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Review of internationally proposed critical levels for ammonia

Conference Background Document

final draft as of 18 March 2022

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by

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List of abbreviations

CATFAC	Controlled Atmosphere Test Facility
CEN	European Committee for Standardization
CLE	Critical Levels
CLRTAP	Convention on Long-Range Transboundary Air Pollution
CSTR	Continuously-Stirred Tank Reactors
DOAS	Differential Optical Absorption Spectroscopy
LML	Landelijk Meetnet Lucht
MAK	Permissible Workplace Concentration
NEC	National Emission Ceilings
NERC	National Emission Reduction Commitments
NPL	National Physical Laboratory
OTC	Open Top Chamber
UNECE	United Nations Economic Commission for Europe

1 Background

Air pollution from ammonia (NH_3) is relevant for human health and ecosystems. The gas is easily converted into NH_4^+, which can act as a plant nutrient, either by assimilation via the plant shoot (after entering the stomata) or after deposition to the ground and the subsequent uptake by the roots (Fangmeier et al. 1994). Together with the oxidized forms of nitrogen, it is significantly contributing to the widespread eutrophication and acidification of ecosystems. As a result, the biodiversity of ecosystems is threatened at the expense of slow-growing nitrogen-sensitive, often rare and protected species (Bobbink et al. 2010).

Ammonia emissions stem to about 95 % from agriculture, especially from livestock farming and the application of slurry or mineral fertilizers (UBA 2021). The odour threshold of ammonia is 5 ppm (3.8 mg m^{-3}) and the permissible workplace concentration (MAK) is 20 ppm (15 mg m^{-3}). Inside stables and after slurry application in the field, peak concentrations will be well above 1 ppm (760 µg m^{-3}), whereas outdoors and close to stables, mean levels will still be around 50 µg m^{-3}. Slightly elevated concentrations of the gas in the range of 10 µg m^{-3} can also be detected near waste-water treatment plants and as line sources along major roads, but concentrations will rapidly drop in the lee of any source (e.g. Bell et al. 2016; Elser et al. 2018). In remote areas, ammonia concentrations are around 1 µg m^{-3} (UBA 2018), while the presence and excrements of animals (urea and uretic acid) and the degradation of plants will elevate levels locally.

Due to its alkaline character, ammonia is rapidly reacting with acids (e.g. sulphuric and nitric acid) creating ammonium salts like $(NH_4)_2SO_4$ and NH_4NO_3, which possess long atmospheric lifetimes as secondary aerosols (PM 2.5) (Fowler et al. 2009). However, the strong reduction of the acidic air pollutants in the last decades has led to more alkaline atmospheric conditions and an increase in the lifetime of ammonia due to the reduced availability of H_2SO_4 to react with NH_3 (Sutton et al. 2020).

CLE describe the concentration of a pollutant above which direct adverse effects on receptors such as individual plants or natural ecosystems may occur. More than ten years ago, revised CLE for ammonia had been discussed in the framework of the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) at a Workshop on Atmospheric Ammonia (UNECE 2007). New evidence was amongst others provided by experiments at Whim Bog in Scotland (Cape et al. 2009) suggesting that the long-term critical level of ammonia needed to be reduced to 3 µg m^{-3} for higher and 1 µg m^{-3} for lower plants (i.e. lichens and mosses), respectively. The UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) accepted these recommendations and replaced the at that time existing CLE of 8 µg m^{-3} (Ashmore and Wilson 1994; UNECE 2007).

To protect European ecosystems from eutrophication, ammonia emissions will have to be reduced significantly in the EU according to the national emission ceilings laid down by the updated NEC Directive 2016/2284/EU and the 2020/2030 national emission reduction commitments (NERC). Most countries are currently developing and applying methods to assess nitrogen effects on ecosystems and vegetation with critical loads, in contrast critical levels are only used sporadically in the UK, Denmark and Germany within the framework of licensing new installations (Reinds et al. 2019).

2 Ammonia research

In order to evaluate the validity of current critical levels and to prepare our own fumigation study, we screened the literature on ammonia effects from the last twelve years, focussing primarily on original publications which cited Cape et al. (2009). We also refer to older publications in present background document, e.g. fumigation studies from the 1990s and before, that are helpful to better differentiate between phytotoxic and chronic effects. Besides the peer-reviewed literature, we also included various reports from studies that monitored ammonia in regional and national projects.

