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Evidence for changing the Critical Level for ammonia

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The long-term critical level for NH_3 has been revised down to 1 µg m^{-3} for the most sensitive plant species.

Abstract
The current Critical Level for ammonia (CLE_{NH3}) in Europe is set at 8 µg NH_3 m^{-3} as an annual average concentration. Recent evidence has shown specific effects of ammonia (NH_3) on plant community composition (a true ecological effect) at much smaller concentrations. The methods used in setting a CLE_{NH3} are reviewed, and the available evidence collated, in proposing a new CLE_{NH3} for different types of vegetation. For lichens and bryophytes, we propose a new CLE_{NH3} of 1 µg NH_3 m^{-3} as a long-term (several year) average concentration; for higher plants, there is less evidence, but we propose a CLE_{NH3} of 3 ± 1 µg NH_3 m^{-3} for herbaceous species. There is insufficient evidence to provide a separate CLE_{NH3} for forest trees, but the value of 3 ± 1 µg NH_3 m^{-3} is likely to exceed the empirical Critical Load for N deposition for most forest ecosystems.

1. Introduction
The Critical Level (CLE) for air concentration of a pollutant gas is defined as "the concentration in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to present knowledge" (Posthumus, 1988). This definition means that when direct adverse effects of a gas are shown to occur at concentrations below the accepted Critical Level, 'present knowledge' must be updated and the Critical Level reviewed. In contrast, the Critical Load (CLO) is defined as "a quantitative estimate of deposition of one or more pollutants below which significant harmful effects on specified elements of the environment do not occur according to present knowledge" (Posthumus, 1988).

The distinction between the definitions is important; it is much more difficult to demonstrate the absence of an effect (to test the CLO) than the presence of an effect (to challenge the CLE). There is a more fundamental difference which is not included in the specific definitions given above, the inclusion of time frames. In general, CLEs are expressed in terms of threshold concentrations not to be exceeded over 1 hour, 1 day, 1 month or 1 year, while the CLO is defined in terms of long-term potential effects (several decades) (van der Eerden et al., 1991). This is because CLOs are usually seen as operating through soil and water rather than directly on vegetation, whereas CLEs refer to direct effects of airborne gases on the vegetation. The differences in applying CLEs and CLOs to nitrogen-containing pollutants (including ammonia) are summarised in Table 1.

Table 1. Current differences in practice between Critical Levels (CLEs) and Critical Loads (CLOs) for N-containing air pollutants.

	CLE	CLO
Summarized definition	Concentration above which effects may occur	Deposition below which effects do not occur
Exposure duration:	Short term (1 yr or less)	Long term (+ 10 yrs)
Effect of peak exposures	Included	Neglected
Agent:	Separate CLE for each N-compound	All N-compounds added
Object of interest:	Individual plant species	Natural vegetation or forests; soils and freshwaters (ecosystems)
No effect concentration:	Generally: the lowest statistically significant response observed in experiments	Generally: estimate of a "safe" deposition level derived from empirical evidence or modelling.
Goal:	Protection of sensitive plant species	Protecting proper functioning of ecosystems
Combination effects	Possibility of synergism is considered	Additivity is presumed (i.e. all forms of N have same effects)

CLEs for NH_3 (CLE_{NH3}) were 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). There have been several subsequent reviews on the effects of NH_3 on vegetation (Fangmeier et al., 1994, Krupa, 2003, van der Eerden et al., 1994, WHO, 1997). The issues involved in addressing the CLE_{NH3} and highlighted in the review articles have been summarised (Cape et al., 2008) in the proceedings of a workshop held in Edinburgh in December 2006 under the auspices of the United Nations Economic Commission for Europe (UNECE) (Sutton et al., 2008a). This paper presents the rationale for reassessing the concept of a CLE_{NH3}, including the procedures used to establish the threshold concentration at which effects are observed, then examines the recent evidence for effects of NH_3 on vegetation at concentrations below the original annual CLE_{NH3} of 8 μg m^{-3}, leading to conclusions and recommendations for new CLE_{NH3} for sensitive vegetation types.

