Final Report

The surface/atmosphere exchange of gaseous ammonia

Special topic in atmospheric chemistry, phase II
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M A Sutton, D Fowler and J B Moncrieff

Institute of Terrestrial Ecology, Edinburgh Research Station, Bush Estate,
Penicuik, Midlothian EH26 OQB.

Institute of Ecology & Resource Management, (previously Department of
Forestry & Natural Resources), University of Edinburgh.

Contents

Abstract

Micrometeorological measurements of the exchange of gaseous NH_3 and NH_4^+ have been made over a wide range of vegetated surfaces. The results are interpreted in temrs 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 NH_3 for different vegetated surfaces. Over unfertilised vegetation in the UK dry deposition of NH_3 is frequently the largest single input of atmospheric N, whereas over ungrazed fertilised agricultural vegetation there is a small net emission of NH_3 (eg < 1 kg N ha^{-1} 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 NH_3 and NH_4^+ over a range of vegetated surfaces.

b)   To use the results of a) to estimate annual exchange budgets of NH_3 and 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 NH_3 concentration data, with, for example, the only published data for Scotland being the total NH_x (NH_3 + 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 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 NH_3 and NH_4^+ using filter pack samplers (Harrison et al, 1986, pers. comm.).

c)   Chemical analysis of 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 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 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 NH_3 surface/atmosphere exchange and micrometeorological theory.

Building and testing of filter pack system and continuous flow analysis for 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 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 NH_3 and particulate NH_4^+, SO_4^{2-}, NO_3^-, Cl- concentrations upwind, downwind and at the summit of Great Dun Fell in the presence and absence of cap cloud.

b)   Comparison of 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). NH_3 and NH_4^+ profiles were measured using the filter pack system and show a high precision of measurement. The decrease in NH_3 concentration towards the ground shows that 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 NH_3 exchange measurements.

As expected from theory (eg Sehmel 1980), gaseous NH_3 was found to exchange much more rapidly than particulate NH_4^+. The mean deposition velocity of particulate NH_4^+ was 1.9 ± 2.5 mm s^{-1} (95% confidence limits). Consequently, the study focussed on the exchange of gaseous NH_3.

The results of the 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
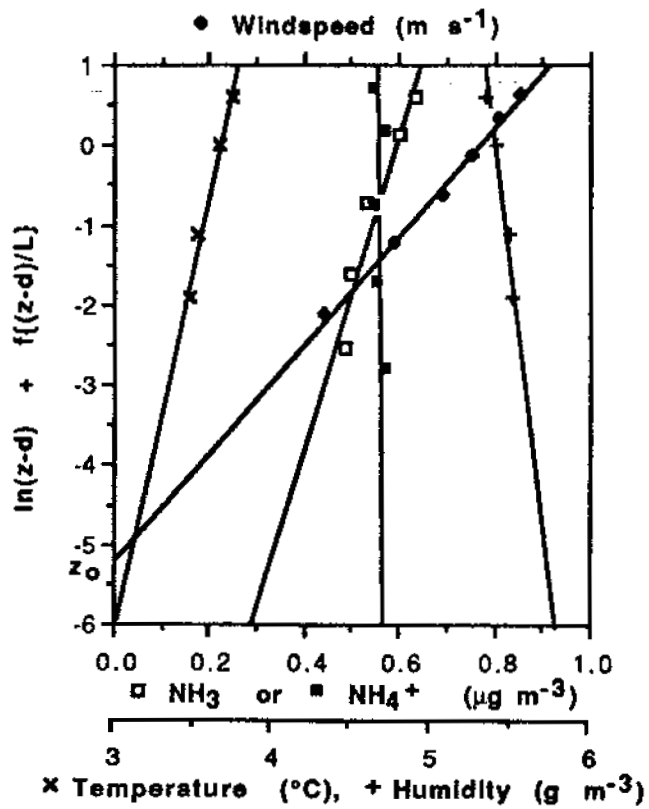
Figure 1. Example profiles measured at Bush, February 1989. Temperature and water vapour profiles measured by aspirated psychrometry. Data are for Run 6 except NH_4^+ which is for Runs 1–6 combined. For height axis, z is in meters; $f\{(z-d)/L\}$ accounts for stability correction.

exceptions to this pattern were seen. In dry conditions a small r_c (< 50 s m^{-1}) was sometimes recorded, while over a surface with exposed calcareous soil (recently harrowed) the mean r_c was 125 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 ng m^{-1} s^{-1} were recorded. In wet conditions in summer r_c was variable (0-130 s m^{-1}), while wintertime measurements showed rapid deposition to wet surfaces ($r_c < 30$ s m^{-1}). During a period of light frost an increased r_c of up to 80 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 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	$u\{1\text{ m}\}$ (m s^{-1})	$T\{z_o'\}$ $(°C)$	r_{a+b} $\{1\text{ m}\}$ * (s m^{-1})	$\chi\{1\text{ m}\}$ $(\mu\text{g m}^{-3})$	Deposition flux NH_3 $(\text{ng m}^{-2}\text{ s}^{-1})$	$V_d\{1\text{ m}\}$ (mm s^{-1})	r_c † (s m^{-1})	$\chi\{z_o'\}$ $(\mu\text{g m}^{-3})$
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) (*Eriophorum* moor)	12	3.9	(7)	45.0	0.67	17.3	19.6	5.9	0.01
Fala Moor 11/1987 (*Eriophorum* 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 (*Calluna* moor)	8	7.0	-0	19.0	0.08	1.71	27.7	17.1	0.05

Table 1. Mean values for 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 NH_3. Values in brackets are means of available data.