2.1 Research in the early years

Experimental exposure of plants to ammonia in the very early years was mainly based on the use of pure (technical) NH_3 supplied from gas flasks to the air inlet of small closed fumigation chambers or continuously-stirred tank reactors (CSTR). Very high concentrations were applied initially to examine whether the growth of crop plants, e.g. sunflowers, could be stimulated in growth by nitrogen containing gases (Faller 1972; Hutchinson et al. 1972; Ewert 1979; Temple et al. 1979; Farquhar et al. 1980). In these short-term experiments with young plants, phytotoxic responses (foliar injury and growth reductions) were observed only at concentrations above 800 µg m^{-3}, depending on the plant species and the soil nitrogen supply. It had also been suggested early that fertilized crops and older plants do not take up ammonia any more at concentrations below 4 µg m ^{3}, but release the gas during senescence (Cowling and Lockyer 1981). Unfortunately, none of the early and more recent studies mentioned sufficient details how the ammonia fumigation was controlled, whether constant levels were achieved and how the realized concentrations were determined. An overview of published ammonia fumigation experiments is given in Table 1.

Dry deposition, bi-directional fluxes and compensation points of ammonia have been studied extensively by Scottish, Dutch and Danish scientists (e.g. Sutton et al. 1993; Duyzer 1994 and Husted and Schjørring 1996). The fluxes are driven by changes to the equilibrium between the ammonia concentrations in the air and in the sub-stomatal cavity of plant leaves and depend on the leaf temperature, stomatal resistances, plant water status, ammonium (NH_4^+) concentration (nutrient status) and pH of the apoplastic solution. Farquhar et al. (1980) and van Hove et al. (1987) obtained compensation points of around 5 µg m^{-3} in crop plants, but suggest that in oligotrophic vegetation, e.g. peatlands, heath and dunes, the uptake of ammonia may occur at lower concentrations. This is principally confirming that low concentrations in the range of the suggested critical levels can be “sensed” by vegetation in pristine areas, but as mentioned above, ammonia concentrations in agricultural and densely populated regions will only rarely be that low. During the lifetime and with the biological activity of plants during seasons, fluxes of ammonia will change. While young N-demanding plants are a sink of ammonia in spring, old senescing plants will be a source and release the gas in the autumn. In addition, ammonia can be transported from a highly fertilized crop canopy to an adjacent natural vegetation with a lower compensation point and vegetation on acidic soil substrates will probably be more prone to the deposition of ammonia.

Following the initial discussion of critical levels for ammonia at the UNECE Workshop in Egham 1992 (Ashmore and Wilson 1994), European research networks had been established in the 1990s to monitor atmospheric processes that lead to the deposition of oxidized and reduced nitrogen species. It became clear that ammonia has a rather short life-time (Asman et al. 1998) reaching acute concentrations only close to emission sources. Further, chronic responses in sensitive wild plants will be driven by the joint deposition of various N-containing compounds mainly in the oligotrophic ecosystems. In order to account for the differences between short-term atmospheric concentrations and the cumulative annual inputs, the concept of critical loads had been introduced.

Ground-breaking research on the adverse effects and dose-response functions of ammonia on the natural (e.g. nitrogen-poor heathland) vegetation came from the Netherlands and served as the basis for the UNECE critical level of 8 µg m^{-3} (van der Eerden et al. 1982; Dueck 1990; van der Eerden et al. 1991; Dueck and Elderson 1992). Research of van der Eerden (1982) was based on the use of diluted exhaust from stables in closed or open top chambers (OTC), while later studies in Wageningen (Dueck and van der Eerden) involved technical ammonia supplied via mass flow controllers. Concentrations were in the range of 50 to 100 µg m^{-3} and were determined with NOx converters/monitors. The only comparable research project performed in Germany dealt with an ammonia fumigation of three grassland species grown in monocultures and mixtures. The experiments were performed in OTCs with diluted technical ammonia using set concentrations of 20 and 50 µg m^{-3} (Jäger et al. 1998). However, the realized concentrations could not be documented due to failures of the NOx converters/monitors. Summaries of the pioneering research of ammonia effects on plants can be found in the reviews of Adaros and Dämmgen (1994), Fangmeier et al. (1994) and Krupa (2003).

Based on the above-mentioned studies, we suggest that ammonia concentrations were probably too high in the early studies restricting the validity of results with respect to the old and new critical levels. Expert judgements and extrapolations from high to low concentrations were used and long-term responses were predicted from short term experiments. None of the early fumigation experiments operated in the range of existing environmental concentrations mainly due to technical reasons. When using pure ammonia without a time and concentration-controlled feedback system, peaks and accidental overdosing may occur that will lead to short-term burdens on plants eventually triggering acute effects. In fact, this will likely also happen in natural vegetation that is exposed to the fumes and plumes from adjacent slurry spreading or livestock housing.