2.   Evidence for reassessing the CLE_{NH3}

Much of the debate over the effects of NH_3 on vegetation arises over the distinction between direct effects of the gas on the above-ground vegetation, and the role of NH_3 in acting as a source of dry-deposited nitrogen (N) to the soil or substrate, adding to the CLO for N. In practice, the current annual CLE_{NH3} of 8 μg m^{-3} does not protect vegetation in Europe because the CLO for N deposition would be exceeded in most ecosystems from the dry deposition of NH_3 long before any direct effects would be expected to occur on the basis of the current annual CLE_{NH3} (Cape et al., 2008). In terms of setting CLEs, the critical question to be answered is whether (in terms of the definition above) a 'direct adverse effect on the receptor' of NH_3 can be demonstrated as distinct from any contribution of NH_3 to N deposition and soil-mediated effects. Although changes in vegetation properties (e.g. tissue N concentrations) can be observed in response to NH_3 (Sheppard et al., 2008b) there is generally no indication of the long-term consequences of such changes, whether adverse or otherwise. The evidence presented below is therefore derived from field-based observations of changes in populations of vegetation, where the evidence for an adverse effect is demonstrated in terms of the loss of one or more species from a community, or radical changes in the proportions of species in a community. This is a very different

approach from that used in the initial setting of the CLE_{NH3}, which made extensive use of laboratory experiments on plants, often species with a high N demand, growing as single species or cultivars in monocultures at constant NH_3 concentrations (Posthumus, 1988).

In deriving a CLE_{NH3} from field observations, the causal relation of the exposure with an ecologically relevant end-point should be clear and quantified. Field observations also can include the interactions (in terms of effects) between NH_3 exposure and environmental conditions. There is evidence of enhanced sensitivity of plants to NH_3 during drought and cold, and vegetation may become more sensitive to insect or pathogen attack, or to strong winds after exposure to NH_3 (Sheppard et al., 2008b, van der Eerden et al., 1991, van der Eerden et al., 2008). However, the field observations used to derive the CLE_{NH3} will not have encompassed the full range of possible environmental conditions. Consequently, exceedance of the CLE_{NH3} does not guarantee that an effect will be observed, nor does it guarantee that no effect will be observed in the presence of particular environmental stresses. Interactions with other gaseous pollutants are also poorly understood. There is experimental evidence of increased deposition rates of SO_2 in response to NH_3 (Cape et al., 1995), and of increased NH_3 deposition in response to SO_2 (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.

Much, but not all, of the evidence presented here is derived from observations made downwind of large intensive animal production units, which are the major point sources of NH_3 in the landscape. Consequently, we need to demonstrate that the causal agent in any effects is likely to be NH_3 rather than another material emitted from such sources. Corroborative evidence will be given from a long-term field fumigation study of an ombrotrophic bog which used pure NH_3 (Leith et al., 2004). In all cases, the evidence is supported by measurements of NH_3 concentrations at the sites of interest.

Emissions from intensive livestock rearing units contain a cocktail of compounds including NH_3, carbon dioxide, gaseous amines and particles containing nutrients, including nitrogen, phosphorous and potassium. It is possible that nutrient-containing particles (dust) could play a part in any observed effects on vegetation. However, the spatial pattern of dust deposition to the landscape is rather different from that for NH_3; large particles ($> 10^{-6}$ m diameter) deposit rapidly, within a few tens of metres, whereas sub-micron particles are inefficiently scavenged by vegetation and may be dispersed over tens or even hundreds of km (Pryor et al., 2008). Ammonia, however, is likely to have effects up to a few hundred metres downwind, depending on the size of the source (Pitcairn et al., 2002). CO_2 is emitted in large quantities in co-occurrence with NH_3, but again its impact on the NH_3 effect is probably negligible (Perez-Soba et al., 1994). Wet N deposition is unlikely to change markedly over short distances from the source; any increases in N deposition measured in throughfall close to point sources are most likely attributable to the removal of soluble dry deposition (mostly NH_3) from plant surfaces (Cape et al., 1995) rather than direct incorporation into falling rain. The evidence presented below relies strongly on observations of lichen and bryophyte communities in response to measured NH_3 concentrations. These

communities are least likely to be influenced by N supply from the substrate, and therefore are good indicators of a direct effect of NH_3 in the gas phase.

