangor, Gwynedd, UK.
- Bietz J.A. (1974) Micro-Kjeldahl analysis by an improved automated ammonium determination following manual digestion. *Analytical Chem.* **46**, 1617–1618.
- Chandler T.J. and Gregory S. (1976) *The climate of the British Isles*. (Eds.) Longman, London. 390 pp.
- Crossley A.C. (1990) Unpublished results. Institute of Terrestrial Ecology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian, UK.
- Garland J.A. (1977) The dry deposition of sulphur dioxide to land and water surfaces. *Proc. Roy. Soc. London. A.* **354**, 245–268.
- Hargreaves K.J. and Atkins D.H.F. (1987) The measurement of ammonia in the outdoor environment using passive diffusion tube samplers. Report AERE-R-12568, Harwell Laboratory, Didcot, Oxon, UK.
- Harrison R.M. (1986) Personal communication. Institute of aerosol science, University of Essex, Colchester, Essex, UK.
- Sehmel G.A. (1980) Particle and gas dry deposition. A review. *Atmos. Environ.* **14**, 983–1012.
- Stevenson C.M. (1968) An analysis of the chemical composition of rain-water and air over the British Isles and Eire for the years 1959–1964. *Quart. J. Roy. Meteor. Soc.* **94**, 57–70.
- Sutton M.A. (1990) The surface/atmosphere exchange of ammonia. Ph.D. thesis, University of Edinburgh, UK.
- Thom A.S. (1975) Momentum, mass and heat exchange of plant communities. In: *Vegetation and the atmosphere*. Volume 1. (Ed: Monteith J.L.) pp 57–109. Academic Press, London.
- Thomas R. (1986) Personal communication. Macaulay Land Use Research Institute, Bush Estate, Penicuik, Midlothian, UK.
- Wesely M.L. and Hicks B.B. (1977) Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation. *J. Air Pollut. Control Assoc.* **27**, 1110–1116.

## LIST OF SYMBOLS

### Roman Alphabet

- $d$  zero plane displacement. Height of apparent (aerodynamic) ground level due to a rough surface such as vegetation (m)
- $F_{\chi}$  flux of trace gas or particulate to or away from a surface ( $\mu\text{g m}^{-2} \text{s}^{-1}$ )
- $k$  von Karman's constant. Constant of proportionality of mixing length ( $l$ ) to height above zero plane in neutral conditions (0.41)

$L$	Monin-Obukhov stability length. Estimate of atmospheric stability above a surface. Independent of height within the constant flux layer (m)
$r_t\{z-d\}$	total resistance to deposition of a trace component, from a defined height above the zero plane. Inverse of deposition velocity ( $\text{s m}^{-1}$ ).
$r_a\{z-d\}$	atmospheric resistance of a trace component to turbulent transfer between the atmosphere and a surface ( $\text{s m}^{-1}$ )
$r_b$	resistance to transfer for entrained properties across quasi-laminar sub-layer surrounding roughness elements of a surface ( $\text{s m}^{-1}$ )
$r_c$	surface or canopy resistance to deposition. A residual or excess resistance between $r_t$ and $(r_a + r_b)$ , assuming surface concentration is zero.
$r_{sE}$	stomatal resistance to water vapour transfer ( $\text{s m}^{-1}$ )
$r_{sEb}$	bulk stomatal resistance to water vapour transfer ( $\text{s m}^{-1}$ )
$T$	temperature ( $^{\circ}\text{C}$ or $\text{K}$ ).
$u$	mean horizontal windspeed ( $\text{m s}^{-1}$ ).
$u_*$	eddy (or friction) velocity ( $\text{m s}^{-1}$ )
$u\{z-d\}$	mean horizontal windspeed at a given height above the zero plane ( $\text{m s}^{-1}$ ).
$V_d\{z-d\}$	deposition velocity of gaseous or particulate species at a given height above the zero plane ( $\text{mm s}^{-1}$ )
$V_m\{z-d\}$	maximum value of the deposition velocity permissible by turbulence, $1/(r_a + r_b)$ ( $\text{mm s}^{-1}$ )
$z$	distance; height above the ground; diffusion tube path-length (m)
$z_\chi$	apparent height above zero plane of predicted zero concentration, from linearized concentration profile (m).
$z_0$	roughness length. Apparent height above zero plane of predicted zero windspeed, from linearized wind profile. Mean point of absorption of momentum (m)
$z_0'$	apparent height above the zero plane of the mean point of exchange of entrained properties with a surface, accounting for $r_a$ and $r_b$ (m)
$z_0''$	as $z_0'$ but also accounting for a surface resistance e.g. $r_{sEb}$ (m)