Early Ammonia Research

- Focus on high concentrations and crop species, mainly in the Netherlands
- Short-term experiments
- Pure (technical) NH_3 supply

2.2 Research after 2009

Whereas first experiments dealing with plant exposure to ammonia were mostly studying the effects of higher concentrations, more recent projects tried to investigate low-range ammonia effects in order to study potential responses in sensitive plant species.

A screening of newer literature dealing with the recommended CLE and contributing new data from the UK and other European countries will be presented in this subchapter. We present an overview of 103 peer-reviewed references (as of December 2020) that cited Cape et al. 2009 according to the databank Scopus®. Figure 1 (top) gives an overview on how many citations per year were recorded and how many of these did not stem from the Scottish research group that also authored the Cape et al. publication. After a decline in the numbers of citations until 2019, the topic “critical levels” peaked again recently and we can observe that 80 % of the citations were from groups not involved in writing the cited paper.

When looking at the country of residence of the main author and her affiliation (Figure 1 below), we can see that most publications which cited Cape at al. (2009) stemmed from the UK, China, Canada and the US, being followed by three Mediterranean countries mostly studying lichen diversity among ammonia gradients. Interestingly, in the Netherlands, Denmark and Germany, the research on effects of ammonia is not of major importance, although the countries have a very large livestock production sector and severe problems with eutrophication. It must be noted that until the late 1990s, most of the ground-breaking research on ammonia had been performed in the Netherlands (the research group of Dr. Ludger van der Eerden at Plant Research International in Wageningen). The old CLE of 8 µg m^{-3} had originally been derived from fumigation studies from that institute and in those years there were many ammonia-related research programs funded by the Dutch, UK and German governments. An even stronger absence of research was noted in France, a country with a strong livestock sector in the EU, where no peer-reviewed literature on the effects of ammonia was published.

When looking at the specific topics dealt with in the 103 articles, the study of the presumed ammonia sensitivity of lichens plays an overwhelming role. 27 articles focus on the mapping of nitrogen sensitive lichens and many of these studies stem from Southern European countries, although intensive livestock farming does not play a prominent role there. Another quarter of the citing articles dealt with the modelling of N deposition and 20 articles were presenting data from ammonia measurements using passive samplers. 16 studies investigated changes in the species composition while only 11 studies reported about “bioindication” methods, addressing ecophysiological changes in lower and higher plants along ammonia gradients. Only a few of these studies made use of pre-cultivated higher plants, which were actively exposed in the field at locations, where ammonia was measured.

Besides the agricultural emissions also the industrial and traffic related emissions as well as the wastewater treatment sector are responsible for the losses in biodiversity of certain cryptogams and lichens. Sutton et al. (2020) have recently suggested that the successful reduction of SO_2 pollution in Europe and elsewhere has led to a general alkalinisation of rain and air that will be harmful to naturally acidophytic species. On the other hand, in the 1990s and early 2000s the elimination of acidification often favoured the return of rare basiophytic lichens. The impacts of the recent and ongoing changes in air quality have also been investigated in Sweden and showed a very slow recolonization of sensitive species due to existing dispersal limits (Weldon and Grandin 2021).

Only in the 1990s, research on the phytotoxicity of air pollutants moved to field-based fumigation systems to study the effects of ammonia on pre-cultured plants or established natural vegetation. Such systems should operate under the normal ambient climates and should not create concentration peaks. Examples are the FACE (free air carbon dioxide enrichment) experiments and the use of open top chambers (OTC) e.g. to study adverse effects of ozone. The only field fumigation system worldwide for ammonia is being operated since the year 2002 in the Scottish Whim Bog (Southwest of Edinburgh). It relies on a gradient system with the wind-controlled release of ammonia into an ombrotrophic bog. Peak concentrations of 1600 µg m^{-3} have been reported in the lee of the ammonia release point, explaining the severe bleaching effects that were observed on *Calluna* shrubs, reindeer lichen and *Sphagnum* mosses (van Dijk et al. 2017; Levy et al. 2019). A recent study observing the N-sensitive lichen *Cladonia portentosa* at Whim Bog revealed that no major effects occurred any more after ceasing the long-term constant exposure to NH_3 (Munzi et al. 2020).

A new generation of experiments mimicking the dry gaseous deposition of ammonia in established ecosystems is currently on the way in China (Pan et al. 2020) and will be recognized under the name Free-Air NH_3 Enrichment (FANE).