Chemical species	no of runs	$u\{1\text{ m}\}$ (m s^{-1})	$T\{z_o'\}$ $(°C)$	r_{a+b} $\{1\text{ m}\}$* (NH_3)	$V_m\{1\text{ m}\}$ (NH_3) (mm s^{-1})	$\chi\{1\text{ m}\}$ $(\mu\text{g m}^{-3})$	Deposition Flux $(\text{ng m}^{-2}\text{ s}^{-1})$	$V_d\{1\text{ m}\}$ (mm s^{-1})	r_c † (s m^{-1})	$\dfrac{V_d(\chi)}{V_m(NH_3)}$
NH_3	4	3.3	(6)	9.7	103	0.20	11.0	65.9	5.5	0.64
NH_4^+	5	3.5	(6)	10.0	100	1.14	9.7	16.6	—	0.17

Table 2. Mean values for NH_3 and NH_4^+ exchange measurement over coniferous forest at Dunslair Heights, Peebles. Equivalent $V_m(NH_3)$ given for NH_4^+ data to compare rates by V_d/V_m.

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

Table 3. Summary of 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/mean V_d); ¶ negative fluxes imply 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.
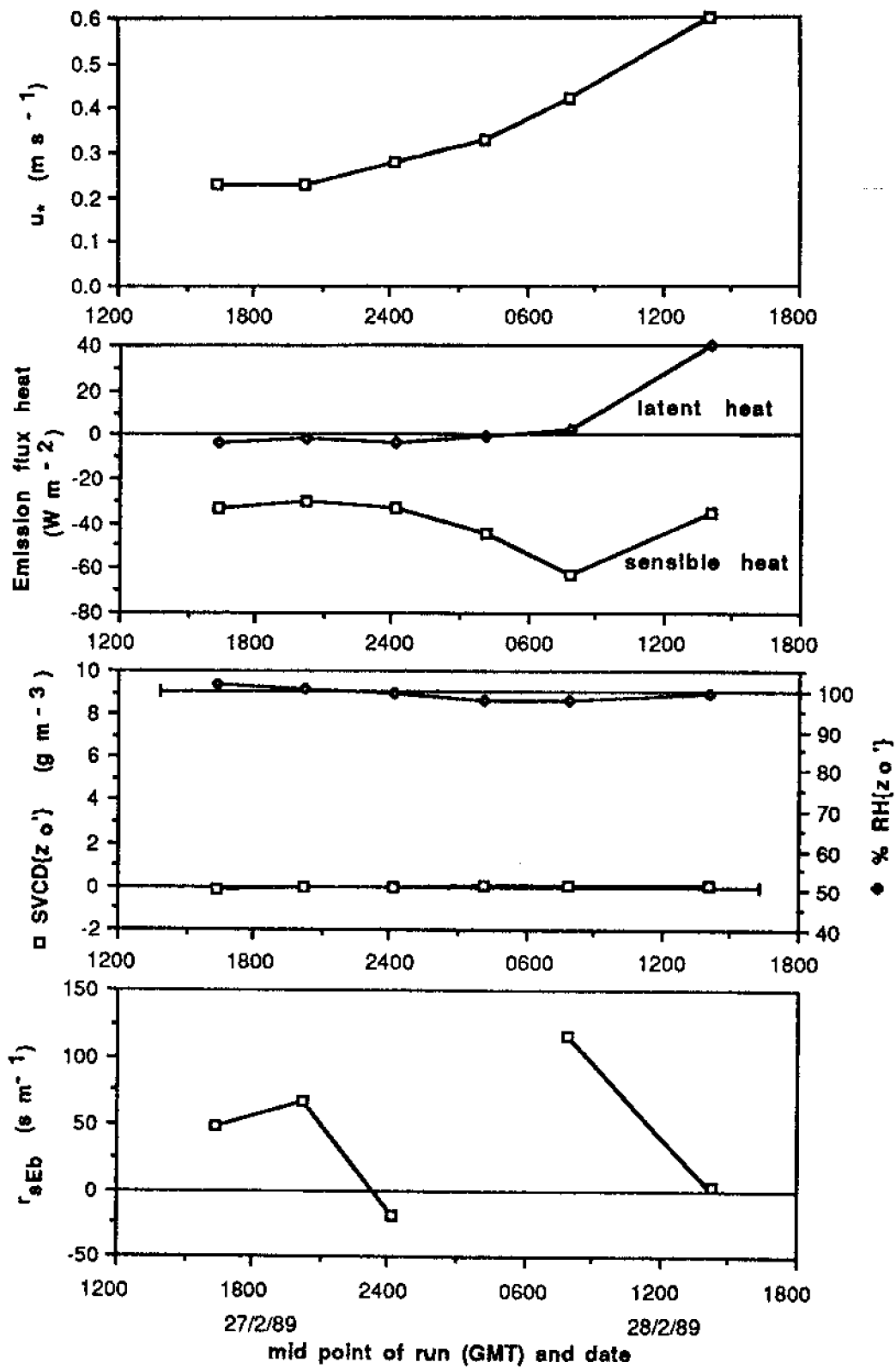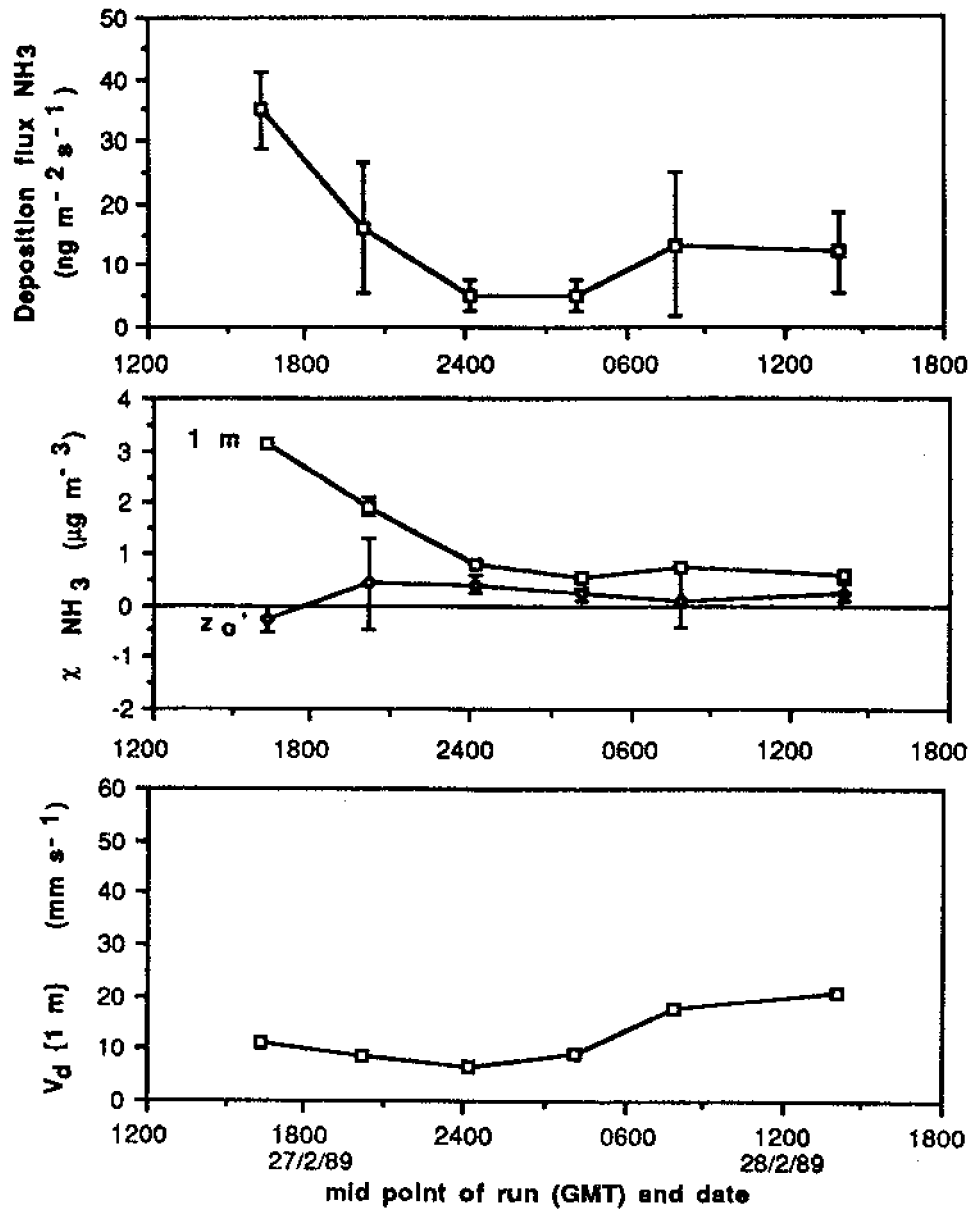
Figure 2b. Course of ammonia exchange and environmental conditions measured over fertilized cut grassland at Bush, February 1989. Note: positive fluxes of NH_3 denote deposition. Error bars (not given for V_d) are 95% confidence limits. Figure continued overleaf.