#### Greek alphabet

$\chi\{z-d\}$	mean concentration of trace gas or particulate in the atmosphere at a defined height $\{z-d\}$ above the zero plane of the surface ( $\mu\text{g m}^{-3}$ )
$\chi_*$	eddy concentration ( $\mu\text{g m}^{-3}$ )
$\chi_{cp}$	compensation point concentration. Supposed concentration in atmosphere in equilibrium with vegetated surfaces ( $\mu\text{g m}^{-3}$ )
$\psi\{(z-d)/L\}$	empirically estimated integrated profile correction factor for non-neutrality in the aerodynamic gradient method. Subscripted: M, momentum; H, heat; $\chi$ , trace components (dimensionless)



## Abstract of Sutton (1990) Ph.D. thesis

Measurements of the exchange of gaseous ammonia ( $\text{NH}_3$ ) and particulate ammonium ( $\text{NH}_4^+$ ) between the atmosphere and a range vegetated surfaces were made using micrometeorological techniques. The aerodynamic gradient method was applied to estimate fluxes, and these interpreted using a resistance analogy and estimates of surface concentration. The results are used to develop an understanding of exchange processes with a view to estimating annual budgets for different surfaces.  $\text{NH}_4^+$  was found to deposit very slowly so that the study focused on the exchange of  $\text{NH}_3$ .

Over natural and unfertilized vegetation,  $\text{NH}_3$  was generally found to deposit rapidly with near zero surface resistance ( $r_c$ ). Some exceptions were seen for dry vegetation ( $r_c < 50 \text{ s m}^{-1}$ ) and over vegetation with exposed calcareous soil (mean  $r_c = 125 \text{ s m}^{-1}$ ). Over fertilized agricultural vegetation both emission and deposition fluxes were recorded, with emission being favoured in warm dry conditions, and deposition in cool wet conditions. In wet conditions in summer  $r_c$  was variable ( $0\text{--}130 \text{ s m}^{-1}$ ), whereas in winter  $r_c$  was small ( $< 30 \text{ s m}^{-1}$ ). During frozen conditions an increased  $r_c$  of up to  $80 \text{ s m}^{-1}$  was observed. In dry summer conditions emission of up to  $24 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$  was recorded. The estimation of the net 'compensation point' for exchange using surface concentration estimates is discussed, and shown to range over  $0\text{--}7 \mu\text{g m}^{-3}$  in the study here depending on surface type and environmental conditions.

The different exchange patterns seen over unfertilized and fertilized vegetation are compared and described in terms of the net exchange with the surface resulting from exchange with leaf surfaces, stomata and the soil. Factors affecting these processes are discussed and include environmental conditions (particularly temperature, wetness and humidity), the presence of acidic pollutants, and the status of the surface (including nitrogen status, stomatal opening, soil pH). Implications are drawn for the concentration dependence of exchange rates and approaches to modelling the atmospheric behaviour of  $\text{NH}_3$ .

In order to estimate annual fluxes, atmospheric concentrations of  $\text{NH}_3$  are needed. Background annual concentrations of  $\text{NH}_3$  measured in this study at several sites in S. Scotland were in the range  $0.4\text{--}1.1 \mu\text{g m}^{-3}$ . Using these and other published data, annual fluxes over different surfaces are estimated. Over an example fertilized surface a small net  $\text{NH}_3$  emission is predicted ( $< 1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ), while over unfertilized surfaces larger deposition fluxes are expected ( $3\text{--}55 \text{ kg N ha}^{-1} \text{ year}^{-1}$  for the background sites considered). Comparison with other sources of atmospheric N shows that dry deposition of  $\text{NH}_3$  is frequently the dominant N input to unfertilized surfaces.

