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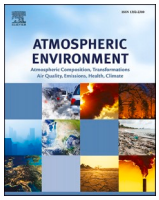

Review article

Synthesis of lichen response to gaseous nitrogen: Ammonia versus nitrogen dioxide

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HIGHLIGHTS

- Evidence supports that lichen community composition is altered at <1-3 μg NO_2 m^{-3} and <1 μg NH_3 m^{-3}.
- The 3-year average (2017-2019) for monitoring sites in the U.S. ranges up to 56.4 μg NO_2 m^{-3} and 6 μg NH_3 m^{-3}.
- Better spatial characterization of NO_2 and NH_3 concentrations, especially near intensive agriculture, are needed in the U.S.

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ABSTRACT

The dominant chemical form of nitrogen pollution in the atmosphere in the U.S. is shifting from oxidized nitrogen, primarily from combustion of fossil fuels, to reduced nitrogen from agricultural animal waste and fertilizer applications. Does it matter to lichens? In this synthesis, we characterize U.S. air concentrations of the most ubiquitous gaseous forms of reduced and oxidized nitrogen, NO_2 and NH_3, respectively, and their direct effects on lichens. In the U.S., the 3-year average (2017–2019) of the annual mean for each monitoring site ranges up to 56.4 μg NO_2 m^{-3} (~30 ppb) and 6 μg NH_3 m^{-3} (~9 ppb). The spatial coverage of current routine monitoring of NO_2 and NH_3 likely does not accurately represent exposures of NO_2 to ecosystems in rural areas or capture spikes of NH_3 concentrations proximal to intensive agriculture, which are documented to exceed 700 μg NH_3 m^{-3} (~1000 ppb) for short durations. Both NO_2 and NH_3 can act as nutrients to lichens, but as exposures rise, both can cause physiological stress and mortality that then change community composition and diversity. There is a growing body of evidence that lichen community composition is altered at current levels of exposure in the U.S. with estimated no effect or lowest effect concentrations from <1 to 3 μg m^{-3} NO_2 and <1 μg m^{-3} NH_3. Better spatial characterization of both NO_2 and NH_3 concentrations, especially near intensive agriculture, would help to characterize the extent of the impacts across the U.S. These findings are discussed in the context of U.S. air pollution policy.

1. Introduction

Humans have polluted the atmosphere with gaseous and particulate forms of reactive nitrogen since industrialization began in the late 1800s. Two main chemical categories of nitrogen air pollutants are nitrogen oxides (NO_Y) and reduced nitrogen (NH_X). The gaseous forms of NO_Y include nitric oxide (NO) and nitrogen dioxide (NO_2), which may be oxidized in the atmosphere to create nitric acid (HNO_3). These NOy species are primarily emitted by combustion of fossil fuels and have been the dominant form of nitrogen pollution emission to the atmosphere in the U.S. (EPA, 2021). However, in the last 30 years, dominance has been shifting from NO_Y to NH_X, which includes NH_3 (ammonia) and NH_4 (ammonium), for two reasons (Aguillaume et al., 2017): decreases in NO_Y emissions due to regulation and (Asta et al., 2002) rising NH_3 emissions from agricultural animal waste and fertilizer applications (Behera et al., 2013; Hoesly et al., 2018).