3.   Procedures for deriving a CLE from an exposure-response relationship

In order to establish a CLE from field observations, the main difficulty is to establish an appropriate background exposure which is below the presumed 'no observed effect concentration' (NOEC). Air concentrations in remote rural areas of Europe are well below 1 µg NH_3 m^{-3}, and, given the relatively short transport distance of gaseous NH_3 in the atmosphere (tens rather than hundreds of km) may be assumed to be close to a true 'background'. However, for many regions of Europe the regional 'background' concentration may be several µg NH_3 m^{-3}, and changes in plant communities may have already occurred many decades ago. For those regions 'background' conditions may have to relate to the 19th century rather than to any currently available. There is documented evidence, for example, of the loss of cyanobacterial lichens in the Netherlands over the past century (WHO, 1997). This problem also arose with some of the early experimental approaches to determining NOECs, where the 'control' NH_3 concentration was several µg NH_3 m^{-3} (van der Eerden et al., 1991).

We therefore need to establish, for any given location where vegetation is exposed to a source of NH_3, the point at which significant changes can be observed. The word 'significant' refers to both *ecological* and *statistical* significance. Responses in terms of growth, vitality, reproductive fitness, competitive ability, shifts in species composition etc. can be regarded as having *ecological* significance. But for some other responses to exposure to NH_3, such as enhanced foliar contents of N, arginine or NH_4^+, Glutathione synthetase activity etc., the relationships with ecological end points and their dependence on environmental conditions are still insufficiently quantified even at the species level for them to be used directly as a basis for setting CLEs. 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 some cases the exposure/response relationship shows a clear break point - the point above which the response deviates from the values observed at low concentrations - and continues to increase in response to increasing concentrations. However, for most of the new information presented here we do not know the true 'background' or 'no-effect' concentration, and so have had to rely on a statistical procedure to identify the point at which an effect is detectable that is statistically significantly different from that observed at the lowest concentrations observed at a given field site.

The method used to identify the apparent NOEC is illustrated in Figure 1. The equation of the line that best fits the response data in terms of the measured NH_3 concentration was established by means of a least-squares analysis. The 95% confidence limits for the relationship can than be calculated. The upper 95% curve at the lowest exposure concentration estimates the largest value of the response variable that falls within the local 'background' range (the lowest concentration measured; point A in Figure 1). If this response value is extended to higher concentrations, the point where it intersects the fitted curve (point B) indicates the lowest concentration that yields 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 NOEC 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. In general, for the data available, either a linear or log-linear response curve has been used, although other forms of response (e.g. sigmoidal) could exist and be used in a similar fashion.

This approach is a pragmatic solution to situations where the true NOEC may already have been exceeded at the point where the lowest concentration was measured. Consequently, the NOEC derived from this approach may be an overestimate. The exact form of the relationship between the response variable and the NH_3 concentration may be uncertain, because of the paucity of sampling points. If an inappropriate response function is fitted, or if the data are subject to large measurement uncertainties, then the 95% confidence intervals will tend to be wide, and the apparent NOEC will again be overestimated. Consequently, the bias in this method is to overestimate the NOEC. Even where a very clear and well-fitted response is observed, the NOEC obtained is specific for the particular site, and includes no 'safety factor' to allow for extrapolation to other sites or conditions, as often used in establishing toxicity thresholds in ecotoxicology.
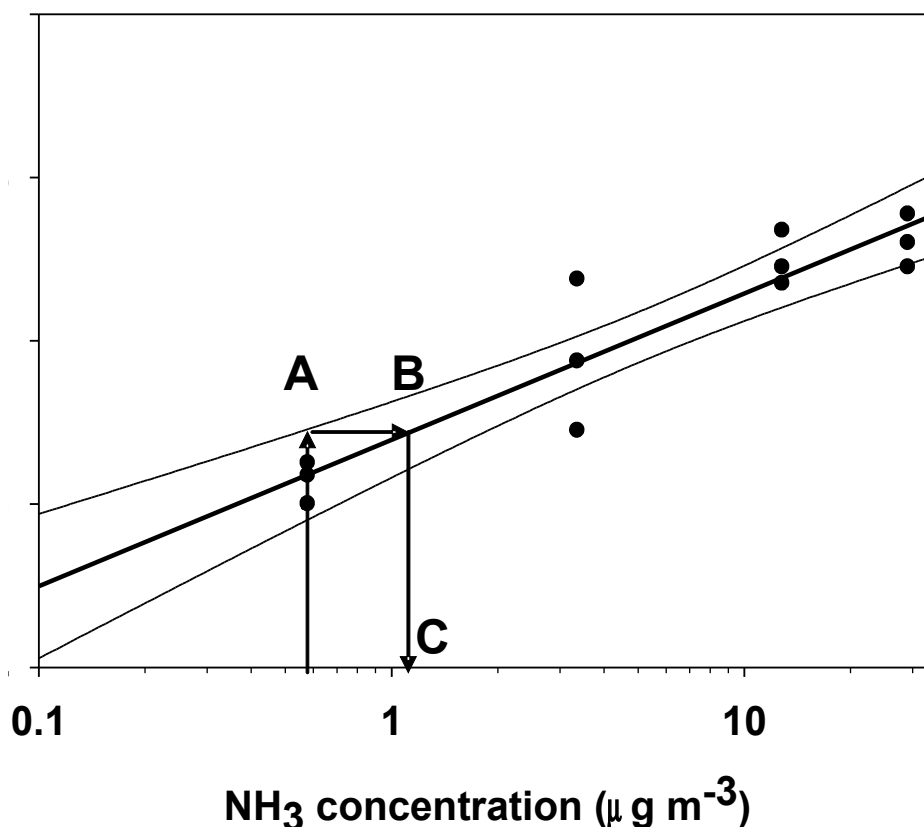