## Summary of Sutton (1990) Ph.D. thesis

- The atmosphere contains trace quantities of ammonia gas ( $\text{NH}_3$ ) and particulate ammonium ( $\text{NH}_4^+$ ) in approximately similar concentrations. Background concentrations are usually in the range  $0.01\text{--}10 \mu\text{g m}^{-3}$ , though near sources much higher  $\text{NH}_3$  concentrations ( $>100 \mu\text{g m}^{-3}$ ) may occur.
- Monitoring of  $\text{NH}_3$  concentrations in this study using passive diffusion tubes showed mean background concentrations in rural areas in S. Scotland to range between  $0.4$  and  $1.1 \mu\text{g m}^{-3}$ .
  - This is much smaller than the concentrations measured, using similar diffusion tubes to those here, by a national monitoring network in the U.K., the results of which have been reported by RGAR (1990). These give a regional average of  $1.5$  to  $3 \mu\text{g m}^{-3}$  for S. Scotland. A sampling comparison performed in this study confirmed that the methods used in the national network provide larger estimates of air concentration than those here. Other available data suggest that the results reported by RGAR (1990) typically over-estimate air concentrations (and therefore deposition) by at least a factor of 2. As a consequence, the national network data are not used here for the estimation of dry deposition budgets (see below).
  - Possible errors in  $\text{NH}_3$  diffusion tube sampling arise from sampling artifacts ( $\text{NH}_3$  deposition to tube walls, capture of  $\text{NH}_4^+$ , wind enhancement of sampling) and analytical artifacts (deposition to samples from laboratory air, inclusion of contaminated samples). Measures to reduce analytical artifacts may account for the difference between the results here and those given by RGAR (1990).
- Evidence in the literature suggests that emissions to the atmosphere occurs as  $\text{NH}_3$ , the main source being from livestock agriculture, which may be converted in the atmosphere to  $\text{NH}_4^+$ .
- The dry deposition of  $\text{NH}_4^+$  particles is expected to be a very slow process, which is confirmed by micrometeorological field measurements in this study. Most of the  $\text{NH}_4^+$  therefore becomes dissolved in precipitation and is returned to earth as wet deposition.
- The major part of this study focused on the measurement of the surface exchange of gaseous  $\text{NH}_3$  using micrometeorological methods. The background exchange over different vegetated surfaces in a temperate climate was considered and included measurements over natural and unfertilized surfaces, and fertilized agricultural surfaces:
  - Measurements over natural and unfertilized vegetation generally recorded rapid deposition of  $\text{NH}_3$  with minimal surface resistance ( $r_c$ ), which shows that the surface behaves largely as a perfect sink, with  $\text{NH}_3$  being deposited onto leaf

surfaces rather than through stomata. Some exceptions to this pattern were seen. In dry conditions a small  $r_c$  ( $< 50 \text{ s m}^{-1}$ ) was sometimes recorded, while over a surface with exposed calcareous soil a mean  $r_c$  of  $125 \text{ s m}^{-1}$  was found.

- Measurements over fertilized agricultural vegetation showed both emission and deposition to occur. Emission was favoured in warm dry conditions, with fluxes in summer of up to  $24 \text{ ng m}^{-2} \text{ s}^{-1}$  being measured. In wet conditions deposition was recorded. Measurements to wet surfaces in summer showed  $r_c$  to be variable ( $0\text{--}130 \text{ s m}^{-1}$ ), while winter-time measurements showed rapid deposition to wet surfaces ( $r_c < 30 \text{ s m}^{-1}$ ). During a period of light frost an increased  $r_c$  of up to  $80 \text{ s m}^{-1}$  was observed.
- The different surface exchange patterns observed are interpreted in terms of the net effect of leaf surface, stomatal and soil exchange processes:
  - Deposition to leaf surfaces is a major uptake mechanism, which may be enhanced in wet conditions. Acid gases, particularly  $\text{SO}_2$ , may enhance leaf surface uptake, often referred to as co-deposition.  $\text{HNO}_3$  and  $\text{HCl}$  may also have some effect. Partial or complete saturation of this sink may occur in very dry (low humidity) conditions or in the presence of very high concentrations of  $\text{NH}_3$ , such as with a crop emitting  $\text{NH}_3$  or in the presence of high atmospheric concentrations.
  - Stomata and soil can act as either sources or sinks of  $\text{NH}_3$ , depending on the Henry equilibria of  $\text{NH}_3$  and  $\text{NH}_4^+$  in plant tissues and soil water with atmospheric concentrations of  $\text{NH}_3$ . The atmospheric concentration in equilibrium with the surface is often referred to as the 'compensation point' ( $\chi_{cp}$ ). Where air concentrations are less than  $\chi_{cp}$  emission occurs, whereas with air concentrations larger than  $\chi_{cp}$  deposition occurs. The compensation point concept is most usually applied to the exchange of  $\text{NH}_3$  through stomata, though equally soil  $\chi_{cp}$  and overall canopy or net  $\chi_{cp}$  may be defined.
  - Over natural and unfertilized vegetation it is probable that the low N status results in small stomatal and soil  $\chi_{cp}$ , with the result that leaf surface deposition dominates and the net  $\chi_{cp}$  is small. Where  $r_c = 0$  the net  $\chi_{cp}$  is by definition zero.
  - Over fertilized agricultural vegetation the higher N status results in larger  $\chi_{cp}$ , and emission may occur through either stomata or soil. However, during wet conditions these  $\chi_{cp}$  have little effect on the net exchange as leaf surface deposition dominates, and the net  $\chi_{cp}$  again approaches zero.
  - Surface concentrations may be predicted by extrapolation of the concentration gradient using a modified resistance analysis, and these may be used as estimates of  $\chi_{cp}$ . Where emission is through stomata alone and stomatal resistance known,

estimates of the stomatal  $\chi_{cp}$  may be made (referred to as  $\chi(z_0)$ ). For an agricultural crop in dry summer conditions  $\chi(z_0)$  was 2–7  $\mu\text{g m}^{-3}$ . Given that some leaf surface deposition may also have been present, this may be an underestimate of the stomatal  $\chi_{cp}$ .