Critical Levels Research

- Until 2020, Cape et al (2009) had been cited over 100 times
- Most citations stem from UK, China, Canada and the US
- Relevant number of publications in several Mediterranean countries
- Low number of publications from the Netherlands, Denmark, Germany and France, although the countries have a large livestock sector and eutrophication problems in common
- Citing studies deal with lichen mapping, modelling N deposition, ammonia measuring, changes in species composition and the investigation of ecophysiological changes in lower species
- Critical loads research is more prominent than the study of ammonia or nitrogen dioxide

Figure 1: Citations of Cape et al. (2009) in the peer-reviewed literature, broken down after years (top) and countries of residence of the main author (below)

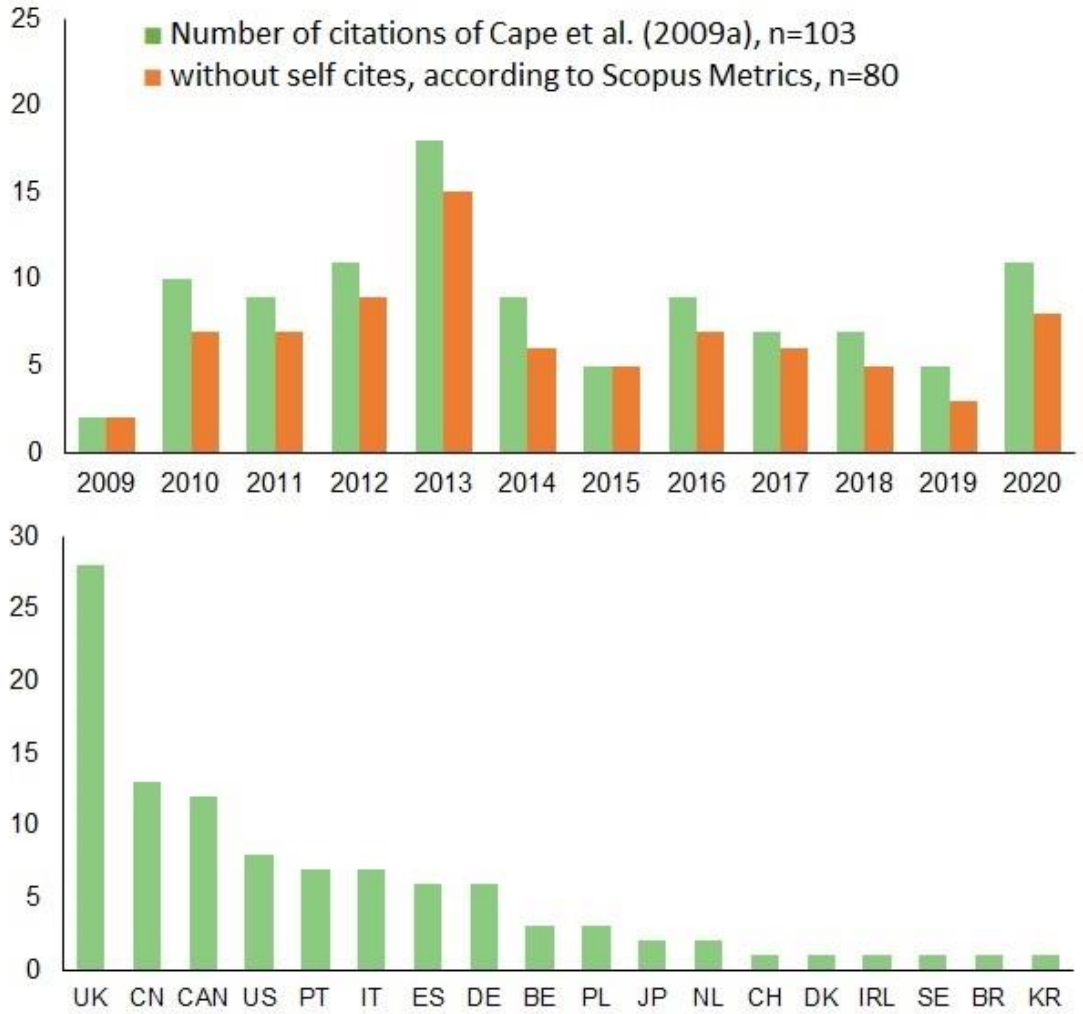

Table 1: Overview of ammonia fumigation experiments in closed and open chambers

Source	Fumigation type	Supply of ammonia	Set range in µg m^{-3}	Method of ammonia measurement	Data on realised concentrations	Duration	Plant species
Faller (1972)	Glass chambers, 0.5 m^3	diluted NH_3, daylight hours	0 - 1600	none, calculated from flow	No	3 weeks	*Helianthus annuus*
Hutchinson et al. (1972)	Plexiglass chambers, 0.3 m high, 0.15 m sides	diluted NH_3,	24-44	trapped in KCl solutions	24-44	24 hrs	*Glycine max, Zea mays, Helianthus annuus*
Ewert (1979)	2 greenhouse chambers 10 m^3	diluted NH_3, 24 hrs day^{-1}	700 - 21000	air sampling, Nessler´s reagent	No	1-500 hrs	48 woody species, 10 crops
Farquhar et al. (1980)	Glass chamber, 0.2 m^3	diluted NH_3, 24 hrs day^{-1}	0 - 50 nbar	air sampling, indophenol method	No	20 minutes	*Phaseolus vulgaris* L. and other
Cowling & Lockyer (1981)	Exposure chambers	diluted NH_3, 16 hrs day^{-1}	0, 148 and 550	air sampling, Nessler´s reagent	No	40 days	*Lolium perenne* L.
van der Eerden (1982)	Open Top Chamber, closed chambers	Exhausts from poultry and pig manure, 24 hrs day^{-1}	600 - 4500	air sampling, Nessler´s reagent	No	3 - 60 days	grasses, trees, *Brassica*, *Lycopersicon*
Lockyer & Whitehead (1986)	Exposure chambers	diluted NH_3, 16 hrs day^{-1}	0, 100 and 500	air sampling, indophenol method	16, 118, 520	40 days	*Lolium multiflorum* Lam.
