UNECE Ammonia Workshop (4-6 December 2006, Edinburgh)
Background Document for Working Group 1:

IS THERE A NEED TO REDEFINE THE CRITICAL LEVELS FOR AMMONIA?

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1. Introduction

The history of the evolution of Critical Levels for ammonia (NH_3), first defined at the UNECE Bad Harzburg workshop [*Posthumus*, 1988] and then revised at the UNECE Workshop in Egham, UK, in 1993 [*Ashmore and Wilson*, 1994], is summarised in the discussion paper by van der Eerden [*van der Eerden et al.*, 2006]. The 1993 Workshop agreed Critical Levels for different averaging times as follows: 1 hour: 3300 µg NH_3 m^{-3}; 1 day: 270 µg NH_3 m^{-3}; 1 month: 23 µg NH_3 m^{-3}; 1 year: 8 µg NH_3 m^{-3}. These were based on a statistical analysis of the available experimental data at the time using the Ecotox model. The lowest experimental concentrations producing effects (on heathland species) were around 20 µg NH_3 m^{-3} over 3 months. For a list of earlier Critical Levels see [*Fangmeier et al.*, 1994].

Since then, and particularly in the past 5 years, experimental data have become available that show measurable effects of NH_3 on vegetation over long time periods (months to years) at air concentrations of much less than 8 µg NH_3 m^{-3}. This background document presents some of these data, and raises questions for discussion that are relevant to a review of the current Critical Levels. Many of the comments made at the Egham meeting, and in subsequent reviews [*Fangmeier et al.*, 1994; *Krupa*, 2003], are still relevant today. Selected extracts from review papers are shown in Box 1. In 1993, almost all the information on effects of NH_3 on vegetation came from experiments or observations in the Netherlands, where background concentrations of NH_3 were high compared with many places in Europe and elsewhere. As experiments have been conducted in regions with much lower background concentrations, it has become clear that effects can be measured at very much lower long-term average NH_3 air concentrations. This is not perhaps surprising, given that many of the ecological changes resulting from enhanced N deposition in the Netherlands had already occurred, long before experiments were conducted specifically to investigate the role of NH_3.

This discussion paper raises the question of what is an appropriate 'No Observable Effect' concentration (NOEC) for NH_3 in general terms (i.e. in pristine environments). It appears that a NOEC will be very much less (in the long term) than the current annual Critical Level of 8 µg NH_3 m^{-3}. However, the discussion must then consider whether and how to provide region-specific or habitat-specific Critical Levels, based on the most sensitive components of an ecosystem, that can be most useful as a management tool relevant for policy development and application. It is interesting to note (Box 1) the comment that the current critical levels for NH_3 "…are probably only valid for temperate oceanic climatic zones." [*WHO*, 1997] This implies that we may not have sufficient data to establish Critical Levels for warmer, drier or continental climates.

Does the current annual Critical Level of 8 µg NH_3 m^{-3} protect vegetation?

The solid diagonal line in Figure 1 shows the predicted deposition for an air concentration of 8 µg NH_3 m^{-3} as a function of deposition velocity. For tall vegetation, this equates to 80 kg N $ha^{-1}y^{-1}$, well above most critical loads. The Critical Level is therefore not protecting vegetation from N deposition. Even for short vegetation, where deposition is less efficient, the predicted dry deposition for 8 µg NH_3 m^{-3} is 45 kg N $ha^{-1}y^{-1}$, which is higher than the empirical Critical Loads for semi-natural ecosystems; again the Critical Level is does not protect the ecoystem. In other words, one would expect that most habitats would exceed the Critical Load for N deposition before "direct effects" of NH_3 on vegetation would be expected to occur, based on the current annual Critical Level of 8 µg NH_3 m^{-3}.

Box 1: Points already made in previous documentation of NH_3 critical levels

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"NH_3 primarily acts as a fertilizer, usually increasing shoot growth while reducing or not affecting root growth"

"Internal consequences of exposure to NH_3 are increased nitrogen and often altered concentrations of nutrients, amino acids and carbohydrates"

"…long term exposures may ultimately affect the plant's ability to endure other environmental stresses, reducing the chances for survival"

"A future improvement might be the choice of a standard set of effect parameters which are ecologically relevant for the survival of each species within the ecosystem."

[*van der Eerden et al.*, 1994]

"..the amount of available data must still be regarded as too small, i.e. the number of observations was too small in many cases, to calculate critical levels for NH_3 for certain plant groups."

"…only a very limited number of experimental data to calculate critical levels are available."

"…the range of susceptibility to NH_3 is suggested to be as follows: natural vegetation > forests > crops".

"The concept of critical levels and critical loads is based on the assumption that the system does not respond to exposures below a certain threshold. However, for nitrogenous air pollution there are good reasons to assume that this threshold is equal to the natural background deposition, because with a low nitrogen input the system will use additional nitrogen."

[*Fangmeier et al.*, 1994]

"…of the plants threatened by increased nitrogen deposition, 75-80% are indicator species for low-nitrogen habitats."

"No-observed-effect concentrations (NOECs) are usually lower than critical levels."

"…critical loads focus on functioning of the ecosystem, while critical levels focus on protection of the relatively sensitive plant species."

"Observation of NH_3 injury to plants also indicates that this is greatest in winter."

"…growth stimulation is often considered an adverse effect in most types of natural vegetation."

