Potential for the further development and application of critical levels to assess the environmental impacts of ammonia.

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DEFINITIONS AND BACKGROUND

1. A critical level is the concentration of an air pollutant below which environmental effects do not occur according to current knowledge[1]. The critical level for ammonia currently set by the UNECE is 8 µg m^{-3} for an annual mean, 23 µg m^{-3} for a monthly mean, 270 µg m^{-3} for a daily mean and 3300 µg m^{-3} for an hourly mean[2]. This range of values as for other pollutant gases reflects the fact that at increasing NH_3 concentrations environmental effects may be seen over shorter exposure periods.
2. Much of the ecological response to ammonia occurs through it contributing additional nitrogen or potential acidity to ecosystems. As a result, the impacts of ammonia are also assessed through the use of critical loads for nitrogen or acidifying deposition. A critical load is the total deposition of an air pollutant (e.g. nitrogen or acidity) below which environmental effects do not occur according to current knowledge.
3. Nitrogen deposition consists of both oxidized and reduced nitrogen components. Reduced nitrogen (NH_x) includes both ammonia (NH_3) and ammonium (NH_4^+), which are deposited through wet and dry deposition. Oxidized nitrogen (NO_y) includes nitrogen oxides ($NO_x = NO + NO_2$), nitric acid (HNO_3) and nitrate (NO_3^-).
4. Analysis of the components of nitrogen deposition and comparison with empirical critical loads for terrestrial ecosystems shows that exceedance of critical loads occurs when NH_3 concentrations are much smaller than the NH_3 critical level. For example, applying a typical deposition velocity (rate of uptake by the ground) for semi-natural vegetation of 15 mm s^{-1} and an annual average NH_3 concentration of 2.5 µg m^{-3} would contribute around 12 kg ha^{-1} yr^{-1} nitrogen deposition. Critical loads for many UK ecosystems are currently estimated to lie in the range 10-15 kg N ha^{-1} yr^{-1}. Hence, even if the additional contributions to N deposition from NH_4^+ and NO_y are not counted, the critical load can easily be exceeded by NH_3 concentrations much smaller than the annual NH_3 critical level.
5. Given that NH_3 makes a major contribution to critical load exceedance, and that this exceedance occurs at NH_3 concentrations less than the critical level, much more attention has been focused on the development of N critical loads rather than the NH_3 critical level. Using the current UNECE values noted above, the NH_3 critical levels are generally only exceeded in the UK in the immediate vicinity of large livestock farms. This applies both to the annual critical level and the short-term critical levels (e.g. hourly, daily, monthly).
6. On the basis of the above, it might be thought that there was little potential in pursuing further development of the critical levels approach for ammonia. By contrast there are several reasons why the critical levels approach has significant potential to help the development and implementation of air quality policies. This paper aims to raise the issues for discussion with DEFRA, Devolved Administrations and the relevant agencies.

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[1] This report was drafted in 2003 and points of correction and clarification made in June 2006 are added at the end of the document. Care is needed with the precise definitions of critical loads and levels: while the critical load refers to "below which effects do not occur" the critical level is formally defined as "above which effects may occur" (see the Mapping Manual, downloadable from http://www.oekodata.com/icpmapping/).

[2] It should be noted that the monthly and hourly critical levels are no longer recommended for use in the ICP Mapping Manual, in accordance with the practice adopted by the WHO, although the reason is not stated in the WHO Air Quality Guidelines (2000) (http://www.euro.who.int/document/e71922.pdf)

