Chapter (non-refereed)

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Estimating the relative contribution of SO_x, NO_y and NH_x inputs to effects of atmospheric deposition

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INTRODUCTION

Atmospheric pollutant inputs to ecosystems include sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and their reaction products. Emissions of these gases derive from very different sources. Most of the SO_2 and NO_x derives from combustion sources, such as in electricity generation and from vehicles. By contrast, NH_3 is primarily a consequence of livestock agriculture, with over 80% estimated to derive from the volatilisation of animal wastes (Buijsman, Mass & Asman 1987). Emission controls of these pollutants, therefore, require very different strategies, so that it is of interest to identify the relative contribution of each component to atmospheric deposition. This information is useful in identifying the most efficient way of reducing deposition to meet critical and target loads. Effects of atmospheric deposition loads may be divided into three issues: eutrophication effects of total nitrogen deposition, effects of total acidifying deposition, and effects of ammonia deposition on base cation uptake.

Total nitrogen deposition is important where ecosystem effects are a consequence of eutrophication from fixed atmospheric N (eg Bobbink *et al.* 1992). The relative contribution of NO_x and NH_3 emissions may be found by summing the deposition of total reactive oxidised nitrogen (NO_y) and reduced nitrogen (NH_x), where these groups include the precursor gases and their products following atmospheric transformation (eg NO_2, HNO_3, NO_3^-, NH_3 and NH_4^+). The dry deposition inputs must be quantified for each of the gases and aerosols, as well as inputs in precipitation (wet deposition).

Total acidifying deposition derives from each of NO_y, NH_x and oxidised sulphur inputs (SO_x), which include SO_2 and sulphates (SO_4^{2-}) formed by atmospheric transformation. Assessing the relative contribution to acidification from SO_x, NO_y and NH_x is a more uncertain task because acidification from deposited N depends on its fate within the receiving ecosystem.

Ecological effects of NH_x deposition *per se* have also been recognised, such as nutrient imbalances with base cations (K^+, Mg^{2+}, Ca^{2+}), but have received less attention in their own right, being usually included with N eutrophication effects (eg Bobbink *et al.* 1992). They are considered separately here because they are a particular consequence of NH_3 emissions. In this case, it is of interest to examine the relative contribution of the different forms of NH_x deposition.

In the following sections, the different components of deposition are considered, with dry deposition of NH_3 taken as an example to show how annual inputs may be estimated. This and other N inputs are summed for example sites in the UK to assess their relative contribution to N deposition. Ecosystem processes affecting the acidification deriving from N compounds are then considered, and the same UK examples used to provide ranges for the relative contribution of NO_y and NH_x to acidification. The results are discussed in relation to the implementation of critical loads and requirements for emission controls.

QUANTIFYING THE COMPONENTS OF DEPOSITION

The different components of atmospheric deposition include dry deposition of gases (eg SO_2, NO_2, HNO_3, NH_3) and aerosols (eg SO_4^{2-}, NO_3^-, NH_4^+), as well as wet deposition of the ionic species in precipitation. A further input is the direct impaction of cloud droplets on to vegetation (cloudwater deposition). Wet deposition is the best quantified of these terms, with extensive results from precipitation monitoring networks allowing regional deposition fields to be mapped (eg UK Review Group on Acid Rain (UKRGAR) 1990). Cloud droplets exist in the size range 5-30 μm diameter, which permits efficient impaction on to vegetation surfaces. Coupled with the large concentrations in such droplets, high-altitude sites that are frequently enshrouded by cloud may receive significant pollutant inputs by this mechanism (Fowler, Cape & Unsworth 1989). Atmospheric aerosols provide the condensation nuclei for the formation of cloud droplets, but because these particles exist in much smaller size ranges, typically 0.1-1 μm, impaction is very inefficient. Other mechanisms for deposition are also inefficient in this size range, so that such aerosols

deposit very slowly and are generally only a small component of the total deposition.