- This understanding is used with the results of the air concentration monitoring from this study and other published values to estimate annual budgets for different example U.K. ecosystems. Examples are for typical exchange not affected by local sources.

- Over the natural and unfertilized surfaces examined, estimated  $\text{NH}_3$  deposition ranges from 3 to 55  $\text{kg N ha}^{-1} \text{ year}^{-1}$ . Estimates are sensitive to air concentration, site roughness (e.g. short grass or forest) and prevailing windspeed at a site.

- The largest deposition is expected to forests in lowland Britain where  $\text{NH}_3$  concentrations are frequently higher than in upland areas. However, estimates over forests are very sensitive to the value of the laminar boundary-layer resistance,  $r_b$ , which is a major uncertainty in the calculations.

- Where a  $\chi_{cp}$  exists for fertilized surfaces it is attractive to be able to include this in models of exchange alongside monitored air concentrations and transfer resistances. However, given the spatial and temporal variability of the net  $\chi_{cp}$ , this is beyond the scope of simple models with only long term air concentration inputs.

- To model annual exchange over an agricultural surface a simplified approach is used in this study. The percentage time the surface is dry, wet or frozen in different seasons is found, and fluxes for each condition summed to provide net seasonal and annual fluxes. Typical emission estimates are used for dry conditions, while a deposition velocity approach is used in wet and frozen conditions.

- A calculated example budget of background exchange for a fertilized agricultural surface shows that in summer net emission occurs, whereas the other seasons show net deposition. If the emission following fertilizer application and probable extra losses during crop senescence or hay drying are included, the net annual  $\text{NH}_3$  emission of is  $< 1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . Large uncertainty applies in using this as typical for fertilized crop surfaces in the U.K. Other sites with larger levels of N fertilization may show emission of  $> 5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ .

- Implications for atmospheric models are drawn from the difference between fertilized and unfertilized surfaces and it is concluded that applying a fixed deposition velocity for all land surfaces contributes to the discrepancy between predicted and observed deposition.

- The total N inputs into specific natural and unfertilized ecosystems are estimated and comparisons made of the contribution from different sources. Dry deposition

of  $\text{NH}_3$  is frequently the largest single N input, which emphasizes the importance of understanding  $\text{NH}_3$  surface exchange processes. Including wet deposited  $\text{NH}_4^+$ ,  $\text{NH}_x$  accounts for 60–80 % of the total N input to the examples considered, as compared to 20–40 % from oxidized N species ( $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{NO}_3^-$ ), giving a total deposition of 10–75  $\text{kg N ha}^{-1} \text{ year}^{-1}$ . Near sources of  $\text{NH}_3$  emission (mainly livestock agriculture) the deposition could be several times larger than this.

◦ A comparison of the relative acidifying inputs into the example ecosystems is also given, though since the acidifying effect of pollutants depends on their fate when deposited only general conclusions may be made. In particular nitrification of deposited  $\text{NH}_x$  to  $\text{NO}_3^-$  is an acidifying process. Comparison may be made either of the suite of deposited pollutants, or according to the origin of the acidity as emitted pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ). Because of atmospheric neutralization of oxidized S and N by  $\text{NH}_3$  to form  $\text{NH}_4^+$ , much of the acidifying deposition in the examples (up to 60–80%) is as  $\text{NH}_x$  rather than free acidity. Emission of  $\text{NH}_3$  accounts for between a maximum of 30–70% of the potential acidity. Plant uptake of deposited N may reduce these figures substantially. This applies for the products of both  $\text{NO}_x$  and  $\text{NH}_3$ , so that  $\text{SO}_2$  emission is frequently the dominant acidifying input. Conversely, where N deposition exceeds plant uptake,  $\text{NH}_3$  emission may have a sizeable or even dominant acidifying effect.

• A comparison of the background deposition estimates of total N with current estimates of critical loads given in the literature shows that N deposition in the U.K. is typically in excess of the critical loads. This is especially clear for forests in lowland Britain where deposition may be several times the critical load. Given the importance of  $\text{NH}_3$  in dominating the N deposition and contributing to the acidification of natural and unfertilized ecosystems, it is clear that emission control policies aimed at reducing  $\text{SO}_2$  and  $\text{NO}_x$  emissions will only have limited effectiveness. In order to achieve major reductions in deposition, particularly in the case of N inputs, additional policies controlling  $\text{NH}_3$  emission are required. Given the agricultural origin of the  $\text{NH}_3$  emission, measures would require changes in farming practice. Major reductions in emission may be achieved by soil incorporation or injection of surface spread liquid manure, acidification of manure, and the use of closed manure storage.