EFFECTS OF AMMONIA ON SENSITIVE PLANT COMMUNITIES

7. Exceedance of a critical level is often taken to represent a *direct* toxic effect[3] on a specified biological component. This contrasts with exceedance of a critical load, which usually represents an *indirect* response, where there may be no direct effects. For example, in adding nitrogen to an ecosystem from the atmosphere, the additional nitrogen may simply modify the competitive ability of different plant groups, leading to a change in species composition. From this perspective, it might be concluded that the critical load remains the correct way to treat the N and acidity effects of low levels of ammonia deposition.
8. By contrast, a critical level may be seen as simply a measure of the impact of elevated *concentrations*, as contrasted to a critical load being a measure of the impact of elevated *deposition*. In this case, it could be argued that expressing indirect environmental effects directly in response to NH_3 concentrations would also be appropriate. In the case of nitrogen deposition, a criticism is that the NH_3 concentration at which indirect effects occur depends on the magnitude of the other components of nitrogen deposition. Hence applying a critical load of 15 kg N ha^{-1} yr^{-1} an *implied critical level for indirect effects* of NH_3 could be calculated, but would depend on local conditions. Using the estimated NH_3 dry deposition of 12 kg N ha^{-1} yr^{-1} from above: with a background NH_4^++NO_y deposition of 3 kg N ha^{-1} yr^{-1}, the NH_3 critical level (indirect effects) would be around 2.5 $\mu g\ m^{-3}$; with a NH_4^++NO_y background deposition of 9 kg N ha^{-1} yr^{-1}, the NH_3 critical level would be around 1.25 $\mu g\ m^{-3}$.
9. In assessing the *direct effects of* NH_3, however, it may be noted that the UNECE critical level has stood for nearly a decade without reassessment. Recent data suggest that direct effects of NH_3 may occur at smaller concentrations. While the UNECE critical level was based on a toxicological assessment for bryophytes (mosses and liverworts), the recent experience suggests direct effects of NH_3 on lichens at small atmospheric concentrations. An extensive analysis of tree living lichens for the Netherlands suggests that lichens may be classified into species favouring N-poor, naturally acidic bark (*Acidophytes*) and those species favouring N-rich, more basic bark (*Nitrophytes*). The occurrence of nitrophytes and the disappearance of the acidophyte species has been shown to be directly proportional to atmospheric NH_3 concentrations. The effects appear to relate to direct toxicity in addition to interspecies competition. In particular, NH_3 (being a base) is shown to reduce the acidity of tree bark, leading to the species changes. Among the different deposited nitrogen species, this effect is unique to ammonia.
10. The effects of ammonia concentrations on nitrophyte lichens in the Netherlands have been detected in the range 5 to 35 $\mu g\ m^{-3}$, with most of the data being above the currently agreed critical level. Recent data from the UK showing the increase in nitrophyte species are consistent with changes above 8 $\mu g\ m^{-3}$. By contrast, the UK data suggest that the most sensitive acidophyte lichen species are lost at concentrations in the range 0.6 to 3 $\mu g\ m^{-3}$.

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[3] It should be noted that the Mapping Manual defines the critical level according to direct effects, so that there is no concentration-based threshold currently defined for indirect effects. However, clarification is needed as to what was originally meant by an "indirect effect", e.g. an effect mediated through the soil, rather than directly on plants. Since NH_3 is dry deposited directly to plants, it could be argued that even long-term effects are 'direct'.

11. These data indicate that the current critical level for NH_3 is set much too large to allow protection of the most sensitive lichen species. Further data are clearly needed to refine the critical level for ammonia, which could even be as small as 1 $\mu g\ m^{-3}$.

TIMESCALES OF CRITICAL LOAD AND CRITICAL LEVEL RESPONSES

12. Although both critical loads and critical levels may be expressed with annual values, it is important to consider that the timescales of each are not strictly comparable. The annual critical level refers specifically to a single yearly value, which should not be exceeded. By contrast, the empirical critical loads for nitrogen refer to long term deposition expressed as kg N ha^{-1} yr^{-1}. Indicatively, this long term period is considered to represent a period of 20-30 years[4] in the definition of empirical critical loads. Because both the critical level and the critical load are expressed on a "yearly" basis, confusion is easy.
13. The relationship between the UNECE critical levels and the time constant is nearly linear on a scale of $\log_{10}$(critical level) vs $\log_{10}$(time). If the curve is fitted with a polynomial ($\log_{10}(\text{Critical Level}) = 0.0623\ [\log_{10}(\text{time})]^2 - 0.9184\ [\log_{10}(\text{time})] + 3.5341$) then the critical level for a period of 20 to 30 years would be 2.7 to 2.4 $\mu g\ m^{-3}$, respectively. Accounting for uncertainty in the extrapolation, the long-term critical level based on the same dataset would be around 2.5 $\mu g\ m^{-3}$ (+/- 0.5 $\mu g\ m^{-3}$).
14. It is relevant to consider the issue of timescale in relation to monitoring the exceedance of critical limits. Although it is considered to take an indicative 20-30 years for the effects of critical load exceedance to become apparent, the values reflect an appropriate limit for the assessment of annual or 3-year estimates of deposition and exceedance. In the same way, although exceedance of the 1-year critical level can be tested annually, the long-term (20-30 year) critical level reflects an appropriate level for assessment of future pollution abatement policies.