Dry deposition of the precursor gases represents a major contribution to total deposition, and provides the most uncertain term in its calculation, particularly for NH_3 dry deposition, which has only recently been studied using methods allowing regional extrapolation for a range of ecosystem types (see Sutton, Pitcairn & Fowler 1993). From micrometeorological measurements, the affinity of vegetation for dry deposition may be described using a 'canopy resistance' (r_c). By coupling estimates of r_c, derived from short-term flux measurements, with resistances for the turbulent atmosphere (r_a) and the quasi-laminar boundary layer at leaf surfaces (r_b), a total resistance (r_t) can be found. The reciprocal of r_t is referred to as the deposition velocity (V_d) and may be coupled with monitored air concentrations (c) to estimate long-term (eg annual) deposition fluxes (F_g):

$$r_t = r_a + r_b + r_c = V_d^{-1} \quad (1)$$

$$F_g = -V_d \chi \quad (2)$$

Figure 1 shows an example of measured NH_3 V_d and r_c for a moorland in southern Scotland (Sutton, Moncrieff & Fowler 1992). The large V_d and small r_c indicate that the vegetation is an efficient sink for NH_3, with deposition limited by atmospheric resistance.

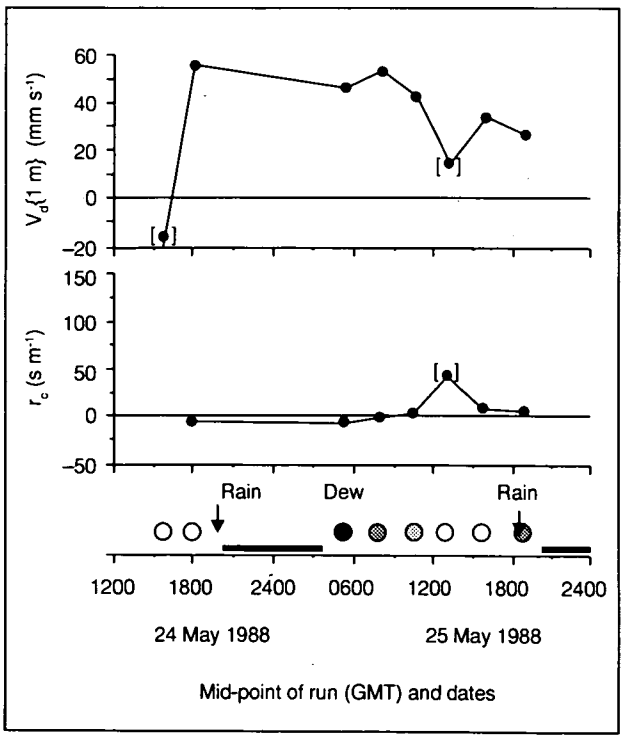

Figure 1. Deposition velocity (V_d) and canopy resistance (r_c) measurements of NH_3 at Fala Moor, southern Scotland. Canopy wetness is shown at the foot of the graph, from dry conditions (open circle) to fully wet (black circle). A horizontal bar denotes night-time. Runs with a large measurement uncertainty are shown in brackets

The mean r_c for these measurements was 5 s m^{-1}. Ammonia exchange is, however, highly dependent on land use, and both NH_3 emission and deposition occur over other vegetation types, such as grazed grassland and fertilized croplands, which are less efficient for NH_3. On a regional scale, ammonia exchange reduces the overall input by NH_3 dry deposition. However, larger air concentrations are maintained, allowing an increased deposition to semi-natural ecosystems.

An example of the use of such measurements is shown in Table 1, where monitored air concentrations are combined with calculated average V_d to provide estimates of annual NH_3 dry deposition fluxes. Four examples of unfertilized sites in Britain are shown to reflect a range of input fluxes and land uses. Air concentrations are larger at the eastern England sites, allowing increased fluxes. In addition, because of the small size of r_c and increased turbulence over rougher forest vegetation, which provides smaller r_a and r_b, dry deposition is much larger over forests compared with short vegetation. Rural background air concentrations are used in these calculations, so that dry deposition may be much larger near local NH_3 sources.

Table 1. Estimated annual NH_3 dry deposition to example unfertilized sites in the UK (further details provided by Sutton *et al.* 1993)

Site	χ NH_3 (μg m^{-3})	V_d* (mm s^{-1})	NH_3 deposition (kg N ha^{-1} yr^{-1})
Southern Scotland			
Upland forest, eg Glentress	0.58	38.1	5.7
Upland moor, eg Fala Moor	0.55	18.5	2.6
Eastern England			
Lowland forest, eg Thetford	3.2	50.2	41.1
Lowland heath, eg Breckland	2.6	13.8	9.3

*Calculated using r_c = 5 s m^{-1}

RELATIVE CONTRIBUTIONS TO TOTAL NITROGEN AND NH_x DEPOSITION

The different components of nitrogen deposition may be summed to estimate the relative contribution of NO_y and NH_x, as shown in Table 2 for the same example sites considered above. Dry deposition fluxes of NH_3 from Table 1 are combined with NH_4^+ inputs in wet deposition, and with aerosol and cloud-water deposition. A similar approach is used to calculate total NO_y deposition, accounting for dry deposition of NO_2 and HNO_3 as well as wet, cloud and aerosol deposition of NO_3^-.