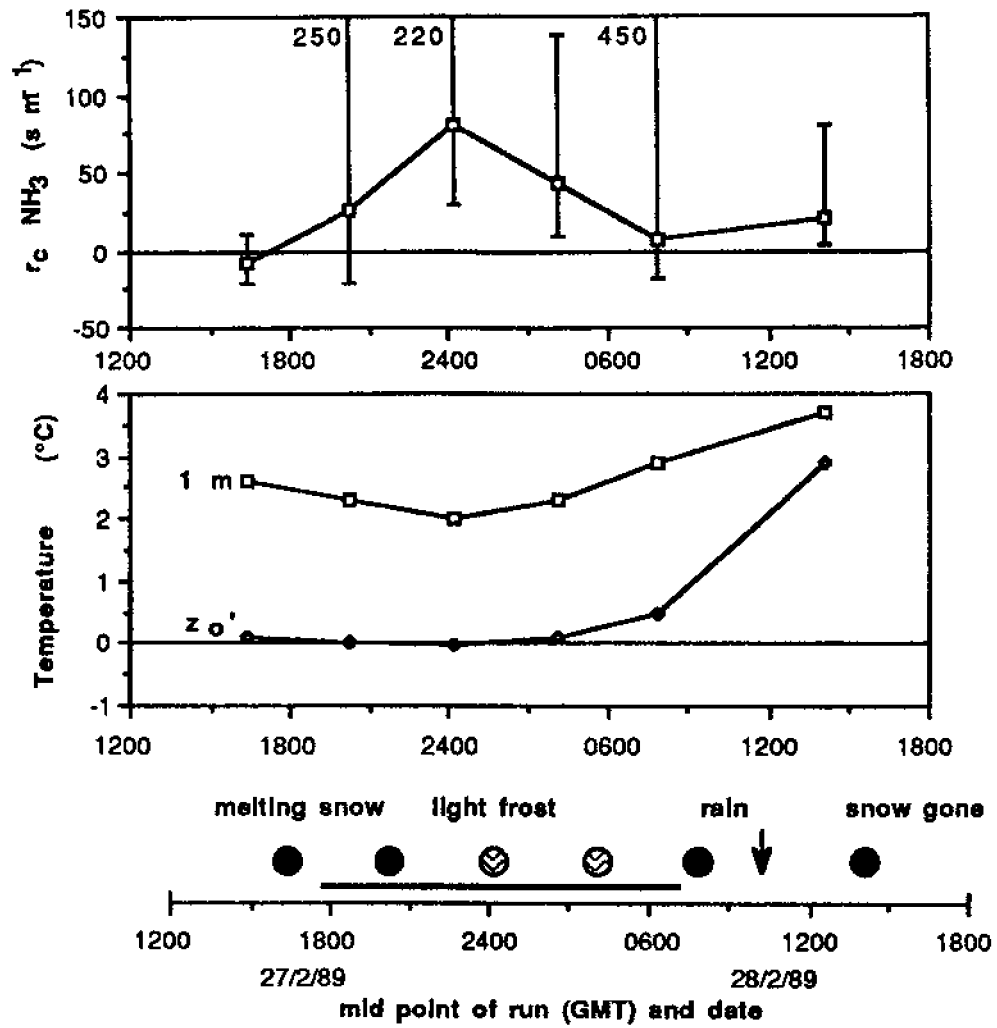
Figure 2c. Course of ammonia exchange and environmental conditions measured over fertilized cut grassland at Bush, February 1989. Error bars for r_c are 95% confidence limits. Surface conditions were assesed visually; black circles denote a wet surface and hatched circles a frozen surface. The horizontal 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 (*Pinus sylvestris*) 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_3 ($\mu g\ m^{-3}$)				
	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 $\mu g\ m^{-3}$.
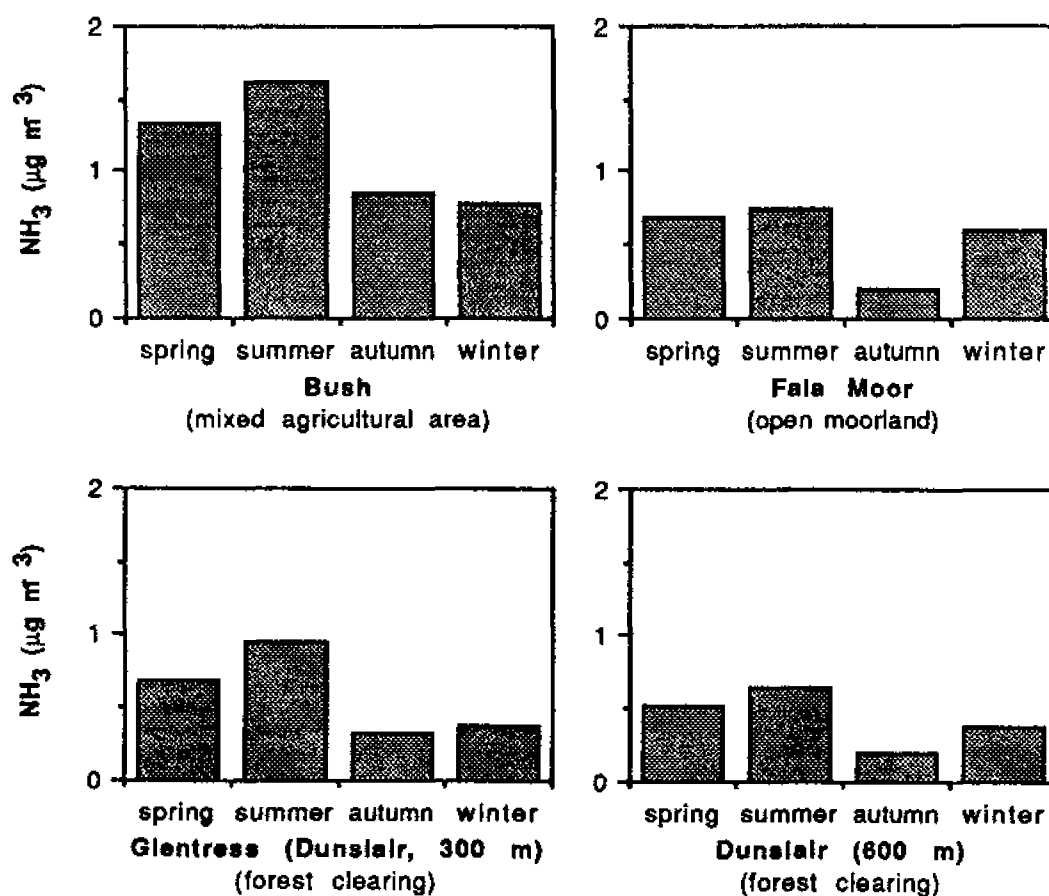