van Hove et al. (1987)	Leaf Chamber	diluted NH_3, short term	0 - 400	Chemiluminiscence after converting NH_3 to NO	No	some days	*Phaseolus vulgaris* L.
Whitehead & Lockyer (1987)	Exposure chambers	diluted NH_3	0 - 700	air sampling, indophenol method	14 - 709	33 days	*Lolium multiflorum* Lam.
Dueck (1990)	Open Top Chambers	diluted NH_3, 24 hrs day^{-1}	0, 53 and 105	Chemiluminiscence after converting NH_3 to NO	No	9 months	*Calluna vulgaris*
Dueck & Elderson (1992)	Open Top Chambers	diluted NH_3, 24 hrs day^{-1}	0, 50	Chemiluminiscence after converting NH_3 to NO	No	9 months	*Arnica montana, Viola canina, Agrostis capillaris*
Husted & Schjørring (1996)	Glass cuvette, 0.45 m^3	diluted NH_3, 24 hrs day^{-1}	0 - 25 nmol mol^{-1}	Chemiluminiscence after converting NH_3 to NO	No	twice a day, 7 days	*Brassica napus* L.
Jäger et al. (1998)	Open Top Chambers, 3.15 m diameter	diluted NH_3, 24 hrs day^{-1}	20 and 50	Chemiluminiscence after converting NH_3 to NO	No	3 years	Monocultures and mixtures of *Bromus erectus* Huds, *Brachypodium pinnatum* P. Beauv. and *Arrenatherum elatius* P. Beauv.
Geßler et al. (2002)	Borosilicate twig chambers	diluted NH_3, 24 hrs day^{-1}	100	continuous wet flow denuder AMANDA	No	several hours	*Picea abies*
Adrizal et al. (2006)	Exposure chambers	diluted NH_3, 24 hrs day^{-1}	2800 - 5000	Photoacoustic NH_3 detector	No	12 weeks	*Juniperus virginiana*, *Gleditsia triacanthos*, *Phalaris arundinacea*, *Populus* spec. *Salix* spec.
Jones et al. (2008)	Flux chamber, 1.84 m^3	release of ^{15}N labelled NH_3 from $(^{15}NH_4)_2SO_4$ with NaOH	16 - 20	continuous wet flow denuder AMANDA	daily resolution	15 days	*Calluna vulgaris*
Franzaring et al. (2012)	Mini greenhouses	diluted NH_3, 24 hrs day^{-1}	0 - 200	Passive samplers	2.2 -195	88 days	*Brassica napus* L.
Ilogu Chibuzo (2012)	Exposure chambers	controlled evaoporation of NH_4Cl solutions	0 - 84	Passive samplers	3, 25, 84	30 days	*Echinochloa crus-gallii* and *Lolium multiflorum*
Jones et al. (2013), presenting results from PhD Thesis of Jonathon Foot from 1998	Open Top Chambers	uncontrolled evaporation of NH_4OH solutions containing 0-10 % of ammonia	0 - 35	Passive samplers	Yes	28 weeks	Mixtures of *Dactylis glomerata, Plantago lanceolata, Festuca rubra, Centaurea nigra* etc.