"…nearly all of the information (*used to calculate critical levels)* originating from one Dutch research group. Only a few pollution climates were considered."

"More experiments with lower concentrations are required."

"The assumption that all deposited nitrogen-compounds…act additionally in their impact on vegetation is poorly based on experimental results and is probably not valid for the short term."

"The critical levels for NH_3…are probably only valid for temperate oceanic climatic zones."

"In the Netherlands, for example, all cyanobacterial lichens that were present at the end of the 19th century are now absent. In Denmark, 96% of the lichens with cyanobacteria are extinct or threatened."

[*WHO*, 1997]

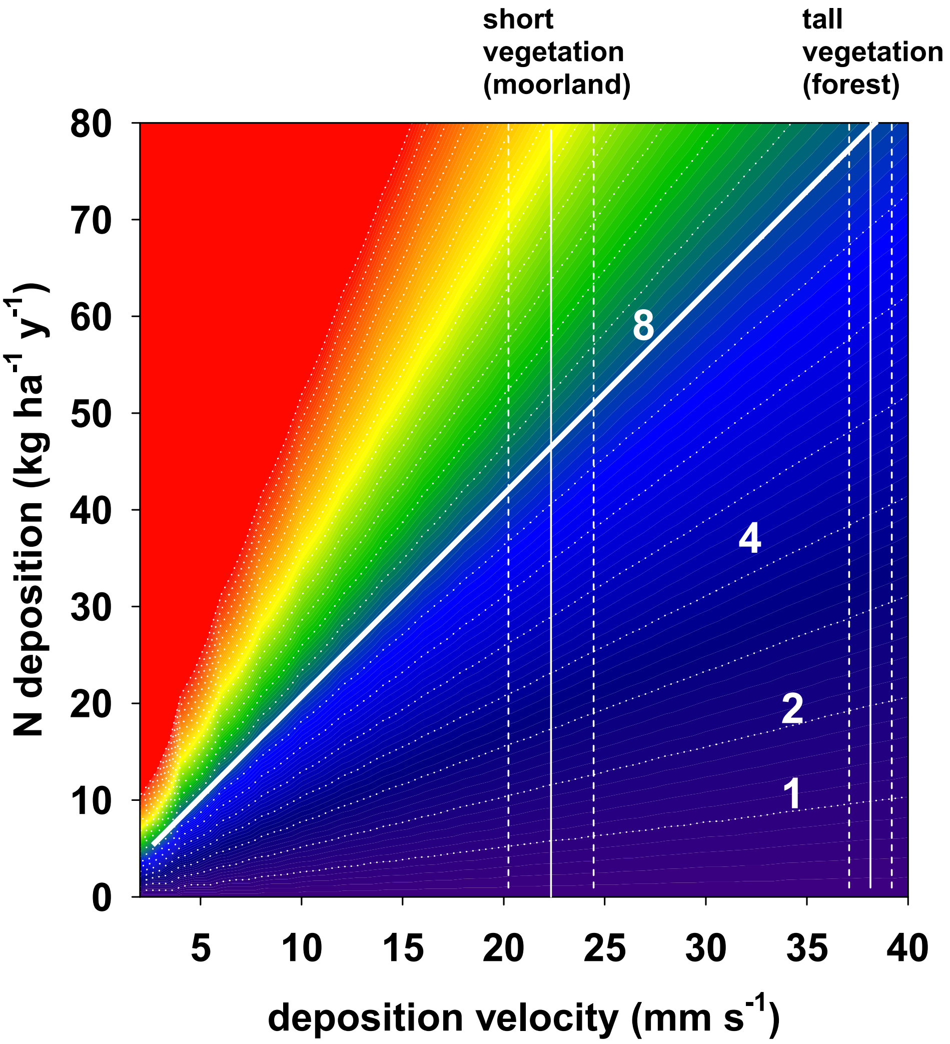

Figure 1. The relationship between annual N deposition and deposition velocity for NH_3 for a range of annual average NH_3 concentrations (diagonal dotted lines). Vertical lines show mean, dashed lines interquartile range, of UK NH_3 deposition velocities for moorland and forest based on 5 km grid square averaged annual wind speeds. Range for moorland is 16-32 mm s^{-1}; for forest is 33-44 mm s^{-1}.

The translation between empirical Critical Loads [*UNECE*, 2003] and equivalent NH_3 concentrations in air for different vegetation types is given in Table 1. This shows that even in the absence of other components of nitrogen deposition, NH_3 concentrations much lower than the critical level are expected to have significant adverse effects on a wide range of habitats.

Table 1. NH_3 concentration at which empirical critical load [*UNECE*, 2003] would be exceeded. (These are maximum values, representing the case where other components of nitrogen deposition are set to zero)

The range of deposition velocities assumed is based on the annual average wind speed dependent data for the UK for each 5 km grid square, separated as 'short vegetation' (16-32 mm s^{-1}) and 'tall vegetation' (33-48 mm s^{-1}).