UNCERTAINTIES IN APPLYING THE CRITICAL LOADS APPROACH FOR NH_3

15. While the critical loads approach for nitrogen necessarily needs to include NH_3, there are also a number of uncertainties that need to be considered when making the comparison with critical levels for NH_3.
16. The first and most important uncertainty in the critical loads approach for nitrogen is that different forms of nitrogen may not have the same level of environmental impact per kg of N deposited. Recent evidence from CEH suggests that there are substantial differences. For a given amount of N input (expressed as kg N ha^{-1} yr^{-1}) there is mounting evidence that dry deposition has larger impacts on sensitive plants that wet deposition and that NH_x has larger impacts than NO_y. Although further data are required, the evidence is sufficient to doubt the basic assumption of the critical loads approach, that all forms of N have the same magnitude of impact.
17. An important additional uncertainty in applying the critical loads approach is the requirement for accurate estimates of atmospheric deposition. Firstly, the experimental and survey studies used to establish empirical critical loads estimates are highly sensitive to varying quality in the atmospheric deposition estimates. Secondly, the quality of mapped critical loads exceedance estimates depends centrally on the

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[4] There appears to be debate on the agreed protection period of critical loads. It seems that critical loads using the mass balance approach have been defined for ~100 years protection, while the empirical critical loads have been defined for a shorter period of protection. Many of the documents on empirical critical loads for N do not clearly state the protection period. However, the Grange-over-Sands Workshop (Hornung et al., 1995, p4) concluded that the empirical approach cannot be assumed to provide a protection period longer than to 20-30 years.

accuracy of the deposition maps. While substantial effort has been placed to develop robust deposition models for mapping across the UK, at a landscape level (sub 5 km) there are large uncertainties due to variability in NH_3 concentrations. Quantifying deposition rates to complex elements of the landscape (e.g. park trees, hedgerows) is also very uncertain.

COMPLEMENTARY BENEFITS OF THE CRITICAL LEVELS APPROACH FOR NH_3.

18. The critical loads approach for nitrogen is well established, and despite the uncertainties it provides an important tool to combine the risk analysis of environmental impacts for different forms of nitrogen and acidifying pollutants.
19. Part of any response to the uncertainties in the critical loads approach must be further refinement of the methods: effort is needed in quantifying landscape level variability of N deposition, as well as rates of deposition to specific landscape elements. At the same time, information needs to be collected that quantifies the relative dose response relationships of different forms of nitrogen.
20. Critical levels for NH_3 have received little attention recently, due to the high limits that have been set by the UNECE. Conventional wisdom, based on the existing limits, is that the main issue for NH_3 is exceedance of critical loads for nitrogen.
21. In contrast to conventional wisdom, several strands of new information combine to suggest that there is merit in revisiting the critical levels approach for NH_3:
    a. Indirect effects of NH_3 to specific vegetation receptors can be expressed in terms of the NH_3 concentration. Based on typical critical loads values, a critical level (expressed as long-term average concentration) for indirect effects would be of the order 1.25 to 2.5 $\mu g\ m^{-3}$.
    b. There is growing evidence of direct effects of NH_3 on sensitive lichen species, which are related to changes in bark pH independent of N availability (e.g. at 0.6-3 $\mu g\ m^{-3}$).
    c. If the current NH_3 critical level is expressed on the same timescale as empirical critical loads, the critical level for NH_3 becomes much smaller. Based on the UNECE data, a long-term average (20-30 year) NH_3 critical level would be around 2.5 (+/- 0.5) $\mu g\ m^{-3}$.
    d. The increased sensitivity of vegetation to NH_3 compared with other forms of N deposition suggests that further attention be given to quantifying the specific impacts of NH_3.
    e. With appropriate measurement techniques, concentrations of NH_3 can be monitored with much greater accuracy than can rates of N deposition. This means that monitoring of the exceedance of a critical level for NH_3 becomes operationally a much easier target than monitoring atmospheric deposition inputs on a site basis. This is especially the case when N deposition inputs are uncertain in the case of proximity to local NH_3 sources or when assessing deposition to complex landscape elements (e.g. single trees or hedgerows).

POTENTIAL OPERATIONAL APPLICATION OF A REVISED AMMONIA CRITICAL LEVEL

22. Further work is necessary to provide the basis to formally revise the UNECE critical level for NH_3. However, *based on the information summarized here, it is expected the critical level would be around 1-3* $\mu g\ m^{-3}$ (long term site average concentration).

23. The critical level might be expected to differ broadly between major vegetation types, reflecting differences in deposition rates. It is, however, emphasized that the prime purpose of the critical level for NH_3 should be as a complementary tool to the critical loads approach. Given that the detail linked to deposition differences is best treated in the critical loads approach, the critical levels approach for ammonia should be seen in contrast as a *simple operational tool*.
24. The benefits of the critical level approach for NH_3 are particularly expected for site-level environmental impact assessment and for setting of air quality targets.
25. In estimating the potential impact of new development on sensitive ecosystems, it needs to be shown that the development would not lead to exceedance of either critical loads or the NH_3 critical level. Use of the NH_3 critical level (with a realistic value) would provide an additional tool to monitor compliance to emissions/air quality standards. This would be particularly appropriate for sources where the prime emission is of ammonia (e.g. livestock farms).
26. The critical level for NH_3 is also well suited to inclusion in the revision of air quality policies. For example, a standard could be set that the critical level NH_3 concentration is not exceeded within the boundaries of relevant sensitive Sites of Special Scientific Interest (SSSI's) and Special Areas of Conservation (SAC's).
27. The key advantage of the critical level in each of these respects is that it is much easier to monitor NH_3 concentrations than deposition. This would encourage rapid assessment of the impacts of ammonia, which would complement the approach based on estimating deposition and critical loads.
28. Current NH_3 monitoring in the UK is conducted with a monthly time frequency. This makes it possible to assess easily each of the monthly, yearly and long-term critical levels. By contrast, daily and hourly monitoring of NH_3 concentrations is best done by continuous sampling, which because of costs, is prohibited to 1 or 2 sampling sites in the UK. Available hourly NH_3 monitoring data in the UK monitoring suggest that it is more likely for the monthly or annual critical level to be exceeded than the hourly or daily critical level. This further justifies the focus on monthly, yearly and long-term means.