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Lichens are mutualistic symbioses between a fungus (mycobiont) and a photosynthetic partner(s) (photobiont). Lichens are generally more sensitive than vascular plants to air pollution because lichens lack stomates and waxy epidermis to control influx to interior cells (Nash, 2008), although lichen species fall along a continuum of N-sensitivity to N-tolerance that reflects interspecific differences (Jovan, 2008; Geiser et al., 2021). Lichen communities are affected by several forms of N (i.e., gaseous and particulate, measured as air concentration or deposition, respectively), so it can be difficult to isolate response to any one chemical species. For example, a study from 22 forest sites in southern California in the U.S. indicated lichen community composition was significantly related to air concentrations of gases (NO_2 $r^2 = 0.42$, NH_3 $r^2 = 0.47$, HNO_3 $r^2 = 0.59$), yet a better predictor was total dry N deposition ($r^2 = 0.62$), while the best predictor is total throughfall N ($r^2 = 0.94$) (Jovan et al., 2012). Total N throughfall was the most integrative measure considered in the study because it captured the deposition mixture of all gases and particulates, a similar metric being total N deposition. Although integrated metrics of N atmospheric exposure may always be the most robust indicator when compared to individual reactive N-containing chemicals, specific mixtures of chemical species in the air at individual sites will influence which form of nitrogen gas has the most dominant relationship to lichen community composition. For example, the amount of variation in lichen communities that was significantly attributed to NO_2 ranged from 5 to 77%, in sites dominated by NH_3 and NO_2, respectively (Cepeda Fuentes and Barcia Rowe, 1998; Van Dobben and Ter Braak, 1998).

Air pollution is generally measured as concentration in the ambient air or as load once it has deposited to an ecological surface. Thresholds of N air pollution may be set as critical loads (CLO), which are thresholds of atmospheric deposition below which harmful ecological effects do not occur, or as critical levels (CLE), ambient air concentrations of reactive N gases that can be averaged daily or annually. By definition, CLEs describe "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). However, sometimes CLEs are based different thresholds like the lowest and no observed effect concentrations (LOEC and NOEC, respectively).

Lichen N CLOs for ecoregions across the U.S. were initially synthesized (Pardo et al., 2011) and more recently calculated in a sophisticated and comprehensive review (Geiser et al., 2021) that shows a CLO of 1.5 kg N ha/yr corresponds to the initial shifts in community composition from pollution-sensitive toward pollution-tolerant lichen species in the U.S. While CLOs are useful recommendations on loads of N deposition that preserve lichen biodiversity, they are not national-scale legal rules, nor do they set limits for individual chemical species that contribute to N deposition. In contrast, National Ambient Air Quality Standards (NAAQS) are legal rules stipulating allowable air concentrations for specific criteria air pollutant (thresholds), such as NO_2, that are set by the U.S. Environmental Protection Agency and reviewed for possible revision every 5 years based on the evolving scientific evidence base.

To date, the methodology to relate deposition measurements for total N to ambient air concentrations of specific N-containing gases and particulates yields highly uncertain results across the national landscape due to incomplete understanding of the relationship between concentration of gases and particulates in the air and N deposition to a surface (Schwede and Lear, 2014). Moreover, studies that only quantify how N deposition exposure affects lichens, although ecologically meaningful, are not useful when precise quantification of the exposures to NO_2 or NH_3 that cause adverse effects on lichens are needed to inform policy. Studies that identify quantified relationships between exposure of gases and effects on lichens inform quantitative thresholds for ambient air concentrations. Considering these factors, in this paper we focus on the effects of the most the most ubiquitous NH_Y and NO_Y gases, NH_3 and NO_2, on lichen physiology and biodiversity. Typically, pollutant driven effects on physiology underlie changes in community composition and biodiversity, and all these ecological outcomes are useful in setting threshold values used in policy making, therefore we focus on these outcomes. The goals of this paper are to synthesize information from the peer reviewed literature to qualitatively characterize how NO_2 and NH_3 exposures alter lichen physiology and identify CLEs and similar quantitative exposure levels that alter lichen community diversity. To better understand current vulnerability of lichens in the U.S., we compare the exposure levels known to cause shifts in lichen community biodiversity to empirically-measured ambient concentrations in the U.S. Finally, we compare levels of ambient air exposures affecting lichen diversity to currently established NAAQS.

2. Concentrations in the U.S.

In the U.S., concentrations of NO2 and NH3 are routinely monitored by a network of measurement stations. Coverage is sparse and the area between monitors is often geographically and meteorologically heterogeneous, making it difficult to assess concentrations between monitors and the overall spatial variability of concentrations. Despite this lack of detail, the current monitors provide some baseline empirical information to characterize the NO_2 and NH_3 concentrations that ecosystems in the U.S. are exposed to.