Ecosystem type	**Empirical CL kg N ha^{-1} y^{-1}**	**NH_3 µg m^{-3}**	**Comments**
Forest			
Forest trees	15 - 20	1.3 - 2.3	Forest canopy and exposed surfaces
Ground vegetation	10 - 15	1.2 – 1.8	Probably higher; low dep. vel.
Lichens and algae	10 - 15	0.9 – 1.8	For exposed surfaces, high dep. vel.
Heathland, scrub and tundra			
Tundra	5 - 10	0.6 – 2.4	
Arctic, alpine and subalpine scrub	5 - 15	0.6 – 3.6	Lower concentrations for rougher surfaces
Northern wet heath *Calluna* dominated	10 - 20	1.2 – 4.8	
Northern wet heath *Erica* dominated	10 - 25	1.2 – 6.0	
Dry heaths	10 - 20	1.2 – 4.8	
Grasslands and tall forb habitats			
Sub-atlantic semi-dry calcareous grassland	15 - 25	1.8 – 6.0	
Non-mediterranean dry acid and neutral closed grassland	10 - 20	1.2 – 4.8	
Inland dune grasslands	10 - 20	1.2 – 4.8	
Low and medium altitude hay meadows	20 - 30	2.4 – 7.2	
Mountain hay meadows	10 - 20	1.2 – 4.8	
Moist and wet oligotrophic grasslands *Molinia*	15 - 25	1.8 – 6.0	
Moist and wet oligotrophic grasslands *Juncus*	10 - 20	1.2 – 4.8	
Alpine and subalpine grasslands	10 - 15	1.2 – 3.6	
Moss and lichen dominated mountain summits	5 - 10	0.6 – 2.4	Possibly lower for exposed locations
Mire, bog and fen habitats			
Raised and blanket bogs	5 - 10	0.6 – 2.4	
Poor fens	10 – 20	1.2 – 4.8	
Rich fens	15 – 35	1.8 – 8.4	

Ecosystem type	Empirical CL kg N ha^{-1} y^{-1}	NH_3 µg m^{-3}	Comments
Mountain rich fens	15 - 25	1.8 – 6.0	
Coastal habitats			
Shifting coastal dunes	10 - 20	1.2 – 4.8	
Coastal stable dune grasslands	10 - 20	1.2 – 4.8	
Coastal dune heaths	10 - 20	1.2 – 4.8	
Moist to wet dune slacks	10 - 25	1.2 – 6.0	
Marine habitats			
Pioneer and low-mid salt marshes	30 - 40	3.6 – 9.6	

In general, mean wind speeds are greater over much of the UK than mainland Europe. Consequently, particularly for rapidly absorbing (wet) surfaces, dry deposition velocities are likely to be higher in the UK than elsewhere. Consequently, the NH_3 concentrations required to exceed the Critical Load are likely to be nearer the upper end of the range, or even higher, in other regions of Europe, particularly for sites with low rainfall and low frequency of mist or fog. By contrast, these calculations are made assuming zero background (non-NH_3) N deposition, so represent upper limit NH_3 concentration thresholds.

With the exception of marine habitats (Table 1), the current annual Critical Level of 8 µg m^{-3} is redundant, i.e. the empirical Critical Load for N deposition will be exceeded on the basis of NH_3 concentration alone before the Critical Level is reached, often by a very large margin.

Is one year long enough to establish a Critical Level?

The foregoing discussion and calculations (Table 1) confound two different time-scales: the Critical Level for one year and the empirical Critical Load for a longer period. The latter explicitly considers the long-term potential for (harmful) effects on ecosystems or ecosystem components. In the Grange-over-Sands Critical Loads Workshop[*UNECE*, 1995], it was noted that the empirical critical loads for nitrogen "cannot be assumed to provide a protection period of longer than 20-30 years". However, the Critical Level philosophy considers an exposure of one year as sufficiently long to establish the appropriate limit value. This is understandable in that many Critical Levels were derived for annual crop plants, where exposure for longer than a single growing season was not relevant. However, for perennial semi-natural species there is no *a priori* reason to suppose that the cumulative effects of NH_3 are restricted to a single year. If one extrapolates the relationship between averaging time and Critical Level derived by van der Eerden [*van der Eerden et al.*, 1994] to longer averaging times, the 25-year Critical Level (analogous to the empirical Critical Load) would be around 2.5 µg NH_3 m^{-3}. Even if this extrapolation is not valid, data are now appearing that show a progressive effect with time of exposure to small NH_3 concentrations [*Sheppard et al.*, 2006].

Direct effects of NH_3 on vegetation at concentrations lower than the current Critical Level.

The question is then whether direct effects on vegetation can occur at smaller annual average air concentrations than the current Critical Level. If so, then such effects might be observed even if the Critical Load were not exceeded. For example, if direct effects were observed at 1 μg NH_3 m^{-3} on short vegetation, the annual dry deposition of NH_3 would only be 5 kg N ha^{-1} y^{-1}, below most existing Critical Loads, and therefore this concentration would not be thought to pose a risk.

A related question is whether "direct effects" vs "indirect effects" can actually be distinguished, since in many cases the boundary between the two becomes blurred. Even what is meant by "direct effects" remains a matter for debate. When the critical load/level definitions were originally agreed, there was the suggestion that "indirect" related to effects mediated via the soil (with ecosystems then being affected by different soil conditions, T. Spranger, pers. comm.). If this definition were adopted, then most effects of ammonia concentrations and dry deposition would be considered as "direct" since most NH_3 is directly taken up by plant surfaces, with only a small fraction reaching the soil surface. Given these uncertainties, it is most practicable to consider all effects of gaseous NH_3 (whether considered direct or indirect) where these have been observed in the field.

This section therefore reviews recent experimental and observational data that demonstrate measurable changes in vegetation, compared to 'background' conditions, which are directly attributable to (measured) exposure to NH_3. Results from measurements on vegetation where the NH_3 gas concentration has not been measured are not included (for example, studies where NH_3 concentration was only indicated by quoting data relative to distance from a point source), although they may have a bearing on the spatial range over which such effects can be observed.