Figure 3. Bar charts of seasonal atmospheric NH_3 concentrations at four background rural sites in S. Scotland. Data from Table 5.

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 NH_3 exchange measured by micrometeorological, controlled chamber and throughfall/stemflow methods.

It was concluded that the exchange of 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 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, NH_3 deposition at the sites considered varies between 3-10 kg N ha^{-1} 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 NH_3 air concentrations for effects of near surface depletion (Table 7). For the background sites

site type	location	$-z_0$ (m)	$u\{10\,m\}$ (m s^{-1})	ref. height (m)	V_d [b] (mm s^{-1})	χ NH$_3$ (μg m^{-3})	Deposition flux NH$_3$-N [b] (kg ha^{-1} year^{-1})
Moorland S. Scotland, upland	Fala Moor, Midlothian [a]	0.03	4.2 [d]	1.5	20.4	0.55 [f]	2.9
N. Scotland, remote	Lerwick, Shetland	0.03	7.1 [e]	1.5	33.0	≈0.4 [h]	3.4
Unfertilized meadow S. England, lowland	SSSI, Huntingdon [a]	0.02	3.6 [d]	2.5	16.0	≈2.6 [g]	10
Forest S. Scotland, upland	Glentress forest (300 m) [a]	0.5	3.3 [e]	1.5	34 (61)	0.58 [f]	5.1 (9.2)
	Glentress forest (600 m) [a]	0.3	5.3 [e]	1.5	48 (81)	0.44 [f]	5.4 (9.3)
C. Scotland, lowland	Glencorse wood, Bush [a]	1.0	3.9 [d]	1.5	46 (120)	1.1 [f]	13 (34)
E. England, lowland	Thetford forest, Norfolk	1.0	3.9 [d]	2.5	42 (99)	≈2.6 [g]	29 (67)
Agricultural crop C. Scotland, lowland Bush [a]	Calculations for when grass wet (see Table 7.5) winter ($r_c = 0$ s m^{-1})	0.02	3.9 [d]	1.5	17.2	0.77 [f]	—
	spring ($r_c = 50$ s m^{-1})	0.04	3.3 [d]	1.5	9.3	1.3 [f]	—
	summer ($r_c = 100$ s m^{-1})	0.06	3.3 [d]	1.5	6.6	1.6 [f]	—
	autumn ($r_c = 50$ s m^{-1})	0.02	4.4 [d]	1.5	9.8	0.85 [f]	—

Table 6. Ammonia surface exchange budgets for a range of U.K. natural and unfertilized vegetated surfaces. Calculations referenced at the height of NH$_3$ 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^{-1}; for Spring and Autumn $r_c = 50$ s m^{-1}. 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$_x$ data (see Table 1.5, Sutton, 1990), assuming 1/3 NH$_x$ = NH$_3$.

site	$V_d\{10\,m\}$ (mm s^{-1})	$\chi\{10\,m\}$ (μg m^{-3})	Deposition flux NH$_3$-N (kg ha^{-1} year^{-1})
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 $1/(r_a\{10\,m\} + r_b)$. Concentrations are rescaled for surface depletion assuming monitoring is made over short unfertilized vegetation where $r_c = 0$. To a good approximation $\chi\{10\,m\} = 1.32\,\chi\{1.5\,m\} = 1.21\,\chi\{2.5\,m\}$ (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 NH_3 dry conditions ($ng\ m^{-2}\ s^{-1}$) [a]	mean flux NH_3 wet conditions ($ng\ m^{-2}\ s^{-1}$) [b]	mean flux NH_3 frozen conditions ($ng\ m^{-2}\ s^{-1}$) [c]	% time surface: dry, wet, frozen [d]	mean seasonal flux NH_3 ($ng\ m^{-2}\ s^{-1}$) [e]
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 ($ng\ NH_3\ m^{-2}\ s^{-1}$):						4.3
Annual background flux ($kg\ NH_3\text{-}N\ ha^{-1}\ year^{-1}$):						1.1
Additional emission following fertilization with NH_4NO_3 ($kg\ NH_3\text{-}N\ ha^{-1}$):						-1.2
Additional emission during senescence/hay drying ($kg\ NH_3\text{-}N\ ha^{-1}$):						-0.3
Overall annual flux ($kg\ NH_3\text{-}N\ ha^{-1}\ year^{-1}$):						-0.4

Table 8. Example exchange budget of 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 $r_c = 100$ 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, NH_3 deposition to forests varies between 5 and 55 kg N ha^{-1} year^{-1}.