Figure 1. Illustrative example of estimation of the NOEC from measurements at several locations differing in NH_3 concentration. The lowest measured concentration (A) is taken as representative of the local 'background' concentration.

4.   Evidence for adverse effects below the CLE_{NH3} of 1993

This section 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.

One of the most comprehensive datasets is from Whim Bog (Sheppard et al., 2008a), reproduced as Figure 2, where the tissue %N of the moss *Hypnum jutlandicum* (Holmen and Warncke) is plotted in response to long-term average NH_3 concentrations after 4.5 years exposure in the field-fumigation experiment at Whim Bog, 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 CLE_{NH3}, as defined above, of 0.8 µg NH_3 m^{-3}.
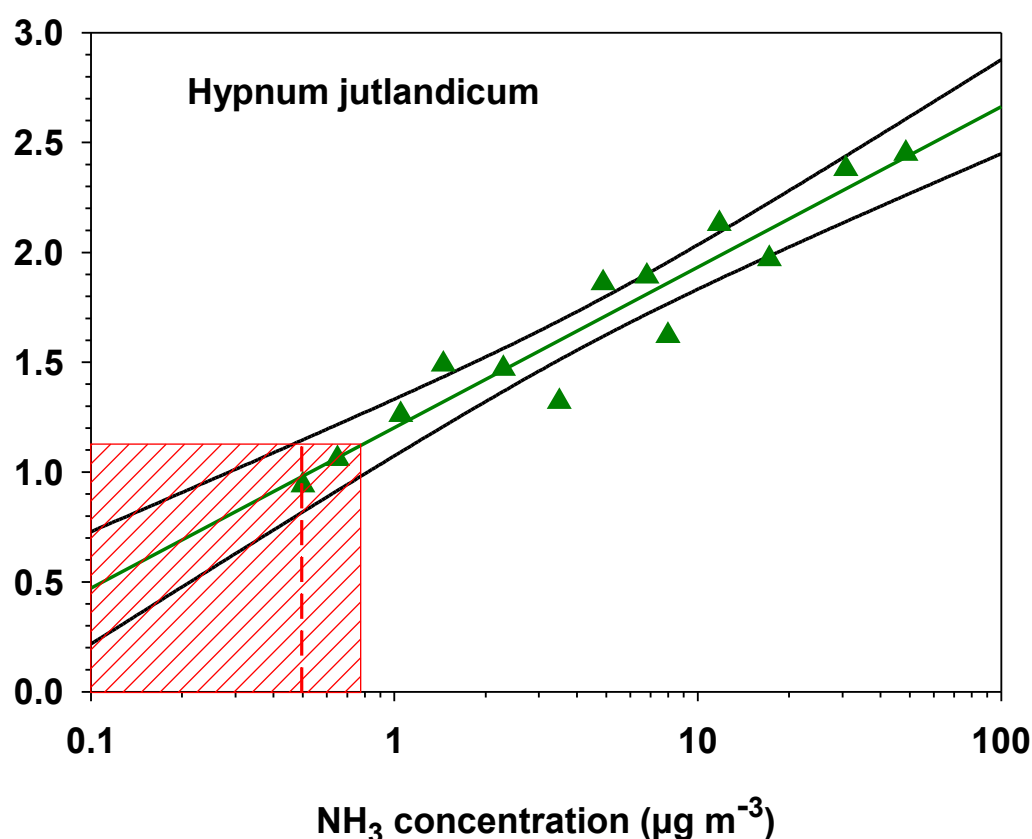

Figure 2.   Increase in tissue N concentration of the moss *Hypnum jutlandicum* in response to experimental field-fumigation with NH_3 after 4.5 years of treatment (data from Sheppard et al., 2008a).