How to determine whether a 'measurable difference' exists.

If one accepts that the existence of a 'measurable difference' from background conditions (a NOEC) is an adequate metric to establish a Critical Level, it is implicit that the 'background' reference level truly represents the non-disturbed state of the system. Unfortunately, much of the research on the effects of NH_3 comes from the Netherlands, where the 'background' state in terms of average NH_3 concentrations is somewhat greater than other areas of Europe. Indeed, as shown in Box 1, for the Netherlands 'background' conditions may have to relate to the 19th century rather than to any currently available region. Consequently, we are in a position where any effects of low concentrations have already occurred at some time in the past, and the reference levels for controlled experiments at several μg NH_3 m^{-3} are many times greater than air concentrations in remote rural areas in other parts of Europe.

Given this constraint on field-based experiments, where the lowest measured concentration has to be regarded as the local 'background' value, we are faced with the task of establishing when a measurement at another location is significantly greater than the 'background'. The word 'significant' here has two meanings, and it is important to differentiate them: in *statistical* terms, 'significant' means that the measurement exceeds the 'background' value, and has only a small probability (e.g.

<5%) of falling within the range of possible values regarded as 'background' – this depends *inter alia* on the inherent uncertainty of the measurement method and the spatial (and temporal) variability of the measured vegetation; in *biological* terms, 'significant' should be understood as meaning a change that will cause a measurable difference in the growth, vitality, reproductive fitness or competitive ability of an organism – this is in general more difficult to establish. In terms of the discussion below, it is proposed that any *statistically* significant difference in properties that can be attributed directly to exposure to NH_3 be used to define the thresholds for setting a Critical Level.

The statistical technique used below relies on the relationship between the measured endpoint (e.g. foliar N content) and the measured NH_3 concentration. In general, there will be insufficient data to postulate other than a linear or log-linear response curve, although other forms of relationship (e.g. sigmoidal) could exist and be used in a similar fashion. The first step is to establish the equation of the line or curve that best fits the data, by means of a least-squares analysis – this is best done on untransformed data by fitting the appropriate explicit form of equation (on the assumption that the measurement error is well represented by the replicate measurements at each concentration point). This may mean using more complex statistical software than a simple least-squares linear fitting routine as found in many spreadsheet applications. The appropriate 95% limiting curves should also be calculated – this gives an envelope (e.g. Figure 2) showing the 95% confidence limits for the relationship. For a relationship where the measured value increases with exposure concentration, the upper 95% curve at the lowest exposure concentration estimates the largest value that might be expected to fall within the local 'background' range at the lowest concentration measured (point A in Figure 2). If this measured value is extended to higher concentrations, the point where it intersects the fitted curve (point B) indicates the lowest concentration that would be predicted to yield a measurement value above the local 'background' (read from the x-axis at point C). This limiting concentration (C) is then an indication of the 'Critical Level' obtained from that data set. This procedure utilises all the information available (in fitting the relationship) while focussing on the lower end of the exposure scale. A measure of the appropriateness of the sampling regime (number of samples at any location) can be ascertained from the relationship between the spread of measurement data about the mean and the range of the fitted curve. If the true background conditions are not represented (i.e. the lowest measured concentration is above the background concentration) then this technique will tend to overestimate the Critical Level.

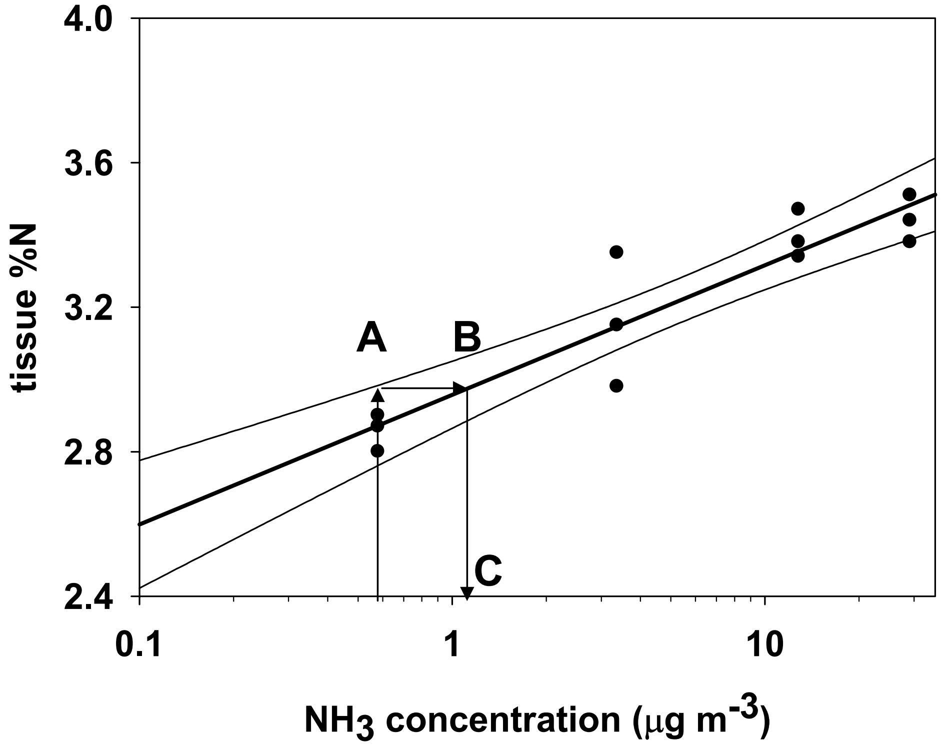

Figure 2. Illustrative example of estimation of Critical Level from measurements (of tissue %N) at several different locations (different NH_3 concentrations) where the lowest measured concentration is taken as representative of the local 'background' conditions.