3. NH_3 concentrations

We evaluate the long-term average air concentrations by calculating the NH_3 concentration 3-year average of the annual mean (2017–2019) for each monitoring site, which was below 6 μg NH_3 m^{-3} (~9 ppb), with one exception in rural Utah that is almost 3 times higher, and is highest in agricultural regions like the Midwest, the Eastern Great Plains, eastern North Carolina and California (Fig. 1a). Maximum 2-week averaged NH_3 concentrations range up to 40 μg NH_3 m^{-3} (~57 ppb, Fig. 1b). These values do not account for spikes of NH_3 concentrations that are spatially localized, such as those observed in the proximity of intensive agricultural sources, like concentrated animal feeding operations [CAFOs (Walker et al., 2006; Wilson and Serre, 2007; Hiranuma et al., 2012; Golston et al., 2020),], which may have concentrations above 700 μg NH_3 m^{-3} (~1000 ppb) over short periods of time, with yearly averages undocumented (Golston et al., 2020). NH3 monitors were generally sited in more rural areas, and a clear increasing trend in NH_3 concentrations in agricultural areas in the U.S. has been observed with satellite-based remote sensing (Warner et al., 2017; Guo et al., 2021); similar trends are observed globally (Behera et al., 2013). The relationship between NH_3 emissions and concentrations is poorly understood in general, as illustrated by the increasing ambient concentrations but relatively flat emissions estimated from inventories in the U.S. during the past few decades (EPA, 2020). Reasons for the poor relationship between emissions and ambient concentrations include (Aguillaume et al., 2017) poorly characterized emissions from intensive agriculture (Asta et al., 2002), decreases in atmospheric concentrations of sulfate and nitrate, which remove NH3, in recent years due to emission controls (Warner et al., 2017) (Attanayaka and Wijeyaratne, 2013), unknown daily fluctuations of NH_3 concentrations which are collected at 2 weeks intervals at U.S. monitoring networks (Behera et al., 2013), poorly characterized effects of temperature on NH_3 emissions and (Cape et al., 2009) uncertainty in bidirectional flux (EPA, 2020).

4. NO_2 concentrations

Air regulations have effectively reduced nationally calculated NO_2 concentrations by 53% between 1990 and 2017 in the U.S. (EPA, 2020). Concentrations of NO_2 are highest in populated regions like California and the Northeast corridor, as well as the Front Range in Colorado, with the 3-year average (2017–2019) of the annual mean of each monitoring site ranging up to 56.4 μg NO_2 m^{-3} (~30 ppb, Fig. 2a) Fig. 3with daily maximum concentrations ranging above 188 μg $NO_2 m^{-3}$ (~100 ppb, Fig. 2b). NO_2 data are based on continuous measurements from the