2.2.1 Gradient Studies

Most field experiments dealing with the effect of ammonia used passive approaches working with the reaction of established vegetation on ammonia input. Sheppard et al. (2011) described a dramatic loss of higher and lower plants at Whim Bog after three years of relatively modest NH_3 deposition. Several lichen mapping studies also showed effects of ammonia with regard to lichen diversity along natural gradients. The number of oligotrophic lichen species decreased significantly with increasing atmospheric ammonia concentrations whereas nitrophytic species increased and/or replaced some species (Pinho et al. 2011; Pinho et al. 2012; Pinho et al. 2014). The authors suggested CLE of ammonia for Mediterranean evergreen woodlands to be 1.9 µg m^{-3} (2012) and two years later they suggested a lower level of 0.69 µg m^{-3}. Experiments from Canada revealed that most lichen species studied were affected above 1.5 µg m^{-3} (Watmough et al. 2014). Izquieta-Rojano et al. (2018) describe effects of an ammonia gradient (distance to a swine livestock facility) on mosses (especially tissue N content) in an oak woodland with an estimated site-specific CLE of 3.5 µg m^{-3}. The results imply that mosses might stand higher concentrations of ammonia than lichens, but it must be noted that there is less information on mosses compared to lichens at the moment. Other passive approaches like the use of oak leaf characteristics as a biomonitoring tool (Wuytack et al. 2013) revealed no differences and therefore seem not to be suitable for ammonia monitoring programs.

Active (biomonitoring) studies are mainly addressing the effects of ammonia from agricultural sites on lower plant species, i.e. lichen and/or moss diversity and vitality. Sensitive moss (Freiberger et al. 2021) or lichen species like *Evernia prunastri* (Paoli et al. 2010; Paoli et al. 2014; Munzi et al. 2014) are transplanted from non-polluted sites (sites with low ammonia background concentrations) to natural ammonia gradients and the vitality e.g. in form of chlorophyll fluorescence is determined. Munzi et al. (2014) found that ammonia concentrations above 3 µg m^{-3} would abruptly decrease plant fitness and frequency but the authors approve the same NH_3 CLE (1 µg m^{-3}) as proposed by Cape et al (2009) because of possible cumulative effects after longer exposure than tested. However, a more recent study observing the N-sensitive lichen *Cladonia portentosa* at Whim Bog revealed that no major effects occurred any more after ceasing the long-term constant exposure to NH_3 (Munzi et al. 2020).

Morillas et al. (2021) studied detrimental cumulative effects of solar radiation and increased nitrogen treatments on lichens via immersing samples into N solutions. Studies about ammonia effects are rarely including additional climatic factors to date.

Gradient studies making use of higher plants are mostly focussing on grass species as bioindicators since their upright growth habit and the presence of numerous stalks enable the effective scavenging and accumulation of air pollutants. While Leith et al. (2009) used grasses in the lee of Scottish poultry farms (confirming CLE of 2-3 µg m^{-3}), Ilogu Chibuzo (2012) used grasses and N-demanding weeds in the lee of a pig stable in Southern Germany. In both studies, plant biomass increments and nitrogen concentrations proved to be sensitive indicators for the fertilizing effect of ammonia.

Freiberger et al. (2021) recently suggested that active approaches using uncontaminated moss transplants (*Pleurozium schreberi*) and accumulated N-levels show a much stronger relationship to the ammonia concentrations than moss or lichen mapping (passive approaches).

Gradient Studies

- Most field studies make use of passive approaches, i.e. investigate the reaction of established vegetation on ammonia concentrations in a natural gradient
- Many studies show a decrease of N-sensitive lichen species with increasing NH_3 concentrations
- Mosses seem to be more tolerant than lichens
- Most active study approaches with lichen transplants confirm low CLE
- Fewer findings suggest that lichens might stand higher NH_3 concentrations than expected
- Only very few studies address higher plants

2.2.2 Fumigation Studies

Apart from the free-air exposure at Whim Bog, which uses the release of technical ammonia along a wind gradient, only two peer-reviewed papers on ammonia fumigation could be found that had been published after 2009. In our own experiment (Franzaring et al. 2012), we studied the effects of sub-acute concentrations of ammonia on the re-growth of winter oilseed rape. We could show that the crop is well able to benefit from the gaseous fertilizer at a concentration of 195 µg m^{-3}, but we did not test whether slightly raised or low concentrations of ammonia would be able to significantly interact with the physiology of the species.

The second study on ammonia fumigation was published by Jones et al. (2013). The authors investigated the effects of ammonia deposition to plants from Welsh sand dune ecosystems and exposed mesocosms of plant mixtures in OTCs. Shoot biomass and tissue nitrogen increased significantly with increasing concentrations of ammonia. A significant biomass increase of the plant mixture was already observed when increasing the ammonia concentrations from 0.4 to 4.3 µg m^{-3}, i.e. dose equivalents of 2 and 24 kg N ha^{-1} y^{-1}.