This approach relies on the form of the relationship between the measured response variable and the NH_3 concentration. In most of the examples given in Table 2 there are relatively few data points, making it difficult to be certain of the appropriate relationship. In general, the best fit is with a linear response to the logarithm of NH_3 concentration, although for some situations a linear:linear response may be better.

One of the most comprehensive datasets is from Sheppard *et al.* [*Sheppard et al.*, 2006], reproduced as Figure 3, where the tissue %N of the moss *Hypnum jutlandicum* is plotted in response to long-term average NH_3 concentrations after 4.5 years exposure in the field-fumigation experiment at Whim, in south-east Scotland [*Leith et al.*, 2004]. In this case, the large number of data points clearly shows the linear response to a logarithmic increase in NH_3 concentration, and a calculated Critical Level, as defined above, of 0.8 μg NH_3 m^{-3}.

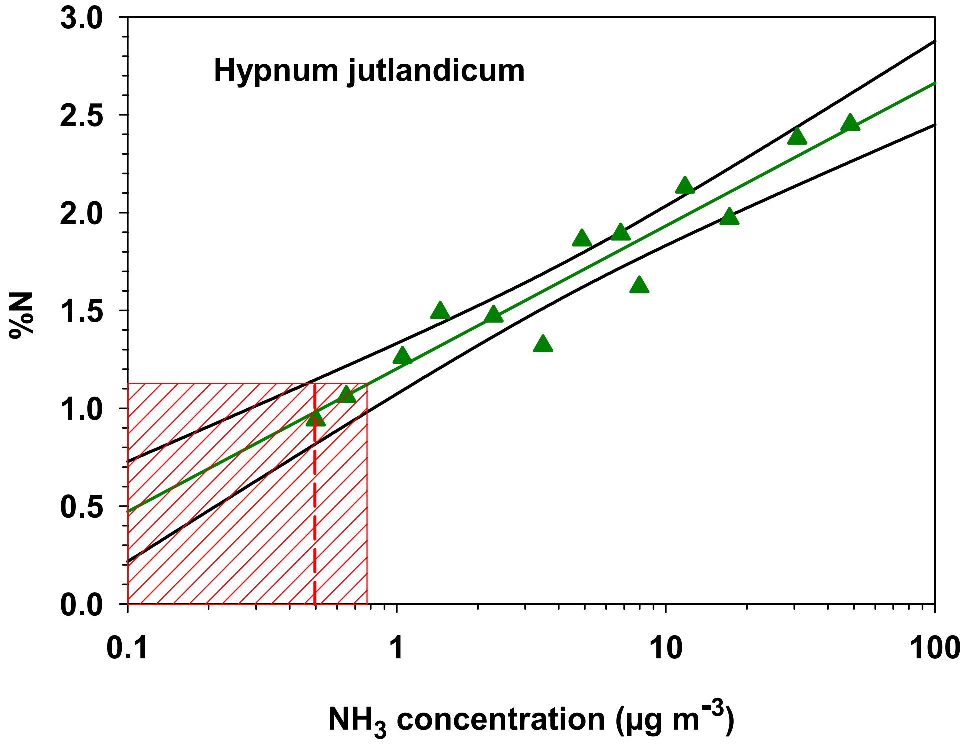

Figure 3. Increase in tissue N concentration of the moss *Hypnum jutlandicum* in response to experimental field-fumigation with NH_3 after 4.5 years of treatment (data from Sheppard et al., 2006).

Experiments in which the response to low concentrations of NH_3 have been recorded are summarised in Table 2, with an indication of the lowest NH_3 concentration measured (the 'background' level) and the calculated 'Critical Level' using the method described above. These data come from a variety of sources, including measurements around point sources, experimental fumigations and regional gradients. It should be noted that the degree of correlation in the experimental datasets affects the Critical Level values derived by this method. Hence high values shown in Table 2 do not necessarily indicate that the receptor was insensitive to NH_3; they simply reflect that in those examples the quality of the relationship is not sufficient to imply significant effects at lower NH_3 concentrations. It should also be noted that, the values in Table 2 do not include any "assessment factors" [*van der Eerden et al.*, 2006], which might mean that actual critical levels were set to lower values.