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# MEASUREMENT OF ATMOSPHERIC AMMONIA AND THE ASSESSMENT OF ITS EXCHANGE WITH VEGETATED SURFACES

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## ABSTRACT

Two methods of gaseous  $\text{NH}_3$  measurement have been used in a study to assess surface / atmosphere exchange, and to monitor ambient concentrations. Fluxes measured using the aerodynamic gradient method with filter packs, showed  $\text{NH}_3$  to be deposited efficiently over most natural vegetation studied. Arable surfaces gave either deposition or emission, with dry, warm conditions favouring the latter. Monitoring  $\text{NH}_3$  using diffusion samplers provided air concentrations in S.E. Scotland, which were  $0.5\text{--}1.5 \mu\text{g m}^{-3}$  at rural sites. From this, two example budgets for natural sites in the U.K. are considered.

## 1. INTRODUCTION

Interest in atmospheric  $\text{NH}_3$  has grown recently because of its apparent effects, both on atmospheric chemistry and ecosystems. (eg Allen et al, 1988; Nilgardt, 1985)

It is therefore necessary to quantify the transfer of  $\text{NH}_3$  between the atmosphere and the ground and to monitor ambient concentrations. This paper reports the use of two methods for  $\text{NH}_3$  measurement and the results of  $\text{NH}_3$  surface atmosphere exchange studies. The results of gaseous  $\text{NH}_3$  monitoring in S. E. Scotland are also provided. These are then used to discuss mechanisms of exchange, and to estimate budgets for different surfaces.

## 2. SURFACE EXCHANGE MEASUREMENT

### 2.1. Theory

The aerodynamic gradient method is used, which involves making measurements of windspeed, gas concentration and temperature at several heights above a uniform ground surface. The resulting profiles may be then used to infer surface fluxes. (Garland, 1977)

Given a windspeed  $U$ , the flux of  $\text{NH}_3$  ( $F_g$ ), of concentration  $X$ , may be found as the product of the eddy velocity and eddy concentration ( $U^*$ ,  $X^*$ ), where these may be defined by the following

linear functions against height ( $z$ ) above the zero plane of the surface ( $d$ ):

$$U(z-d) = \frac{U^*}{k} \left[ \ln(z-d) + f_u \left( \frac{z-d}{L} \right) \right] - \frac{U^*}{k} \ln(z_0)$$

$$X(z-d) = \frac{X^*}{k} \left[ \ln(z-d) + f_x \left( \frac{z-d}{L} \right) \right] - \frac{X^*}{k} \ln(z_x)$$

Here  $k$  is von Karman's constant, 0.41,  $z_0$  and  $z_x$  are the extrapolated zero heights of wind and concentration, and  $f_u$ ,  $f_x$  are profile corrections for non neutral conditions, based on the Monin-Obukhov stability length,  $L$ .

Assuming zero surface concentration a deposition velocity ( $V_g$ ) may be defined, at a reference height of 1 m:

$$V_g(1 \text{ m}) = F_g/X(1 \text{ m}) = 1/r_t(1 \text{ m})$$

Here  $r_t$  represents the total resistance to transfer. A residual surface resistance,  $r_c$ , may also be deduced from the difference between  $r_t$  and the resistance to transfer through the atmospheric boundary layer (Garland, 1977):

$$r_c = r_t(1 \text{ m}) - (r_a(1 \text{ m}) + r_b)$$

Here  $r_a$  and  $r_b$  are the turbulent and laminar boundary layer resistances respectively. Another way of interpreting the excess described by  $r_c$  is to assume rapid transfer limited by a non-zero surface concentration at the effective height of absorption ( $z_0'$ ):

$$X(z_0') = X(1 \text{ m}) - F_g(r_a(1 \text{ m}) + r_b)$$

Both  $r_c$  and  $X(z_0')$  are useful in interpreting exchange rates.

### 2.2 Ammonia measurement

The gradient method requires precise short term estimates of concentration (<3 hr). This may be met by a dual filter system (Harrison et al, 1987). Here 90 mm diameter filters are used, sampling at  $0.75 \text{ m}^3 \text{ hr}^{-1}$ . A teflon membrane filter (1  $\mu\text{m}$ ) removes particulate  $\text{NH}_4^+$ , followed by an acidified paper filter to capture  $\text{NH}_3$  gas. Paper filters are prepared by

repeated pre-extraction of batches of about 100 in 7.5% phosphoric acid, to reduce blank values. They are then dried on racks in a clean air chamber with  $\text{NH}_3$  removed, to prevent redeposition. Exposed filters and blanks are analysed by continuous flow with the indophenol reaction (Bietz, 1974), in a clean air chamber.

### 2.3 Gradient system

Profiles of  $\text{NH}_3$ , using 5 filter packs are made up to 2.5 m above the ground. Profiles of windspeed and temperature are measured by sensitive cup anemometers and fine thermocouples respectively.