The results are compared with other components of N deposition by Sutton (1990) and it is concluded that dry deposition of 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^{-1} year^{-1} (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 NH_3 concentrations. The effect of acid gases (SO_2, HNO_3, 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 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 NH_3 in the atmosphere.

• The validity of passive diffusion tube measurements of NH_3 concentrations.

• The extent of non-conservation of NH_3 fluxes for different exchange situations.

• The magnitude of r_b over forests.

• The effect of CO_2 on reducing NH_3 solubility in water (separate from pH effects).

RECOMMENDED CRITERIA FOR FUTURE MEASUREMENTS OF NH₃ SURFACE/ATMOSPHERE EXCHANGE

Further studies of the exchange of NH_3 over vegetated surfaces should:

• define the vegetation, soil type and management, especially the use or absence of fertilizers.

• measure NH_3 and 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 NH_3 emission.

PUBLICATIONS LIST

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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_χ — flux of trace gas or particulate to or away from a surface (μg m^{-2} 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)
$r_t\{z\text{-}d\}$	total resistance to deposition of a trace component, from a defined height above the zero plane. Inverse of deposition velocity (s m^{-1}).
$r_a\{z\text{-}d\}$	atmospheric resistance of a trace component to turbulent transfer between the atmosphere and a surface (s m^{-1})
r_b	resistance to transfer for entrained properties across quasi-laminar sub-layer surrounding roughness elements of a surface (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 (s m^{-1})
r_{sEb}	bulk stomatal resistance to water vapour transfer (s m^{-1})
T	temperature (°C or K).
u	mean horizontal windspeed (m s^{-1}).
u_*	eddy (or friction) velocity (m s^{-1})
$u\{z\text{-}d\}$	mean horizontal windspeed at a given height above the zero plane (m s^{-1}).
$V_d\{z\text{-}d\}$	deposition velocity of gaseous or particulate species at a given height above the zero plane (mm s^{-1})
$V_m\{z\text{-}d\}$	maximum value of the deposition velocity permissible by turbulence, $1/(r_a + r_b)$ (mm s^{-1})
z	distance; height above the ground; diffusion tube path-length (m)
z_χ	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

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

Abstract of Sutton (1990) Ph.D. thesis

Measurements of the exchange of gaseous ammonia (NH_3) and particulate ammonium (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. NH_4^+ was found to deposit very slowly so that the study focused on the exchange of NH_3.

Over natural and unfertilized vegetation, 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 s m^{-1}) and over vegetation with exposed calcareous soil (mean r_c = 125 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 (0–130 s m^{-1}), whereas in winter r_c was small (< 30 s m^{-1}). During frozen conditions an increased r_c of up to 80 s m^{-1} was observed. In dry summer conditions emission of up to 24 ng NH_3 m^{-2} s^{-1} was recorded. The estimation of the net 'compensation point' for exchange using surface concentration estimates is discussed, and shown to range over 0–7 μg 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 NH_3.

In order to estimate annual fluxes, atmospheric concentrations of NH_3 are needed. Background annual concentrations of NH_3 measured in this study at several sites in S. Scotland were in the range 0.4–1.1 μg m^{-3}. Using these and other published data, annual fluxes over different surfaces are estimated. Over an example fertilized surface a small net NH_3 emission is predicted (< 1 kg N ha^{-1} year^{-1}), while over unfertilized surfaces larger deposition fluxes are expected (3–55 kg N ha^{-1} year^{-1} for the background sites considered). Comparison with other sources of atmospheric N shows that dry deposition of 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 (NH_3) and particulate ammonium (NH_4^+) in approximately similar concentrations. Background concentrations are usually in the range 0.01–10 μg m^{-3}, though near sources much higher NH_3 concentrations (>100 μg m^{-3}) may occur.

* Monitoring of 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 μg m^{-3}.

   o 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 μg 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 are not used here for the estimation of dry deposition budgets (see below).

   o Possible errors in NH_3 diffusion tube sampling arise from sampling artifacts (NH_3 deposition to tube walls, capture of 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 NH_3, the main source being from livestock agriculture, which may be converted in the atmosphere to NH_4^+.

* The dry deposition of NH_4^+ particles is expected be a very slow process, which is confirmed by micrometeorological field measurements in this study. Most of the 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 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:

   o Measurements over natural and unfertilized vegetation generally recorded rapid deposition of NH_3 with minimal surface resistance (r_c), which shows that the surface behaves largely as a perfect sink, with 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 s m^{-1}) was sometimes recorded, while over a surface with exposed calcareous soil a mean r_c of 125 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 ng m^{-2} s^{-1} being measured. In wet conditions deposition was recorded. Measurements to wet surfaces in summer showed r_c to be variable (0–130 s m^{-1}), while winter-time measurements showed rapid deposition to wet surfaces ($r_c < 30$ s m^{-1}). During a period of light frost an increased r_c of up to 80 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 SO_2, may enhance leaf surface uptake, often referred to as co-deposition. HNO_3 and 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 NH_3, such as with a crop emitting NH_3 or in the presence of high atmospheric concentrations.