CONCLUSIONS AND RECOMMENDATIONS

29. It is concluded that:
    a. The critical level for NH_3 is currently set too high. A more realistic value (expressed as long-term (20-30 year) average NH_3 concentration) is probably 1-3 $\mu g\ m^{-3}$.
    b. Per unit of nitrogen deposited, NH_3 appears to be more damaging to flora than other forms of nitrogen.
    c. Lichens are particularly sensitive to NH_3, and respond not just to increased nitrogen availability, but to the reduction of bark acidity caused by NH_3.
    d. The critical level approach for NH_3 complements the critical loads approach, and has the particular advantage that it allows simple operational assessment through monitoring of NH_3 concentrations.
30. It is recommended that:
    a. Further effort be placed in quantifying the dose response relationships for NH_3 compared with other forms of nitrogen and that these data also be interpreted in relation to the critical levels approach.
    b. Any revised definition of the critical level for NH_3 be kept as simple as possible, as the need is for an operational tool, which complements the more detailed critical loads approach.

   c. Efforts are given to formally re-evaluate the UNECE critical level for NH_3. There is a strong case for holding a workshop under the auspices of the UNECE in the next 15 – 18 months (See appendix).

d. Consideration should be given to apply the NH_3 critical level in assessing the protection of statutory nature reserves and in further developing air quality policies.

SUPPLEMENTARY NOTE JUNE 2006

The above document was drafted some time ago, but provides a useful starter for discussion in advance of the UNECE Workshop "Atmospheric Ammonia: detecting emission changes and environmental impacts" (4-6 December 2006). Full background documents on this and the other issues will be provided in advance of the workshop.

In the context of the discussion on critical thresholds for ammonia, a Europe-wide approach needs to be taken, and key questions will include:

- Can all effects of dry ammonia deposition on vegetation be considered as "direct effects", since they primarily occur through direct uptake to plants?
- Where NH_3 has larger effects on vegetation than other forms of nitrogen (per unit of N), does this mean that the total amount of N deposition is not the main driver of effects?
- Practically, how can the thresholds approach handle the finding that NH_3 is in some contexts more damaging than other forms of N input? Is there merit in developing weighting functions for different N forms in the critical loads approach? Or is that too uncertain, so that it is more practical to include the higher sensitivity to NH_3 in setting the long-term critical level?
- It should be recalled that the basis for the critical level and critical loads definitions are different: the critical load refers to the deposition limit *below which* effects do not occur according to present knowledge, while the critical level refers to the concentration in the atmosphere *above which* direct effects may occur according to present knowledge. What was the reason for this, and is it justifiable for NH_3?
- Where a mean NH_3 concentration below which effects do not occur is defined utilizing the findings of critical loads literature and appropriate deposition velocities, what would be the most suitable terminology (e.g. critical level, guideline value etc)?
- In relating NH_3 concentrations to exceedance of critical loads, what non-NH_3 N deposition values should be applied, e.g. zero (giving an upper limit NH_3 concentration) or mid-range non-NH_3 N deposition (giving a lower, more typical NH_3 concentration) below which effects do not occur / above which effects may occur?
- How can we resolve and explain clearly the need to make the averaging periods of critical levels and critical loads comparable, e.g. a "long term mean critical level", also bearing in mind that direct effects of NH_3 can be compounded over periods longer than 1 year?
- From a scientific perspective, what would be the long-term mean air concentration(s) needed for the protection of ecosystems when considering a potential European "Air Quality Standard" for NH_3?

Supplementary reference

Hornung M., Sutton M.A. and Wilson R.B. (1995) *Mapping and modelling of critical loads for nitrogen - a workshop report.* (Eds.) (Report of the UN-ECE workshop, Grange-over-Sands, 24-26 October 1994). Institute of Terrestrial Ecology, Edinburgh, 207 pp. (ISBN 1 870393 24 4).