Table 2 shows that NH_x typically accounts for 60-80% of the total N input for these examples of unfertilized and semi-natural ecosystems. The fraction is largest

Table 2. Relative contribution of NO_y and NH_x to total N deposition for example unfertilized sites in the UK, calculated using NH_3 dry deposition from Table 1. Details of other wet and dry deposited inputs provided by Sutton *et al.* (1993). Inputs in kg N ha^{-1} yr^{-1}

Site	NO_y deposition	NH_x deposition	Total N deposition	% deposition from NH_x
Southern Scotland				
Upland forest, eg Glentress	7.1	11.8	18.9	62
Upland moor, eg Fala Moor	5.5	7.9	13.4	59
Eastern England				
Lowland forest, eg Thetford	12.4	48.4	60.8	80
Lowland heath, eg Breckland	9.9	16.6	26.5	63

for the lowland forest, where NH_x contributes about 80% of the nitrogen input and NO_y only 20%. In addition to showing the importance of NH_x deposition to total N inputs, the Tables also show the relative contribution of NH_3 dry deposition. For these examples, NH_3 contributes 33-85% of the NH_x input. At specific near-source locations (ie adjacent to livestock farms), NH_3 dry deposition is expected to dominate both NH_x and total nitrogen deposition. In general, because NH_3 has a shorter atmospheric residence time than NO_2, sites in NH_3-polluted regions will be most dominated by the NH_x inputs, while remote sites will have the largest NO_y/NH_x deposition ratio.

While these values are only examples, they may be contrasted with estimated emissions of NO_x and NH_3. The UK emission of NO_x has been estimated to be 750 Gg N yr^{-1} (UKRGAR 1990), whereas recent NH_3 emission estimates range between 170 and 390 Gg N yr^{-1} (see Sutton, Pitcairn & Fowler 1993). On the basis of these emissions, the large contribution of NH_x to total N deposition might seem surprising. However, as noted above, NH_3 dry deposition depends on land use, with fertilized agricultural vegetation generally showing net emission or a balance between emission and deposition over the year. Hence, net dry deposition is limited to unfertilized sites which consequently receive larger inputs than might be expected.

CONTRIBUTION OF NO_y AND NH_x TO TOTAL ACIDIFYING DEPOSITION

Biological interactions of deposited nitrogen

Estimating the contribution of N compounds to ecosystem acidification is complicated because of interactions of the deposited ions within the ecosystem. Because N is a major nutrient, much of the deposited input may be taken up by plants or immobilised in soil organic matter, affecting the

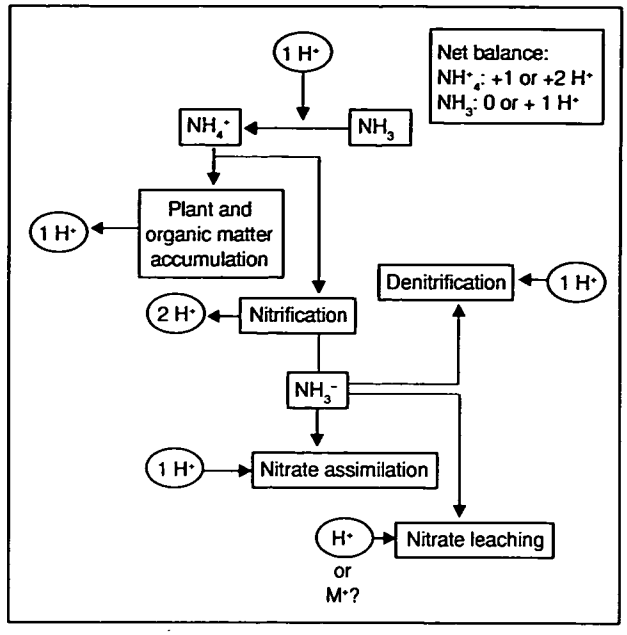

Figure 2. Effects of atmospheric NH_3 or NH_4^+ input on soil acidity. M^+ represents a metal ion that might be leached from the soil

extent of soil acidification (Binkley & Richter 1987). The problem is not so significant with deposition of SO_x, as much smaller amounts of S are accumulated within biomass and soil organic matter. As a consequence, in most ecosystems, outputs of SO_4^{2-} by leaching equate closely with atmospheric SO_x inputs over a few years.