Fumigation Studies

- Apart from the Whim Bog Experiment, only two newer fumigation studies were found
- Both studies showed a biomass increase of the species tested under NH_3 fumigation

Summary

Most recent studies addressing CLE for ammonia work on passive approaches with lichens in natural ammonia gradients, the majority suggesting CLE of 0.69-3.5 µg m^{-3}

Active approaches confirm CLE of 1 µg m^{-3} for lichens and 2-3 µg m^{-3} for higher plants (grasses)

Some findings show higher CLE for lichens than expected

Only few studies (passive or active) include higher plants

Only few studies work with artificial ammonia gradients, i.e. ammonia fumigation

3 Ammonia measuring and monitoring programs

Since the 1990s, pioneering work on continuous ammonia measurements in the ambient air has been done in the Dutch Landelijk Meetnet Lucht (LML) using denuders and differential optical absorption Spectroscopy (DOAS). The latter methodology is well able to determine low background concentrations but until now, only a few sites have been equipped with these rather expensive and support demanding devices in the Netherlands and in Switzerland (Volten et al. 2012a; Volten et al. 2012b; Berkhout et al. 2017; Bell et al. 2017). Pogány et al. (2016) and Niederhauser (2017) therefore formulated the need for more intensive metrological research focusing on the quality assurance, inter-comparability and validation of ammonia in the ppb range. A first international initiative was set up within the European MetNH3 (Metrology for ammonia in ambient air) project. One of the work packages of the MetNH3-Project dealt with the testing and calibrating of ammonia passive samplers. Samplers were tested in the UK's National Physical Laboratory's (NPL) controlled atmosphere test facility (CATFAC) and in the field at the above-mentioned Scottish Whim Bog Experimental site. The inter-comparisons between different sampler types have been presented by Braban et al. (2018) and Martin et al. (2019). Measurement errors of the tested passive samplers varied between 11 and 23 % at the reference concentration of 1 µg m^{-3}, i.e. a concentration representative for the lower critical level. ALPHA passive samplers proved to be the best suited for the lower concentration ranges and have an exposure time of 28 days, whereas e.g. the Radiello® samplers can be used to investigate shorter periods.

Passive samplers have been developed for the determination of gaseous air pollutants in locations without power supply and are the only method to determine gas concentrations in remote areas. In order to assure their quality, devices need to be certified according to CEN (European Committee for Standardization) standards EN 13528-1 to 3 for diffusive samplers. Two types are available, axial (badge type) and radial (tube like) samplers. Latter types have higher sampling rates and can therefore be exposed over shorter times (Puchalski et al. 2011).

Table 2 gives an overview of studies that used passive samplers to study ammonia concentrations in different countries. Only papers and grey literature are listed that were published after 2009. In most of the studies, ammonia concentrations did not decrease over time contradicting the results from modelled concentrations (Wichink Kruit et al. 2017) and the information derived from emission inventories. As previously mentioned, the reasons for higher levels may be the reduced concentrations of SO_2 and increased volatilization of the gas due to the higher ambient temperatures. At the same time, higher concentrations may also stem from previously underestimated emissions, e.g. due to uncertainties in emission factors or activity data in agriculture, from waste water treatment facilities and biogas plants as well as from the increased use of diesel exhaust fluids (DEF, AdBlue). Higher vehicular emissions of NH_3 and ammonia slip have been addressed by Elser et al. (2018), Suarez-Bertoa and Astorga (2016) and Fenn et al. (2018).

In contrast to the pioneering, smaller European countries like the Netherlands (Lolkema et al. 2015; Noordijk et al. 2020), Belgium (VMM, 2017) and Switzerland (Thöni et al. 2018), larger countries with intensive agricultural systems like France, Italy and Germany do not operate national ammonia networks yet, so that regional data are very scarce in these countries. There is only one publication from France that reports on ammonia measurements in five agricultural and six forest regions (Fauvel et al., 2019). In Brittany, a region with intensive livestock farming, ammonia concentrations are on average in the range of 9 µg m^{-3}, while inside forest areas in the south and in the east, concentrations of less than 1 µg m^{-3} are common. In Germany, there have been some efforts in various federal states to monitor ammonia with passive samplers, mainly badge type devices (e.g. Lohrengel et al. 2012; LfU 2019).