Table 2. Summary of recent experimental studies of the impact of NH_3 on vegetation

Measurement	linear/log	lowest NH_3 $\mu g\ m^{-3}$	Crit Lev $\mu g\ m^{-3}$	Source/ location	com
Field measurements close to point sources					
arginine in *Rhytidiadelphus triquetrus*	log	1.6	2.2	Poultry farm/ Scottish Borders	Feb 1995
threonine in *Rhytidiadelphus triquetrus*	lin	1.6	4.0	Poultry farm/ Scottish Borders	Feb 1995
histidine in *Rhytidiadelphus triquetrus*	log	1.6	2.2	Poultry farm/ Scottish Borders	Feb 1995
serine in *Rhytidiadelphus triquetrus*	log	1.6	2.2	Poultry farm/ Scottish Borders	Feb 1995
serine in *Rhytidiadelphus triquetrus*	lin	1.6	4.5	Poultry farm/ Scottish Borders	Feb 1995
glutamic acid in *Rhytidiadelphus triquetrus*	log	1.6	2.8	Poultry farm/ Scottish Borders	Feb 1995
glutamic acid in *Rhytidiadelphus triquetrus*	lin	1.6	5.0	Poultry farm/ Scottish Borders	Feb 1995
aspartic acid in *Rhytidiadelphus triquetrus*	log	1.6	3.5	Poultry farm/ Scottish Borders	Feb 1995
aspartic acid in *Rhytidiadelphus triquetrus*	lin	1.6	5.6	Poultry farm/ Scottish Borders	Feb 1995
NH_4^+ in *Hypnum cupressiforme*	Log	0.6	1.6	Poultry farm/ Scottish Borders	Oct-N
NH_4^+ in *Hypnum cupressiforme*	Lin	0.6	5.5	Poultry farm/ Scottish Borders	Oct-N
NH_4^+ in *Rhytidiadelphus triquetrus*	Log	0.6	1.4	Poultry farm/ Scottish Borders	Oct-N
NH_4^+ in *Rhytidiadelphus triquetrus*	Lin	0.6	4.7	Poultry farm/ Scottish Borders	Oct-N

Measurement	linear/log	lowest NH_3 µg m^{-3}	Crit Lev µg m^{-3}	Source/ location	com
%N in *Eurynchium striatum*	log	2	2.7	Poultry farm/ SW England	86 days
%N in *Eurynchium praelongum*	log	2	2.6	Poultry farm/ SW England	86 days
NH_4^+ in *Eurynchium praelongum*	log	2	2.2	Poultry farm/ SW England	86 days
NH_4^+ in *Eurynchium striatum*	log	2	10.0	Poultry farm/ SW England	86 days
NH_4^+ in *Eurynchium striatum*	log	2	2.8	Poultry farm/ SW England	log:lo
%N in *Dryopteris dilatata*	log	3	7.5	Poultry farm 'L'/ Central Scotland	July 1995
%N in ectohydric mosses	log	3	5.0	Poultry farm 'L'/ Central Scotland	July 1995
%N in ectohydric mosses	lin	3	9.0	Poultry farm 'L'/ Central Scotland '	July 1995
%N in Elder (*Sambucus nigra*)	log	3	9.5	Poultry farm 'L'/ Central Scotland	July 1995
%N in *Flavoparmelia caperata*	log	0.7	1.7	Pig farm/ Italy	2 x 2
Measurements on biomonitors close to a point source					
NH_4^+ in *Lolium perenne*	log	0.6	1.0	Poultry farm/ Scottish Borders	biomonit
total above-ground N per pot	log	0.6	2.0	Poultry farm/ Scottish Borders	biomonit
NH_4^+ in *Deschampsia flexuosa*	log	2	2.5	Poultry farm/ SW England	biomonit
%N in *Deschampsia flexuosa*	log	2	9.0	Poultry farm/ SW England	biomonit

Measurement	linear/log	lowest NH_3 µg m^{-3}	Crit Lev µg m^{-3}	Source/ location	com
Measurements from controlled field fumigation					
%N in *Hypnum jutlandicum*	log	0.5	0.8	Whim experiment/ South-east Scotland	4 year (NI
%N in *Calluna vulgaris*	log	0.5	1.0	Whim experiment/ South-east Scotland	4 year (NI
%Ca in *Calluna vulgaris*	log	0.5	1.0	Whim experiment/ South-east Scotland	4 year (NI
%Mg in *Calluna vulgaris*	log	0.5	1.3	Whim experiment/ South-east Scotland	4 year (NI
Measurements across regional gradients					
%N in epiphytic mosses	log/lin	0.02	<0.1	Atlantic oakwoods, North-western UK	variatio sourc

Comment: Discussed below

Other measures based on community structures may also be used to estimate Critical Levels in the field, in response to gradients in NH_3 concentrations. Pitcairn *et al.* (poster; see also [*Leith et al.*, 2005]) showed parallel gradients in Ellenberg N Index, but the data were not adequate to extract an effective 'Critical Level' as described above. However, the more sensitive index derived from the presence/absence of nitrophobe and nitrophile species [*Pitcairn et al.*, 2006; *Wolseley et al.*, 2006] suggested significant changes in species composition occurred at concentrations between 2 and 3 μg NH_3 m^{-3}.

Comment: This is where Pat Wolseley's data is cited

Discussion

The data presented in Table 2 show that the 'Critical Level' or NOEC as defined above is likely to be in the region of 1-2 μg NH_3 m^{-3} as a long-term average concentration, depending on the specific receptors being considered. Values in this range would also be broadly consistent with the estimates derived from Table 1, indicating a better harmonization with the empirical critical loads. However, there are several caveats to be made in interpreting the data, which are discussed below:

a) NH_3 as the main source of the measured effect;
b) the possibility of using biomonitors;
c) the height at which the NH_3 concentration is measured;
d) the variability in concentrations.

a) Is NH_3 responsible for the observed effects?