The effects of N transformations on acidification are demonstrated for NH_x inputs to soils in Figure 2. Deposition of NH_4^+ followed by accumulation in biomass and soil organic matter is acidifying, because the N is stored as organic R-NH_2 forms. Uptake results in an equivalent net release of H^+ ions back to the soil to maintain electro-neutrality. By contrast, mineralisation of soil organic matter is de-acidifying, so that the actual acidification by this mechanism depends on net accumulation in biomass and organic matter. In the long term, this requires harvesting of biomass or litter removal.

If NH_4^+ is left in the soil and nitrified to NO_3^-, the effect is again acidifying:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (3)$$

Accumulation of NO_3^- in biomass may neutralise this acidity, as the NO_3^- is reconverted to R-NH_2 forms. In addition, any NO_3^- that is denitrified results in an equivalent consumption of H^+, neutralising soil acidity. Alternatively, NO_3^- may be leached from the soil accompanied by base cations or aluminium, resulting in net acidification.

Nitrification of NH_4^+ in the soil does not always occur, however, and, where NH_x deposition is very large or there are shortages of other nutrients (Gundersen & Rasmussen 1988), NH_4^+ may accumulate allowing NH_4^+ leaching. Though not shown in Figure 2, potentially the effect would be de-acidifying, especially where the leached NH_4^+ is derived from

mineralisation of organic N originally deposited as NO_y (M S Cresser, pers. comm.). However, nitrification may be expected in subsequent ground- and surface waters, so this effect is temporary.

Figure 2 also shows that deposition of NH_3 or NH_4^+ has differing effects. Conversion of dry-deposited NH_3 to NH_4^+ consumes one H^+ ion, so that NH_3 has no net acidifying effect if accumulated in biomass or denitrified. Equally, nitrification from deposited NH_3 produces one H^+, rather than two as for NH_4^+. Ammonium is, therefore, more acidifying than NH_3, and in many cases represents a major acidity input compared with free H^+, SO_2 and NO_2 deposition. However, it should be noted that ammonia emission occurs as NH_3, and that NH_4^+ is a product of H_2SO_4 and HNO_3 neutralisation, where these acids derive from SO_2 and NO_x emissions. Hence, while much of the acidifying deposition arrives as neutral NH_4^+ salts, the acidity originates from SO_2 and NO_x.

Because of the effect of atmospheric transformation, it is useful to consider acidifying inputs in two distinct ways. One is to consider inputs of the *actual deposited species.* In this way, the acidification from each of the ions and gases deposited (eg SO_2, SO_4^{2-}, NH_3, NH_4^+, H^+, etc) is summed, and account is taken of the different acidifying effects of each species. This approach is relevant for detailed assessments of the form in which acidity is input to ecosystems. Alternatively, acidifying inputs may be treated in terms of the *equivalent emitted pollutants.* In this approach, the acidifying effect of each of the deposited species is treated as if it were the precursor gas; thus removing the effect of atmospheric transformation; the method is therefore useful for assessing the relative contribution of different emissions (SO_2, NO_x, NH_3) to acidifying deposition.

Critical loads treatment of deposited N interactions in ecosystems

The estimation of critical loads for acidity has largely treated the acidifying deposition in terms of the equivalent emitted pollutants. Hence, all inputs of SO_x, NO_y and NH_x are assigned the acidifying effect of SO_2, NO_2 and NH_3. In the mass balance approach (eg Schulze *et al.* 1989), the nitrogen transformations discussed above are associated with the critical load calculation, rather than with the deposition. All deposited N, apart from that accumulated in vegetation and organic matter, is assumed to be acidifying, and all NH_x left in the soil is assumed to be nitrified. This approach, as outlined by Schulze *et al.*, states that the critical load for acidity is met if (expressed as equivalents):

$$F_{SOx} + F_N < W_{bc} + A_N + I_{Nnet} \quad (4)$$

where F_{SOx} = total deposition of SO_x; F_N = total deposition of NO_y and NH_x; W_{bc} = base cation weathering; A_N = biomass accumulation of N; and I_{Nnet} = net N immobilisation. Further modifications of this approach have been developed (eg Grennfelt & Thörnelöf 1992), such as accounting for acceptable nitrate leaching, base cation deposition and denitrification.