### 3. AMMONIA MONITORING: DIFFUSION TUBES

For monitoring purposes a simple long term method is desirable. A passive system which samples by molecular diffusion is used here, (Hargreaves and Atkins, 1987) and is convenient since no power supply is needed at field sites. Small teflon tubes, 7 x 1 cm, are capped at one end, under which a glassfibre disc (Whatman GF/A), impregnated with dilute acid is placed to absorb  $\text{NH}_3$ . Blanks are minimized by extraction for several hours in a Soxhlet apparatus and drying *in situ* in a clean air stream. The resulting concentration gradient up the tube gives an effective sampling rate of  $1 \times 10^{-4} \text{ m}^3 \text{ hr}^{-1}$ . In general 5 tubes are set out for 3 weeks at each site and compared against

Table 1. Summary of deposition measurements over natural vegetation. Errors in  $X(z_0')$  are 95% limits of the mean of runs. \*The grass had recently been harrowed (soil pH = 8.4).

Site	surface conditions	$\bar{X}$ $\mu\text{g m}^{-3}$	$V_g$ $\text{cm s}^{-1}$	median $r_c$ $\text{s m}^{-1}$	$X(z_0')$ $\mu\text{g m}^{-3}$
Moorlands:					
Great Dun Fell	mostly wet	0.7	2.8	4.9	$0.0 \pm 0.3$
Fala Moor	dry+ wet	0.7	4.7	0.5	$-0.1 \pm 0.2$
Natural Grasslands:					
Huntingdon	dry+ wet	2.0	1.7	-2.6	$-0.1 \pm 0.7$
Harwell*	dry+ wet	1.8	0.8	121	$1.0 \pm 1.1$
Coniferous Forest:					
Glentress	wet+ dry	0.2	6.6	(51)	-0.3

10 blanks, though occasional loss and contamination may reduce this.

### 4. SURFACE / ATMOSPHERE EXCHANGE RESULTS

The wind and temperature profiles were measured to a high precision. The filter pack system also performed well, for the most part giving good profiles at all but the lowest air concentrations. Errors are nevertheless dominated by the  $\text{NH}_3$  profile estimates. Figure 1. shows the profiles for one run, where deposition was occurring.

#### 4.1 Natural Vegetation

A summary of measurements over 'natural surfaces' is given in Table 1. Deposition is occurring to all surfaces measured. Both moorland and the grassland at Huntingdon appear to have a minimal surface resistance ( $r_c$ ) and correspondingly near zero surface concentrations ( $X(z_0')$ ). The effect of surface drying on the uptake appeared to be very small. This is demonstrated for Fala Moor in Figure 2. Over forest, measurements were only very approximate, since air concentrations were small and rapid mixing by turbulence over the rough surface means that the measurable gradients over forests are also very small. However a general trend of rapid deposition was again observed.

The measurements at Harwell over a harrowed calcareous field (pH = 8.4) gave the only unequivocal surface resistance. Since deposition occurred even during periods of low concentration the interpretation via  $r_c$  would seem more appropriate than  $X(z_0')$ .

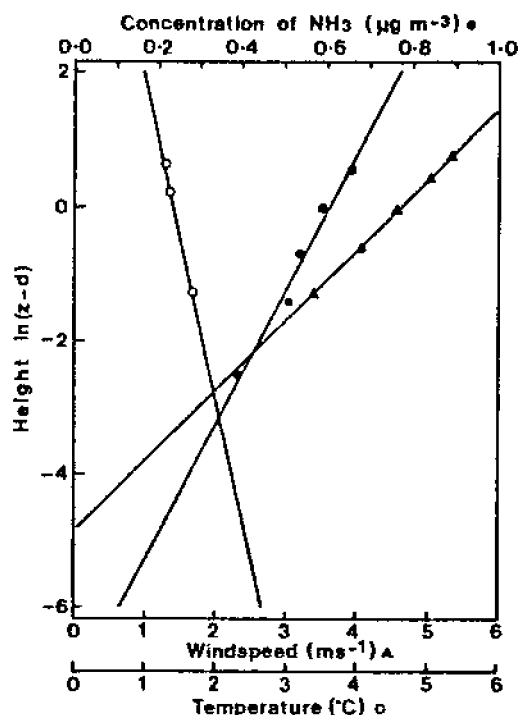


Figure 1. Example profiles for one run at Great Dun Fell. (Deposition:  $r_c = 3.3 \text{ s m}^{-1}$ )