Although this example only shows a measurable response to NH_3, which may not be *ecologically* significant, it illustrates the method using real field data, and shows that plants do respond to NH_3 concentrations very much smaller than the current CLE_{NH3}. Similar data have been reviewed and summarised elsewhere (Cape et al., 2008), and serve as corroborative evidence for NH_3 effects at low concentrations, even though

the measured response may not (yet) have resulted in changes in species composition or other ecologically relevant outcomes.

The same approach can, however, also be used to examine the effects on community structures of measured gradients in NH_3 concentrations downwind of large sources. Several indices of community response have been used: parallel spatial gradients have been shown between NH_3 concentrations and Ellenberg N Index (Leith et al., 2005, Pitcairn et al., 2006). A more sensitive index, derived from the presence/absence of nitrophobe and nitrophile species (Pitcairn et al., 2006, Wolseley et al., 2006), suggested that significant changes in species composition occurred at concentrations between 1 and 3 $\mu g\ NH_3\ m^{-3}$. More recent data, derived from experiments in the UK, Switzerland, Portugal and Italy, all indicate ecologically significant effects in the range of $0.5 - 4\ \mu g\ NH_3\ m^{-3}$ (Frati et al., 2007, Pinho et al., 2008, Rihm et al., 2008, Sutton et al., 2008b) . The results of the statistical approach described above to each of these datasets are shown in Table 2. Lichens and bryophytes represent the most sensitive types of vegetation to NH_3.

Table 2: Summary of NOECs of the impact of long-term exposure to NH_3 on species composition of lichens and bryophytes. NOECs were directly estimated from exposure/response curves or calculated with regression analysis. The data are from recent experimental studies, both field surveys and controlled field experiments on the impact of NH_3 on vegetation.

Location	Vegetation type	Lowest measured NH_3 concentration ($\mu g\ m^{-3}$)	Estimated NOEC ($\mu g\ m^{-3}$)	Reference
SE Scotland, poultry farm	Epiphytic lichens	0.6	0.7 (on twigs) 1.8 (on trunks)	(Pitcairn et al., 2004, Sutton et al., 2008b)
Devon, SW England	Epiphytic lichens diversity (twig)	0.8 (modelled)	1.6	(Wolseley et al., 2006)
United Kingdom, national NH_3 network	Epiphytic lichens	0.1	1.0	(Leith et al., 2005, Sutton et al., 2008b)
Switzerland	Lichen population index	1.9 (modelled)	2.4	(Rihm et al., 2008)
SE Scotland, field NH_3 experiment, Whim bog	Lichens and bryophytes – damage and death	0.5	< 4	(Sheppard et al., 2008a)
Corroborative evidence *				
SW England	Epiphytic lichens	1.5	ca. 2	(Leith et al., 2005)
South Portugal	Epiphytic lichens	0.5	1	(Pinho et al., 2008)
Italy, pig farm	Epiphytic lichens	0.7	2.5	(Frati et al., 2007)

* In these cases NH_3 concentration data were available for less than one year, which is why these results are categorised as "corroborative evidence".

5.   Proposal for new CLEs

The data in Table 2 suggest that the current annual CLE_{NH3} does not protect the most sensitive components of ecosystems, namely lichens and bryophytes, and probably also some of the more sensitive higher plant species. The changes in species composition observed for ecosystems that contain lichens and/or bryophytes suggest

that long-term exposure at concentrations lower than 8 μg NH_3 m^{-3} would lead to changes in species, and possibly species extinction. In this case, 'long-term' refers to a period of several years, sufficient for such changes to occur. Based on the NOEC data in Table 2, a long-term CLE_{NH3} for these systems should be set at 1 μg NH_3 m^{-3}. For higher plants, there is much less new information, but two studies indicate that the current CLE_{NH3} of 8 μg m^{-3} is too high as a long-term threshold for higher plants in natural vegetation.

(1) Changes in woodland ground flora downwind of an intensive animal unit in SW England suggest a threshold of 4 μg m^{-3} (Leith et al., 2005).