The approach, therefore, takes some account of the nitrogen transformations. However, it fails to separate the different possible effects of NO_y and NH_x deposition, which becomes important if, for example, N accumulation is different for NO_3^- or NH_4^+. The approach also entails some circularity, as N accumulation is expected to be a function of F_N. As a consequence of these effects, it becomes harder to examine the relative contribution of SO_2, NO_x and NH_3 emissions to the critical load exceedance.

Relative contributions to ecosystem acidification

A complementary approach to that outlined above is to associate N transformations with the atmospheric deposition side of the equation. This approach is adopted here, the aim being to examine, in a simple manner, the relative magnitude of the different components of acidifying deposition. By examining deposition in this way, it is possible to consider inputs both in terms of the actual deposited species and as the equivalent emitted pollutants.

To demonstrate the different relative contributions of the deposited species, total acidifying inputs are calculated for the same example sites considered in Tables 1 and 2. This calculation is shown first in Table 3 for the suite of *actual deposited species.* The range of possible acidification deriving from NH_3 and NH_4^+ inputs may be found according to Figure 2, and a similar approach is used for NO_y inputs. Nitric acid deposition is acidifying if left in the soil and ultimately leached, but neutral if accumulated in vegetation. Conversely, NO_3^- inputs are neutral if left in the soil, but de-acidifying if accumulated in vegetation. Deposition of SO_4^{2-} is not shown in this Table as, in itself, it has no net acidifying effect, the reason being, as with NO_3^-, that the acidity derives from the associated input of H^+ ions.

Table 3 shows the fluxes of the deposited species in kg (H^+, S or N) ha^{-1} yr^{-1}, and, underneath in italics, ranges of the possible acidification (mmol H^+ m^{-2} yr^{-1}) for each species. The Table is revealing in that it highlights the importance of each of the actual deposited species to ecosystem acidification. If plant uptake and denitrification are assumed to be negligible and nitrification complete, the upper figures are appropriate for the N species. In this case, the largest contribution to acidification at each of the sites is from NH_3 in dry deposition and from NH_4^+ in wet deposition. The contribution to acidification that is deposited as NH_x is shown in the final column. Even assuming complete biomass accumulation and immobilisation of all deposited N, the Table shows that about 40% of the acidity is input as non-acidic NH_x. If accumulation and immobilisation are unimportant, then 60-75% of the acidity is deposited as NH_x.

Table 3. Ranges of possible acidifying deposition to example unfertilized sites in the UK. Inputs expressed as the actual deposited species.. For each site, the first figure is the deposition (kg ha^{-1} yr^{-1}) as H, N, or S. The second figure (in italics) is the equivalent H^+ input (mmol m^{-2} yr^{-1}). Ranges of possible acidification for N components depend on the fate of the deposited species (see Figure 2). Dry deposition of free H^+ in aerosols is assumed to be small and is not calculated

	Wet deposition [a]				Dry deposition					Cloudwater deposition [d]			H^+ input	
Chemical species	H^+	NH_4^+	NO_3^-	SO_2 [b]	NO_2 [c]	HNO_3 [c]	NH_3 [c]	NH_4^+ [c]	NO_3^- [c]	H^+	NH_4^+	NO_3^-	Total H^+ (mmol m^{-2} yr^{-1})	% of positive inputs from NH_x
H^+ produced (mol/mol)	+1	+1 or +2	-1 or 0	+2	0 or +1	0 or +1	0 or +1	+1 or +2	-1 or 0	+1	+1 or +2	-1 or 0	-	-
Southern Scotland														
Upland forest,	0.35	4.5	3.5	3	1	1.5	5.7	0.6	0.2	0.11	1.0	0.9	*76-211*	40-61
eg Glentress	*35*	*32-64*	*-25-0*	*19*	*0-7*	*0-11*	*0-41*	*4-9*	*-1-0*	*11*	*7-14*	*-6-0*		
Upland moor,	0.35	4.5	3.5	3	1	0.6	2.6	0.6	0.2	0.02	0.2	0.2	*66-162*	39-59
eg Fala Moor	*35*	*32-64*	*-25-0*	*19*	*0-7*	*0-4*	*0-19*	*4-9*	*-1-0*	*2*	*1-3*	*-1-0*		
Eastern England														
Lowland forest	0.25	6.5	4.5	10	4.3	3.2	41.1	0.8	0.4				*105-540*	37-74
eg Thetford	*25*	*46-93*	*-32-0*	*63*	*0-31*	*0-23*	*0-294*	*6-11*	*-3-0*	-	-	-		
Lowland heath	0.25	6.5	4.5	10	4.3	0.7	9.3	0.8	0.4					
eg Breckland	*25*	*46-93*	*-32-0*	*63*	*0-31*	*0-5*	*0-66*	*6-11*	*-3-0*	-	-	-	*105-294*	37-58