  ○ Stomata and soil can act as either sources or sinks of NH_3, depending on the Henry equilibria of NH_3 and NH_4^+ in plant tissues and soil water with atmospheric concentrations of NH_3. The atmospheric concentration in equilibrium with the surface is often referred to as the 'compensation point' (χ_{cp}). Where air concentrations are less than χ_{cp} emission occurs, whereas with air concentrations larger than χ_{cp} deposition occurs. The compensation point concept is most usually applied to the exchange of NH_3 through stomata, though equally soil χ_{cp} and overall canopy or net χ_{cp} may be defined.

  ○ Over natural and unfertilized vegetation it is probable that the low N status results in small stomatal and soil χ_{cp}, with the result that leaf surface deposition dominates and the net χ_{cp} is small. Where $r_c = 0$ the net χ_{cp} is by definition zero.

  ○ Over fertilized agricultural vegetation the higher N status results in larger χ_{cp}, and emission may occur through either stomata or soil. However, during wet conditions these χ_{cp} have little effect on the net exchange as leaf surface deposition dominates, and the net χ_{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 χ_{cp}. Where emission is through stomata alone and stomatal resistance known,

estimates of the stomatal χ_{cp} may be made (referred to as $\chi\{z_0"\}$). For an agricultural crop in dry summer conditions $\chi\{z_0"\}$ was 2–7 $\mu g\ m^{-3}$. Given that some leaf surface deposition may also have been present, this may be an underestimate of the stomatal χ_{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 NH_3 deposition ranges from 3 to 55 kg N ha^{-1} 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 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 χ_{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 χ_{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 NH_3 emission of is < 1 kg N ha^{-1} 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 kg N ha^{-1} 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 NH_3 is frequently the largest single N input, which emphasizes the importance of understanding NH_3 surface exchange processes. Including wet deposited NH_4^+, NH_x accounts for 60–80 % of the total N input to the examples considered, as compared to 20–40 % from oxidized N species (NO_2, HNO_3, NO_3^-), giving a total deposition of 10–75 kg N ha^{-1} $year^{-1}$. Near sources of 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 NH_x to 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 (SO_2, NO_x, NH_3). Because of atmospheric neutralization of oxidized S and N by NH_3 to form NH_4^+, much of the acidifying deposition in the examples (up to 60–80%) is as NH_x rather than free acidity. Emission of 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 NO_x and NH_3, so that SO_2 emission is frequently the dominant acidifying input. Conversely, where N deposition exceeds plant uptake, 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 is 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 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 SO_2 and NO_x emissions will only have limited effectiveness. In order to achieve major reductions in deposition, particularly in the case of N inputs, additional polices controlling NH_3 emission are required. Given the agricultural origin of the 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

M.A.Sutton *†, D.Fowler * and J.B.Moncrieff †

* Institute of Terrestrial Ecology, Edinburgh Station, U.K.
† Department of Forestry and Natural Resources, University of Edinburgh, U.K.

ABSTRACT

Two methods of gaseous 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 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 NH_3 using diffusion samplers provided air concentrations in S.E. Scotland, which were 0.5-1.5 $\mu g\ m^{-3}$ at rural sites. From this, two example budgets for natural sites in the U.K. are considered.

1. INTRODUCTION

Interest in atmospheric 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 NH_3 between the atmosphere and the ground and to monitor ambient concentrations. This paper reports the use of two methods for NH_3 measurement and the results of NH_3 surface atmosphere exchange studies. The results of gaseous 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 NH_3 (Fg), 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):

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

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

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 (Vg) may be defined, at a reference height of 1 m:

$$Vg(1\ m) = Fg/X(1\ m) = 1/r_t(1\ m)$$

Here r_t represents the total resistace 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):

$$r_c = r_t(1\ m) - (r_a(1\ m) + r_b).$$

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'):

$$X(z_0') = X(1m) - Fg(r_a(1m) + r_b)$$

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 $m^3\ hr^{-1}$. A teflon membrane filter (1 μm) removes particulate NH_4^+, followed by an acidified paper filter to capture 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 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 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 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 1×10^{-4} m^3 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(zo') are 95% limits of the mean of runs. *The grass had recently been harrowed (soil pH = 8.4).