(2) Comparison of the increasing rate of death of *Calluna vulgaris* at a field fumigation experiment in Scotland (Whim bog) with the death rate of the lichen *Cladonia* spp. indicates consistently that *Calluna* death occurs at a concentration 2.2 times that at which *Cladonia* is killed (Sheppard et al., 2008a); this implies a 'no effect' concentration for *Calluna* of around 2 μg m^{-3}.

On the basis of these results, we propose the long-term CLE_{NH3} for higher plants as 3 μg NH_3 m^{-3}. Although data are sparse, it is likely that the CLE_{NH3} as defined above would protect bogs, heathland, woodland ground flora and probably also oligotrophic grassland, from NH_3-driven shifts in species composition, and the potential for species extinctions.

There is too little experimental information to propose a long-term CLE_{NH3} for all ecosystems or habitats. However, the proposed long-term CLE_{NH3} for higher plants is likely to be no more restrictive than the existing CLO for most habitats, based on estimating the contribution of 3 μg NH_3 m^{-3} to dry deposition of N in most ecosystems. For example, typical values for the UK would be 15-20 kg N ha^{-1} y^{-1} for short vegetation, and up to 30 kg N ha^{-1} y^{-1} for tall vegetation, in addition to the deposition of other N species (wet and dry).

6.   Conclusions and recommendations

The current annual CLE_{NH3} of 8 μg NH_3 m^{-3} is of little practical use because it was not defined in terms of sensitive ecosystems, and because it is not as precautionary as empirical Nitrogen Critical Loads for most of the semi-natural habitat types of Europe. Clear evidence has emerged, especially from field studies in the UK, but also from several other European countries, of effects of NH_3 on vegetation at concentrations well below the current annual CLE_{NH3}. Based on that evidence, a long-term CLE_{NH3} of 1 μg NH_3 m^{-3} can be assumed to be protective for biodiversity of most sensitive ecosystems. A long-term CLE_{NH3} of 3 μg NH_3 m^{-3} is probably protective for biodiversity of systems if bryophytes and lichens are not included.

Despite the progress made in recent years, several uncertainties still remain. Additional work is required to allow inter-conversion of CLEs and CLOs. In particular, uncertainty exists as to the appropriate deposition velocities linking CLEs and CLOs for climatic zones outside the western maritime conditions of western Europe, especially for colder and drier climates. As with the CLO, it is expected that interactions with other plant stresses will modify the CLE, although there are few data on the quantitative interaction with high and low temperatures or drought stress. There are some indications, for example, that cold and drought stress make *Calluna* more sensitive to NH_3 (Sheppard et al., 2008b). The presence of other pollutants may also affect the response of vegetation to NH_3, particularly at low concentrations of NH_3. There are major gaps in our knowledge of the deposition behaviour and compensation

points of NH_3, and the relative importance of the different N compounds that contribute to CLOs.

We recommend:
that the 'long-term' annual average Critical Level (CLE_{NH3}) for lichens, bryophytes, and for ecosystems in which they are important, be set at 1 µg NH_3 m^{-3};
that the 'long-term' annual average Critical Level (CLE_{NH3}) for higher vegetation be set at 3 µg NH_3 m^{-3}, recognizing that this figure is more uncertain, and that it should be expressed as a range of $2 - 4$ µg NH_3 m^{-3}

In defining the CLE_{NH3} in terms of air concentrations, it is assumed that appropriate methods are available to measure NH_3. For long-term averages, passive diffusion samplers provide adequate precision and accuracy (Leith et al., 2004, Sutton et al., 2001, Tang et al., 2001), but care must be taken with their deployment in the field. The CLE_{NH3} defined above are based on NH_3 concentrations measured at a height of 1-2 m above the vegetation surface. Where the surface is an important sink for NH_3 there will be marked vertical concentration gradients (Cape et al., 2008), so that the measurement height in relation to the CLE_{NH3} becomes important, and should also be standardized, for example at 1.5m above the surface of short vegetation.

The proposed CLE_{NH3} are based on empirical evidence for responses of the sensitive species within a community. Directly applicable quantitative information on causal relations and on inter-species variation in sensitivity is still scarce. Deriving methods for linking physiological and biochemical measurements on plants to observed shifts in species composition would greatly assist in detailed analysis of existing information. Ecosystem models that simulate N cycles and biomass production could be useful, but are still in a preliminary state of development for the purpose of assessing CLE_{NH3}.

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