a, from Warren Spring Laboratory (1988)
b, from UKRGAR (1990)
c, from Table 1 and Sutton, Pitcairn and Fowler (1993)
d, from Fowler, Cape and Unsworth (1989)

Alternatively, these deposition data may be viewed as the *equivalent emitted pollutants.* Because all inputs are treated as either SO_2, NO_x or NH_3, the calculation of possible acidification is simplified, and accounting for the range of possible effects of N deposition may be expressed (in moles) as:

$$H^+ = 2F_{SOx} + (0\text{-}1)F_{NOy} + (0\text{-}1)F_{NHx} \quad (5)$$

The results of applying this equation to the same sites as in the previous Tables are shown in Table 4. In this case, the input of free H^+ in rain and cloudwater deposition is not treated separately. It is included implicitly because it is a result of atmospheric reaction of emitted SO_2 and NO_x. Ranges of total acidifying inputs to the soil are given for each site, and agree well with those calculated in Table 3, particularly as the components of deposition are given different weighting in the two approaches to account for atmospheric transformation. Apart from the approximations in estimating deposition, the only difference between the Tables is the small contribution of free H^+ in dry deposited unneutralised SO_4^{2-} aerosols, which is not easily measured and excluded from Table 3. It is expected to contribute less than dry deposition of NH_4^+ aerosols and to have a minor effect on the calculated figures.

The results in Table 4 demonstrate the relative contributions of different emissions to the acidifying input. If all the deposited N is accumulated and immobilised, then, by definition, all acidification derives from SO_2 emissions. By contrast, where these effects are not important, N deposition would contribute approximately 50-80% of the acidifying deposition for these examples. Ammonia emissions are also seen to be the main component of acidifying N deposition, contributing up to 30-60% of the acidifying deposition for the sites shown.

Table 4. Ranges of possible acidifying deposition to example unfertilized sites in the UK. Inputs expressed as the equivalent emitted pollutants

	Deposited species (kg S, N ha^{-1} yr^{-1}) (mmol H^+ m^{-2} yr^{-1})				% acidifying deposition attributable to equivalent emitted pollutants		
Site	SO_x [a]	NO_y [b]	NH_x [b]	Total H^+ input	SO_2	NO_x	NH_3
Southern Scotland							
Upland forest,	12	7.1	11.8				
eg Glentress	*75*	*0-51*	*0-84*	*75-210*	36-100	0-24	0-40
Upland moorland,	12	5.5	7.9				
eg Fala Moor	*75*	*0-39*	*0-56*	*75-170*	44-100	0-23	0-33
Eastern England							
Lowland forest,	20	12.4	48.4				
eg Thetford	*125*	*0-89*	*0-346*	*125-560*	22-100	0-16	0-62
Lowland heath,	20	9.9	16.6				
eg Breckland	*125*	*0-71*	*0-119*	*125-315*	40-100	0-22	0-38

a, from UKRGAR (1990)
b, from Table 2

Tables 3 and 4 show in a simple manner the ranges of possible acidification deriving from deposited inputs. Accordingly, no particular values for N transformations are given. These depend on biomass production and, therefore, on ecosystem type (forest, moorland) and management (harvesting). They are also expected to depend on the magnitude of deposition, as well as on

interactions with other nutrients. For example, short-term increased growth of trees deriving from increased N supply would result in increased base cation uptake by the trees, depleting soil base saturation and increasing acidification, which would limit the mitigating effect of biomass accumulation. Biomass accumulation will, however, have little effect in unharvested ecosystems (eg unharvested forest nature reserves). In this case, N uptake is balanced by mineralisation, so that where nitrification occurs the upper figures for the N contribution to acidification are expected to apply. Equally, in moorland areas where net accumulation of biomass is limited (removal by burning), the N contribution will approach the upper figures.