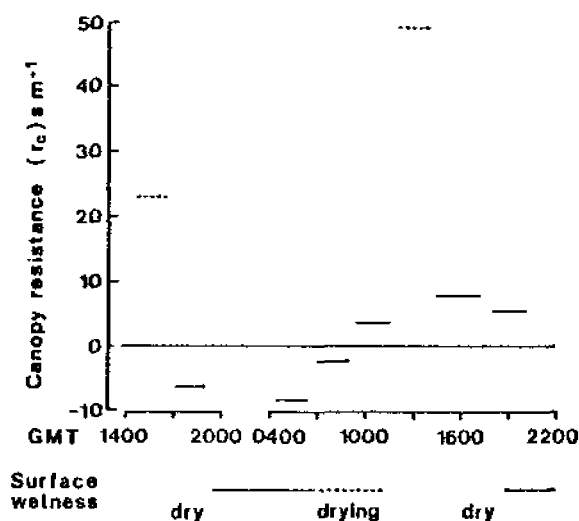


Figure 2. Surface (canopy) resistance for varying surface wetness. Bars show run duration. Dashed bars note poor profiles. For the good data  $r_c$  is consistently small.

#### 4.2 Intensive arable systems

Results were found to vary greatly with environmental conditions. The results are therefore summarized as ranges rather than averages (Table 2.). Figure 3. gives the results for summer crop grass at Bush. Emission predominates and appears to increase in warm and dry conditions. Canopy profiles showed the crop to be the source. A clear relationship with  $X(z_0')$  is seen, since this relates to the surface potential for emission, although if a surface resistance to emission is

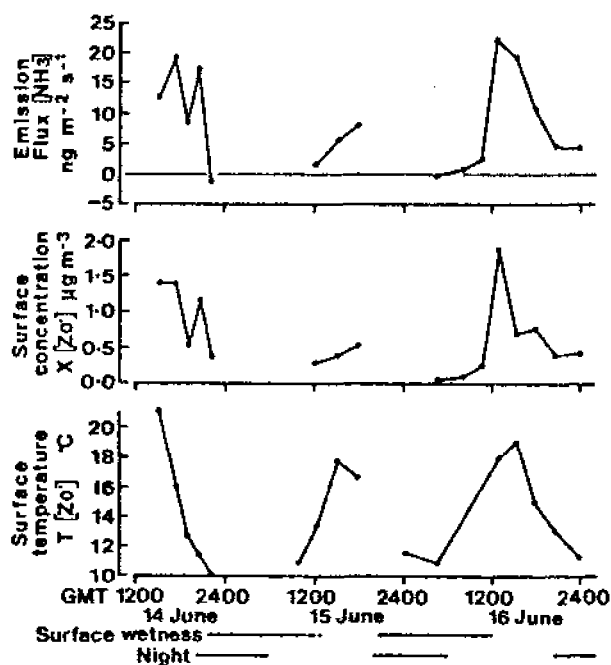


Figure 3. Ammonia fluxes compared with surface concentration and temperature for crop grass at Bush. For explanation see text.

Table 2. Ranges of values measured over intensive arable systems, in summer. A negative flux implies deposition.

Site	emission			
	X $\mu\text{g m}^{-3}$	flux $\text{ng m}^{-2} \text{s}^{-1}$	$X(z_0')$ $\mu\text{g m}^{-3}$	$T(z_0')$ $^{\circ}\text{C}$
Crop Grass - Bush:				
dry+wet	0.0 1.0	-2 20	0.0 1.8	10 22
Barley - Stenton:				
dry+wet	0.5 1.3	-4 19	0.6 1.7	5 19

Table 3. Seasonal means of ammonia concentrations ( $\mu\text{g m}^{-3}$ ) at several sites in S.E. Scotland. \*Inclusion of one dubious outlying run (10.5) would make this 2.5

Sites	winter	spring	summer	autumn
Bush	0.77	1.34	1.62	0.85
Glentress Forest (altitude):				
(600 m)	0.38	0.53	0.65	0.19
(300 m)	0.37	0.68	0.95	0.32
Fala Moor	0.59	0.69	0.74*	0.19
Livestock Farm	3.68	11.2	-	-

also present actual values will be higher.

Other runs at Bush in winter (not described here) support these trends with deposition toward the cold, wet surface. For the barley it was less clear where the emission source lay.

#### 5. AMMONIA MONITORING RESULTS

The diffusion tubes performed well, being simpler to operate than the filter packs. A summary of seasonal concentrations at 5 sites is given in Table 3. Concentrations are clearly seasonally dependent being highest in spring and summer. The farm site (2 km S. of Fala Moor) gave the highest concentrations. Bush, gave the next highest levels, being in an agricultural area. The other sites represent background levels remote from sources.