While in Germany only sporadic measurements are being performed in four Federal States, Belgium, the Netherlands and Ireland have established monitoring sites in a large number of Natura2000 (the EU Habitat Directive) sites (Table 2). Since protected landscapes are often nitrogen limited, the vegetation (e.g. bogs and heathlands) will be an ideal receptor for potentially harmful ammonia.

Table 2: Overview of ammonia monitoring programs using passive samplers

Source	Country	Sampler type	Network name	N of sites	Period	Results
Tang et al. (2018)	UK	Alpha, Delta	UK NAMN	59	since 1998	Reduction of 3% on national level, but ammonia increases in some regions.
Fauvel et al. (2019)	F	Alpha, Delta		11	2009-2019	Selected agricultural and forest locations. High ammonia concentrations in Brittony.
Yao & Zhang (2013; 2019)	CAN-ONT	Ogawa	NAPS	74	2006-2007	Even in remote sites in CAN, 50% of the sites would exceed the critical levels.
Seitler et al. (2018)	CH	Radiello®		13	since 2000	No reductions over time, different levels in different regions. All values exceed the 1 µg level, most the 3 µg critical level.
Puchalski et al. (2011) and Yao & Zhang (2016; 2019)	US	Radiello®, blue diffusion barriers	AMoN	50	since 2007	NH_3 concentrations have increased by 7% between 2008 and 2015 at 18 long-term sites.
VMM (2017)	BE	Radiello®, blue diffusion barriers		100 Natura2000 sites	2015-2016	Country mean: 3.3 µg m^{-3} NH_3, in Western Flanders > 5 µg m^{-3} NH_3, no trends over time.
Lolkema et al. (2015); Noordijk et al. (2020)	NL	Gradko	MAN	82 Natura2000 sites	since 2005	NH_3 concentrations significantly increased in easterly regions and went down in the west and in the south.
Kelleghan et al. (2021)	IRL	Alpha		12 Natura2000 sites	2017-2018	0.47–4.59 µg NH_3 m^{-3}. Agriculture is the main source and ammonia is related to ambient temperatures.
Lohrengel et al. (2012)	DE-NS	Ferm (IVL)		22	2010-2011	Selected rural locations. 0.7 to 13 µg m^{-3} ammonia.
LfU (2019)	DE-BY	Ferm (IVL)		4	since 2006	Selected urban and rural locations. Downward trend.
LANUV (pers. comm.)	DE-NRW	Ferm (IVL)		8	since 2018	Selected urban and rural locations. No trend.
LUBW (internet resource)	DE-BW	Ferm (IVL)	Spot	13 new in 2021	2016-2021	Selected urban and rural locations. High NH_3 at traffic sites.

Ammonia Measuring and Monitoring

- Ammonia monitoring differs between European countries: The Netherlands and Switzerland are well equipped with technologies for continuously measuring ammonia, while countries like Germany, France and Italy do not operate continuous national ammonia networks except their activities in the EMEP programme
- Many countries and studies use passive samplers – a well-accepted, low-cost technique - to measure NH_3

4 Discussion points at the workshop

During the workshop, we aim to collate recent information on the topic and ask the presenters and participants to inform the audience about ongoing research activities. In order to prepare a general discussion, we would like you to answer following questions. You may report back to us prior to the conference.

Discussion 1: Current set-up and future perspective on ammonia monitoring

- With regard to ammonia measuring, is the use of passive samplers suitable? How often should samplers be analysed? Are there (new/suitable/affordable) measuring devices to continuously monitor NH_3 in the low range?
- Which criteria have to be met to set up a national representative ammonia network?
- Which difficulties complicate ammonia monitoring networks? Costs?
- Is there essential knowledge for recommendations to policy makers that is gained (exclusively) with ammonia monitoring networks?
- Ammonia monitoring is beneficial for nature protection and air quality policies, correct?
- Would you support an ammonia monitoring obligation and for what reasons?

Discussion 2: New findings with potential relevance to NH_3 CLE: Future directions

- Do you perform or are you aware of research on ammonia effects on higher or lower plants using controlled fumigation at ammonia levels < 10 µg m^{-3}? What are the technologies involved?
- Do you perform or do you know of ammonia fumigation studies in the field? What are the technologies involved and which are the tested ecosystems?
- Do you perform or do you know of gradient studies using active or passive biomonitoring, i.e. the use of vegetation on-site or plants being actively exposed? What are the involved technologies and plant species?
- Would you support annual, monthly and/or short-term CLE?
- Would you support to include knowledge on Critical Loads into scientific justification of critical levels?
- Based on current research, is there (enough) evidence for changing/keeping the CLE (for lower and higher plants, respectively)?
- Which further steps after the Workshop should be taken in the review of NH_3 CLE?

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