DISCUSSION

The Tables show the contribution of the different deposited pollutants to each of N eutrophication, acidification and NH_x effects. By definition, the latter depend specifically on NH_3 emissions, though the figures show that NH_x also contributes substantially to the other effects. In particular, the deposition of N as NH_x is larger than for NO_y for each of the example sites by a factor of 1.4-4. Although NH_3 emissions in the UK are less than for NO_x, the deposition of NH_x to the example sites is greater because the semi-natural ecosystems of interest for critical loads receive large rates of NH_3 dry deposition, whereas agricultural land is often a net source of NH_3.

Much of the scientific focus has been on the acidifying effects of deposition. In this case, N transformations may mitigate the effect of NO_y and NH_x, so that deposition of SO_x is most important. However, where N removal is limited, NH_3 emissions may make a major contribution (up to 30-60% for the examples given). The magnitude of this contribution has important implications for emission control policy. At present, control is focused on SO_2 and NO_x emissions (eg Commission of the European Communities 1989). From the example figures shown above, it is clear that such measures will have limited effectiveness for both acidification and N eutrophication in the absence of reductions in NH_3 emissions. Additionally, such measures would have no benefit in the case of NH_x-specific ecological effects. Though these NH_x effects have received less attention in their own right, they may be particularly important because of local deposition near agricultural sources. In addition, Bobbink *et al.* (1992) point out that the critical load for NH_x nutrient imbalances can be as small as 11 kg N ha^{-1} yr^{-1} for non-nitrifying soils.

The importance of each of the three pollutant response groups (N eutrophication, acidification and NH_3 effects) also highlights the need for improved integration of different critical loads. Alongside the development of critical loads for acidity, there has been some development of critical loads for N eutrophication (eg Bobbink *et al.* 1992), though there is also a need to further distinguish critical loads for NH_x effects (eg De Vries 1992). This distinction would be useful, because they represent a specific response to NH_3 emissions. A potential constraint is that some deposited NO_y may be assimilated by vegetation and subsequently mineralised to form NH_4^+. In this case, NH_4^+-nutrient imbalances might be defined in response to total N deposition. However, such imbalances would not be completely expected in situations of excess N, particularly for woody plants, which show a preference for uptake of NH_4^+ (Schulze *et al.* 1989), leaving NO_3^- to be leached from the soil. Hence, NH_4^+ effects are expected to be most closely coupled with NH_x deposition.

Separating these three pollutant response groups would allow each critical load to be mapped and compared with the relevant deposition to show exceedances in each case. It would be attractive to overlay these three maps of critical load exceedance (E) and apply the most sensitive effect (E_{max}) for each area in a combined exceedance map, ie:

$$E_{max} = \text{largest of } (E_{acidity} \text{ or } E_{totalN} \text{ or } E_{NHx}) \quad (6)$$

However, this procedure is complicated because each of the different exceedances and underlying critical loads relate to deposition of different quantities: $SO_x+NO_y+NH_x$ for acidity, $NO_y + NH_x$ for nitrogen eutrophication and NH_x for NH_x/base cation ratios, respectively. Reducing deposition on the basis of E_{max} at a particular date would not necessarily reduce the other exceedances. For example, if $E_{max} = E_{acidity}$ and emission controls reduced S deposition only, then the critical load for acidity might be met, but E_{totalN} and E_{NHx} would remain unchanged. As a consequence, protection of an area requires each of the three critical loads to be met. Nevertheless, these issues could be integrated qualitatively in a combined map, showing where each of the three critical loads were exceeded. This map would show up regional patterns in the three effects and the degree to which they overlapped.

One benefit of integrating the critical loads for N eutrophication and NH_x alongside that for acidity is that such integration would allow for ecosystem responses that are currently treated as mitigating effects in the critical load for acidity. For example, where a soil is non-nitrifying, this factor might be seen protecting it from acidification due to NH_x. However, it is in such conditions that the critical load for NH_x, in the context of imbalances in nutrient cation uptake, is most likely to be exceeded. Hence, integrating the three critical load exceedances would mean that the effect was still recognised.

A further example of such an effect is denitrification from forest soils, which is sometimes added to the critical load as a removal mechanism alongside biomass N accumulation (Grennfelt & Thörnelöf 1992). Because denitrification (producing both N_2 and N_2O) emissions increase in response to N deposition, ecosystem acidification from N inputs would tend to be limited (eg Aber *et al.* 1989).