Site	surface cond- itions	$\overline{X}$ μg m^{-3}	$\overline{Vg}$ cm s^{-1}	median r_c s m^{-1}	X(z$_0$') μg m^{-3}
Moorlands:					
Great Dun Fell	mostly wet	0.7	2.8	4.9	0.0±0.3
Fala Moor	dry+ wet	0.7	4.7	0.5	-0.1±0.2
Natural Grasslands:					
Hunting- don	dry+ wet	2.0	1.7	-2.6	-0.1±0.7
Harwell*	dry+ wet	1.8	0.8	121	1.0±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 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 $X(z_0')$.
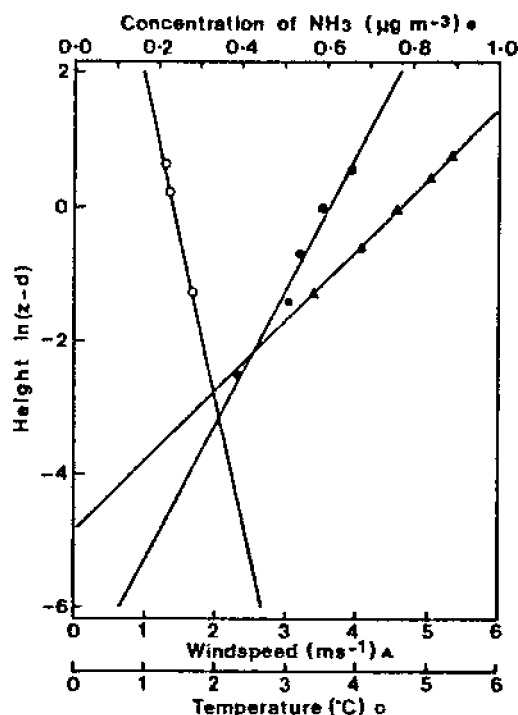

Figure 1. Example profiles for one run at Great Dun Fell. (Deposition: r_c = 3.3 s m^{-1})
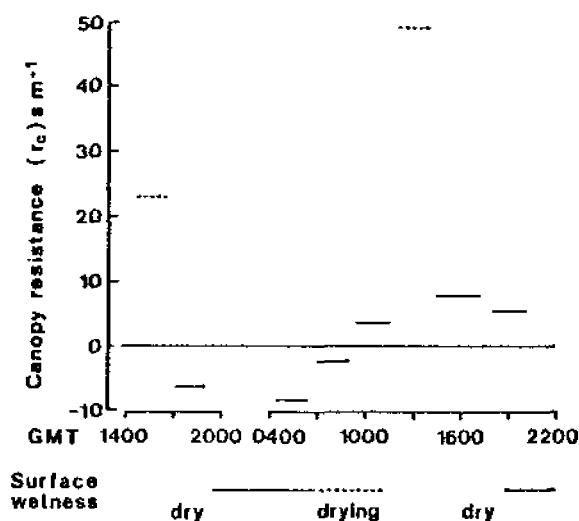
Figure 2. Surface (canopy) resistance for varying surface wetness. Bars show run duration. Dashed bars note poor profiles. For the good data r_c is consistently small.

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
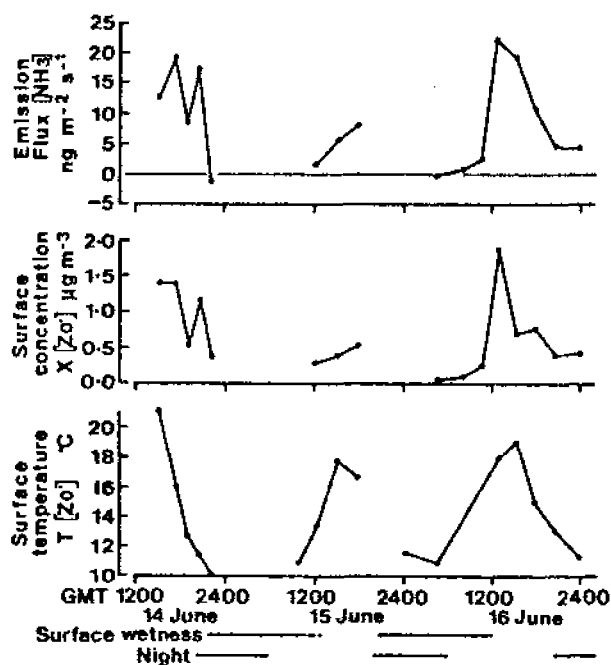

Figure 3. Ammonia fluxes compared with surface concentration and temperature for crop grass at Bush. For explanation see text.

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

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

Table 3. Seasonal means of ammonia concentrations ($\mu g\ m^{-3}$) 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 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_2, rates of NH_3 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_2 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_3 deposition on moorland, with results broadly in agreement with these, however with some tendency toward larger values of r_c. This difference could relate to lower humidities, or a different ratio of NH_3/SO_2 in their experiments. It is reasonable that at high NH_3 levels with only background SO_2, NH_3 saturation of the leaf surfaces could occur. In accordance with this, our most recent studies have included measurements of water vapour and SO_2 gradients. The clear r_c seen in the Harwell data may confirm this interaction, since the elevated pH, due to harrowing the chalk soil, would reduce NH_3 solubility.

Exchange of NH_3 has previously been thought of in terms of a temperature dependent 'compensation point' being the sub-stomatal equilibrium NH_3 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_c is zero,

so is $X(z_o')$. 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 $r_c = 0$. Example budgets for two sites are given in Table 4. Compared with wet deposition dry NH_3 clearly provides a large fraction of total NH_3/NH_4^+ input. Values will depend on site roughness and NH_3 concentration, though, noting the above discussion, some caution is needed about extrapolation to much drier climates and cases of very high NH_3 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 $\mu g\ m^{-3}$	Vg $cm\ s^{-1}$	deposition flux-N Kg ha^{-1} yr^{-1}	
			NH_3 dry	NH_4^+ wet*
Moorland (Fala Moor)	0.64	3.0	5.0	4
Meadow (Huntingdon)	2.6 †	1.7	11.5	5

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