For the field fumigation experiments the link between cause and effect is strongest, because the experiment was designed for that specific purpose. For the purposes of this paper, as argued above, it does not matter whether this effect was a direct effect on foliage, or indirect through the underlying peat. However, the fact that both *Calluna* (an ericoid shrub) and *Hypnum* (a pleurocarpous moss) show similar responses strongly argues for a direct effect of the gas through foliar uptake.

For the field measurements around point sources (intensive agriculture) again it is most likely that NH_3 gas is the causal agent, although it is possible that N-containing dust could play a part. However, it is unlikely that the distribution of dust deposition over distances of several hundred metres would be strongly correlated with NH_3 concentrations, so that NH_3 is again the likely causal agent. Wet deposition is unlikely to change markedly over such short distances.

For the last entry in Table 2, the role of NH_3 is much more difficult to assess. Strong correlations in this study [*Mitchell et al.*, 2005] were also observed with wet N deposition and with throughfall N content. However, this example is a useful reminder of the other factors that may play an important role in affecting the measured properties of vegetation on a regional scale. Despite the strong correlations with wet deposition, it is still possible that the major influence controlling the N content of these epiphytic mosses was the local NH_3 concentration, mediated by the fraction of time that the bark surface on which they were growing was wetted by rain. However, given the strong correlations with other wet deposition and stemflow, it may be considered unsafe to set a very low critical level (0.1 μg m^{-3}) based on this dataset.

b) Can biomonitors be used to show that exposure to NH_3 at low concentrations affects plants?

In any study of the potential effects of air pollutants on vegetation, and in setting the Critical Level, of concern is the most sensitive species or organism present. In general, there is no way of deciding *a priori* which of the components of an ecosystem is likely to be the most sensitive, and it may be sufficient to show the *potential* for an effect, by using a biomonitor, rather than an *actual* effect on one of the components of the ecosystem. This begs the question as to what is an appropriate biomonitor plant to use, and whether it is surprising if a species able to respond to additional N, from whatever source, gives any indication of the likelihood of harmful effects to the natural ecosystem. However, the ability to exploit additional N is not confined to biomonitor species, and differential utilisation of additional N may well lead to changes in competition within communities. The data in Table 2 clearly show that NH_3 *can* influence the N content and growth of biomonitors, even at very low concentrations, and over periods as short as a month, with implications for other species.

c) At what height should NH_3 concentrations be measured?

There is no standard height used in experimental protocols for measuring NH_3 concentrations, although 1.5 m, above ground for short vegetation is usual. If a surface is absorbing NH_3 from the atmosphere, then a marked vertical gradient occurs, with concentrations decreasing towards the surface. The problems caused by the vertical gradient, and the correct methods for assessing the reference height at which concentrations should be measured [*Sutton et al.*, 1997], has been well described for the case of ozone [*Pleijel*, 1998]. The vertical gradient in NH_3 is illustrated in Figure 4, which shows the long-term monthly average concentrations of NH_3 in ambient air at the Whim experimental site at several heights above the canopy; the site and experimental procedures have been described elsewhere [*Leith et al.*, 2004]. The data in Table 2 were recorded at a height of 0.1 m; consequently, the derived 'Critical Level' in Table 2 may be too low by a up to a factor of 2, if referenced to a measurement height of 1.5 m above ground. It should be noted that the concentrations shown in Figure 4 are the long-time average concentrations, which are not the same as the concentrations that would be observed during conditions when micro-meteorological theory is applicable – i.e. the data in Figure 4 cannot be used to infer the NH_3 flux to the surface. The concentration gradient during conditions when micrometeorological flux theory is applicable is likely to be somewhat smaller [*Sutton et al.*, 1997].

These effects do not change the overall conclusion that the 'Critical Level' from the studies shown is ~1-2 $\mu g\ NH_3\ m^{-3}$. However, care must be taken in making NH_3 measurements at an appropriate height above the canopy of the vegetation of interest. This may be of particular concern in complex layered canopies, for example if assessing the concentrations to which forest understorey vegetation is exposed.

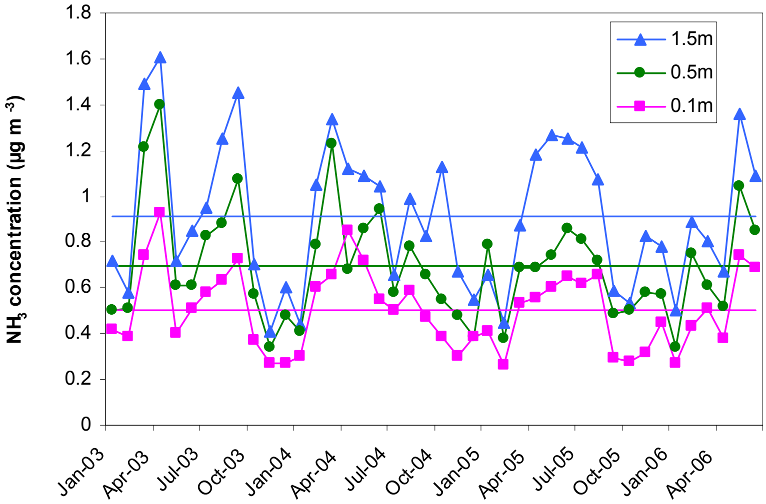

Figure 4. Ambient NH_3 concentrations from Jan 2003 to June 2006 at Whim experimental site, south-east Scotland, at 0.1, 0.5 and 1.5 m above the canopy, showing the average vertical gradient in NH_3 concentration (horizontal lines). The concentrations represent background ambient conditions at a point unaffected by the experimental NH_3 release.