Conversely, enhanced N_2O emission might in itself be considered a detrimental environmental effect and an indicator of having exceeded an N eutrophication critical load. Again, integration of the three exceedances would show which effect was the most sensitive.

There is also some evidence that enhanced N deposition can result in feedbacks which limit net NH_3 dry deposition to semi-natural ecosystems (Sutton *et al.* 1993). The suggestion is that the elevated N supply increases plant nitrogen status, allowing extended periods of NH_3 emission, which may also be associated with increased plant senescence. This process would mitigate against each of the three pollutant responses, as the deposition term used to compare with critical loads would be reduced. Such a response may be visualised as diluting the effects of deposited N by exporting the NH_3 from the most contaminated areas. Clearly, there is a problem for the critical loads approach, as the reduced deposition is itself a response to having exceeded the critical load. A possible solution would be to estimate deposition to damaged sites as if for healthy ecosystems, where NH_3 deposition was more rapid. At present, there is a requirement for further measurements to examine how widespread this phenomenon is, and also to ensure that NH_3 inputs are quantified on the basis of deposition to healthy sites.

CONCLUSIONS

Atmospheric pollutant inputs to ecosystems can be quantified by combining estimates of wet and cloud-water deposition, together with inputs by dry deposition of gases and particles. Dry deposition of gases (SO_2, NO_x and NH_3) is one of the most uncertain terms, especially for NH_3. Rates of NH_3 dry deposition depend on the vegetation type, though rapid deposition occurs for the semi-natural ecosystems of most interest for critical loads. Ammonia deposition is particularly sensitive to the canopy resistance, which for these sites is estimated at 5 s m^{-1}. For the four example sites in the UK, NH_3 dry deposition ranges from 3 to 41 kg N ha^{-1} yr^{-1}, which represents 33-85% of the total NH_x input at these sites.

Such dry deposition inputs may be combined with the other components of deposition to estimate the relative contributions to total nitrogen deposition (NO_y+NH_x) and acidifying deposition (SO_x+NO_y+NH_x). For the same example unfertilized sites, NH_x is estimated to contribute 60-80% of the total N deposition, with the greatest percentage over lowland forest where NH_3 dry deposition is largest. Total N deposition for these examples is estimated to be 10-60 kg N ha^{-1} yr^{-1}, though in practice some UK sites probably receive up to 100 kg N ha^{-1} yr^{-1} at woodlands close to large NH_3 sources.

Estimating the relative contribution to acidification is less simple because interactions within the ecosystem mitigate the acidification from the deposited N species. Nevertheless, ranges of the possible acidifying contributions may be defined. The acidifying inputs may be considered in two ways, as the *actual deposited species* or as the *equivalent emitted pollutants.* The former assesses the contribution of individual gases and ions deposited (eg SO_2, SO_4^{2-}, NH_3, NH_4^+, H^+), while in the latter the acidifying effects of SO_x, NO_y and NH_x are treated as for the precursor gases (SO_2, NO_x, NH_3), removing the effect of atmospheric transformation. Expressed as the equivalent emitted pollutants, NH_x contributes up to 30-60% of the acidifying input, demonstrating the importance of NH_3 emissions. The contribution is even larger when expressed as the actual deposited species (up to 60-75%), showing that most of the acidity is actually deposited as NH_x. The magnitude of each of these figures demonstrates the need to include NH_3 in emission control policy.

Although most attention has been given to acidifying deposition, effects of both total N deposition and NH_x *per se* have also been recognised. It is useful to distinguish these issues because they define three pollutant response groups for SO_x+NO_y+NH_x, NO_y+NH_x, and NH_x deposition, respectively. Separating these three groups defines effects in relation to the appropriate emissions, and also allows combined exceedance maps to be constructed showing areas not protected for each effect. Integrating critical loads for these three groups would also account for responses that tend to mitigate ecosystem acidification, such as non-nitrifying soils which are sensitive to NH_x-nutrient imbalances. Nevertheless, other ecosystem responses may remain untreated by this approach. An example is a possible feedback which limits NH_3 dry deposition to severely polluted semi-natural ecosystems, and which may itself be a response to having exceeded the critical load for N deposition. As a result, some caution is needed when comparing critical loads with deposition estimates that are based on inputs to N-polluted sites.

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