#### 6. DISCUSSION

The near zero  $r_c$  measured for most of the natural sites shows deposition must be to the external surfaces of leaves. For wet conditions this may be explained by the high solubility of  $\text{NH}_3$  in water according to Henry's Law. However deposition was also efficient in dry conditions. This gives field evidence for the chamber work of van Hove et al (1989), who suggested that a bound water layer is present on

leaf surfaces, increasing at higher humidities, which may enable deposition of soluble trace gases. In the presence of SO<sub>2</sub>, rates of NH<sub>3</sub> deposition are enhanced, and *visa versa*. The opposing pH of each is seen as increasing the solubility of the other. It is reasonable that SO<sub>2</sub> also present in the atmosphere, and possibly other acid gases, could have been stimulating the deposition we observed.

Duyzer et al (1988) have recently measured NH<sub>3</sub> deposition on moorland, with results broadly in agreement with these, however with some tendency toward larger values of r<sub>c</sub>. This difference could relate to lower humidities, or a different ratio of NH<sub>3</sub>/SO<sub>2</sub> in their experiments. It is reasonable that at high NH<sub>3</sub> levels with only background SO<sub>2</sub>, NH<sub>3</sub> saturation of the leaf surfaces could occur. In accordance with this, our most recent studies have included measurements of water vapour and SO<sub>2</sub> gradients. The clear r<sub>c</sub> seen in the Harwell data may confirm this interaction, since the elevated pH, due to harrowing the chalk soil, would reduce NH<sub>3</sub> solubility.

Exchange of NH<sub>3</sub> has previously been thought of in terms of a temperature dependent 'compensation point' being the sub-stomatal equilibrium NH<sub>3</sub> level (Farquahar et al, 1980). The direction of exchange depends on the corresponding air concentration. The results here show it not to occur in practice over natural vegetation, because of these surface reactions. By definition if r<sub>c</sub> is zero,

so is X(z<sub>0</sub>'). A form of compensation point is seen though in the arable system at Bush, but this is presumably much modified by the surface and varying wetness as well as by temperature.

It is clear from this that budget estimation over arable surfaces is a complex task. We can still approximate easily for undisturbed natural surfaces however, taking r<sub>c</sub> = 0. Example budgets for two sites are given in Table 4. Compared with wet deposition dry NH<sub>3</sub> clearly provides a large fraction of total NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> input. Values will depend on site roughness and NH<sub>3</sub> concentration, though, noting the above discussion, some caution is needed about extrapolation to much drier climates and cases of very high NH<sub>3</sub> concentration.

Table 5. Dry deposition of ammonia gas compared to wet deposition for 2 British sites: an upland moor (Fala Moor) and an unfertilized lowland meadow (Huntingdon). † Allen et al, 1988; \* Warren Spring Lab, 1989

	X µg m <sup>-3</sup>	Vg cm s <sup>-1</sup>	deposition flux-N Kg ha <sup>-1</sup> yr <sup>-1</sup>	
			NH <sub>3</sub> dry	NH <sub>4</sub> <sup>+</sup> wet*
Moorland (Fala Moor)	0.64	3.0	5.0	4
Meadow (Huntingdon)	2.6 †	1.7	11.5	5

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#### REFERENCES

- Allen, A.G., R.M.Harrison and M.T.Wake, 1988: A meso-scale study of the behaviour of atmospheric NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. *Atmos. Env.*, 42, 1347-1353.
- Duyzer, J.H., A.M.H.Bouman, H.S.M.A.Diederer and R.M.van Aalst, 1987: Measurements of dry deposition velocities of NH<sub>3</sub> and NH<sub>4</sub> over natural terrains. TNO report R87/273. Ministry of Housing Phys. Planning and Env., Delft, The Netherlands.
- Farquahar, G.D, P M Firth, R Wetselaar and B Weir, 1980: On the gaseous exchange of ammonia between leaves and the environment, determination of the ammonia compensation point. *Plant Physiol.* 66, 710-714.
- Garland, J.A., 1977: The dry deposition of sulphur dioxide to land and water surfaces. *Proc. R. Soc.* A354, 245-268.
- Hargreaves, K.J. and D.H.F.Atkins, 1987: The measurement of ammonia in the outdoor environment using passive diffusion tube samplers. UKAEA Report 12568, Harwell, Didcot, Oxon, UK.
- Nihlgard, N., 1985: The ammonium hypothesis: an additional explanation to the forest dieback in Europe. *Ambio*, 14, 2-8.
- Bietz, J.A., 1974: Micro-kjeldahl analysis by an improved automated ammonia determination following manual digestion. *Anal. Chem.*, 46, 1617-1618.
- Hove, van L.W45.A., E.H.Adema, W.J.Vredenberg and G.A.Pieters, 1989: A study of the adsorption of NH<sub>3</sub> and SO<sub>2</sub> on leaf surfaces. *Atmos. Env.* 23, 1479-1486.
- Warren Spring Laboratory, 1987: United Kingdom acid rain monitoring. Div. Air Pollution, WSL, Department Trade and Industry, Stevenage, U.K.