Comment: Check above ground or above canopy

d) How important is the temporal variability of NH_3 concentrations?

Much of the data represented in Table 2 comes from environments (point sources) where the long-term average concentration conceals the variability that is a feature of exposure to NH_3 close to agricultural point sources. Apart from the regular cycles of production (e.g. in broiler chicken houses), the exposure of vegetation is likely to be strongly dependent on wind direction, with alternating exposure to high concentrations when the wind is blowing from the source, and low 'background' concentrations when the wind is blowing towards the source. If, for example, the wind direction leading to fumigation of a site close to a source occurs only 10% of the time, then the average concentration during such episodes will be (approximately) 10 times the measured long-term average value. In conditions with low wind speeds, or when dispersion is poor, short-term concentrations for an hour or more may be even higher still. There are no experimental data that have explicitly considered the differential effect (if any) of exposure to constant low concentrations or intermittent higher concentrations with the same mean value. It is therefore a debatable point as to whether the observed effects are caused by the intermittent higher concentrations, or to the long-term average. This may not be a problem if the earlier formulation of Critical Levels [*Ashmore and Wilson*, 1994] is considered to apply – where the 1 hour Critical Level is 3300 µg NH_3 m^{-3}, or over 400 times the annual Critical Level of 8 µg NH_3 m^{-3}. Burkhardt et al. [*Burkhardt et al.*, 1998] showed that for long-term continuous measurements of NH_3 concentrations in an agricultural region the ratio of hourly maximum to annual maximum concentrations was only around 30, suggesting that the annual average value was the more strict criterion under these conditions (i.e. the ratio of the measured maximum annual average to the Critical Level (0.18) was greater than the ratio of the measured maximum hourly average to the hourly Critical Level (0.013). This finding was repeated at the Whim experimental site, where the point of exceedance of the annual NH_3 critical level occurred at a greater distance from the source than the point of exceeding the monthly critical level.

Interactions with other factors

The effects of NH_3 on vegetation may be enhanced by interaction with drought or frost [*van der Eerden et al.*, 1991]. Low temperatures increase the solubility of NH_3 in water, and whether the active component of dissolved NH_3 is the undissociated molecule or the ammonium ion, concentrations will be enhanced in the leaf at low temperatures; the equilibrium concentration of undissociated NH_3 is twice as great at 5 °C as at 20 °C. Moreover, at lower temperatures, the processes which lead to assimilation or detoxification of NH_3 inside the leaf may be less effective than at higher temperatures. There is some field evidence for interactions of low concentrations of NH_3 with both low temperature (frost) and drought.

A reduction in the cover of green shoots of *Calluna* at the Whim experimental site in south-east Scotland has been observed after each winter when the shoots had a bleached appearance. The NH_3 concentration at which this type of damage occurred has decreased with each year of exposure [*Sheppard et al.*, 2006]. The bleaching observed in *Calluna* is most likely due to an interaction between NH_3 and a secondary stress, winter desiccation [*Sheppard and Leith*, 2002], and implies that NH_3 has affected several aspects of the metabolism of *Calluna*, in addition to increasing susceptibility to desiccation. Frost hardiness experiments conducted in years one and two indicated that ammonia reduced shoot hardiness, as shown by warmer LT_{50}s (lethal temperature causing 50 % shoot death). However, the effect was not sufficient to explain the damage observed following the winter temperatures experienced by these plants in the field, which did not fall below –10 ^{0}C.

Interactions with other pollutants are also poorly understood. There is experimental evidence of increased deposition rates of SO_2 in response to NH_3 field fumigation [*Cape et al.*, 1995], and of increased NH_3 deposition in response to SO_2 field fumigation [*Shaw and McLeod*, 1995]. However, interaction with SO_2 might be expected to lead to increased deposition to external leaf surfaces, and localised depletion of gas-phase NH_3 near stomata, thereby reducing internal uptake and NH_3 effects. However, NH_3 deposited to leaf surfaces can subsequently migrate into the leaf [*Sutton et al.*, 1995], while there would be increased net deposition of N to the ecosystem, with implications for Critical Load exceedance.

Interactions with biotic stresses (pathogens, insects) are known to occur at high NH_3 concentrations; see reviews [*Fangmeier et al.*, 1994; *Krupa*, 2003], but little is known about effects at low concentrations.

Conclusions

1. The current annual Critical Level of 8 µg NH_3 m^{-3} is currently of little practical use because it is not as precautionary as empirical Critical Loads for most of the semi-natural habitat types of Europe.
2. Uncertainty exists in appropriate deposition velocities for climatic zones outside the western maritime conditions of western Europe, especially for colder and drier climates.
3. There is clear evidence of effects of NH_3 on vegetation at concentrations well below the current long-term Critical Level, even below 1 µg NH_3 m^{-3} for UK ecosystems.
4. The use of biomonitors to evaluate Critical Levels for NH_3 should be investigated.
5. The measurement height for NH_3 measurements should as far as possible be standardised because of the pronounced vertical gradients in NH_3 concentrations close to vegetation surfaces.
6. Little is known of the quantitative interaction with cold and drought stress, particularly at low concentrations of NH_3.
7. Little is known about interactions with other pollutants.
8. It remains a matter for discussion in the expert workshop, whether to combine information from experiments looking at NH_3 effects directly with others used to estimate empirical critical loads, and thereby consider habitat specific NH_3 critical levels.

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