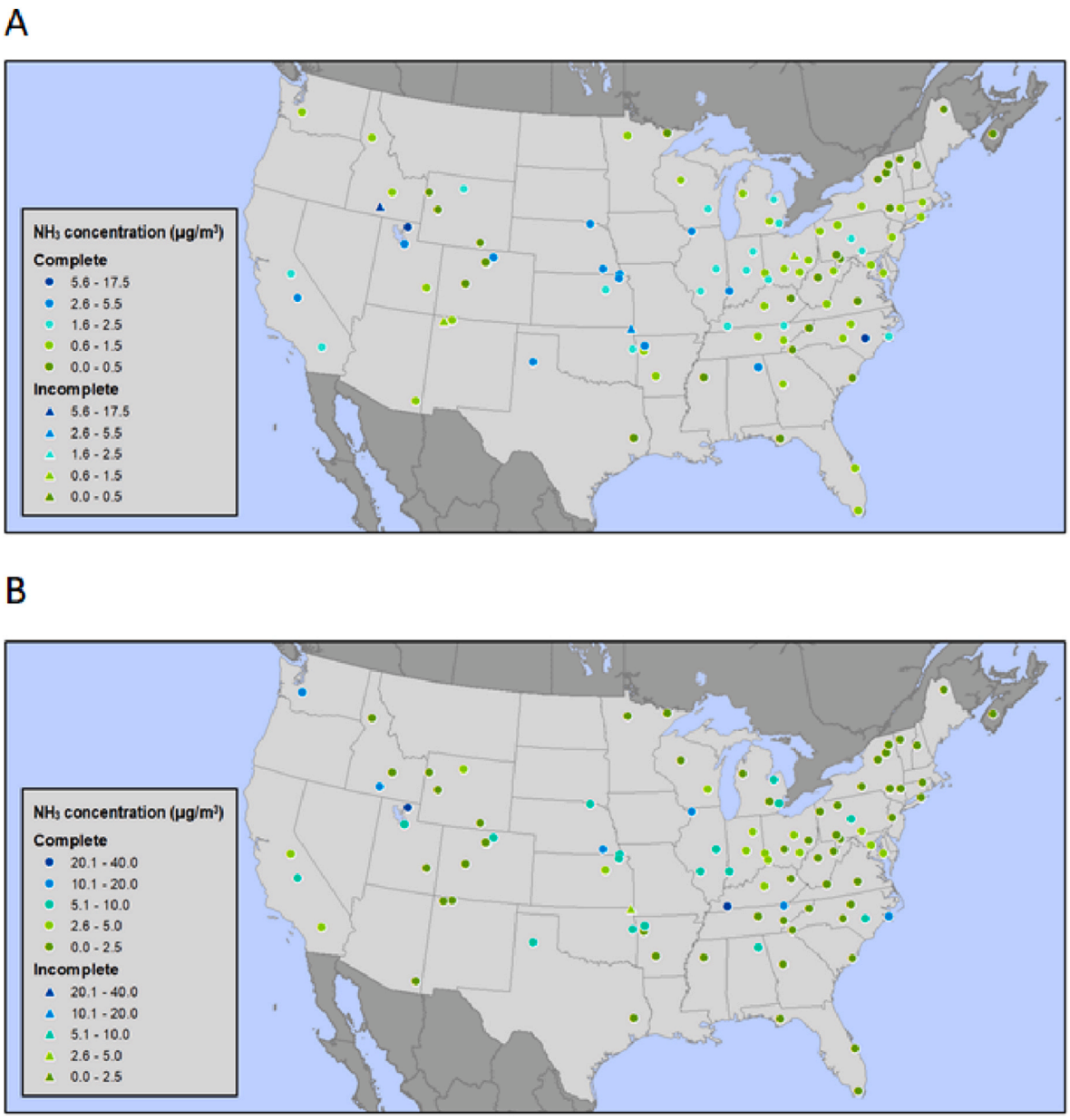

Fig. 1. State and Local Air Monitoring and Clean Air Status and Trends network of A) 2017–2019 3-year average NH_3 and B) 2019 maximum 2-week average NH_3 (https://aqs.epa.gov/aqsweb/airdata). Monitor sites with a "complete record" have >75% of observations/records for each year. Sites that met the 75% data capture for of all samples collected for both State and Local Air Monitoring and Clean Air Status and Trends (national) networks are shown with circles and those that are incomplete with triangles.

regulatory-based state and local air monitoring sites network for NO_2.

5. Is NO_2 a good indicator for gaseous NO_Y?

As NO_2 is only one form of gaseous NO_Y, it leads to the question of how well NO_2 approximates total loading of gaseous NO_Y to lichens. To address this, we analyzed NO_Y vs. NO_2 annual average concentrations in 2017 (Figure S-2) and found that NO_2 accounted for most of the mass of gaseous NO_Y at most monitoring sites. However, total NO_Y was on average 50% greater than NO_2 alone for sites with both measurements. Much of the additional NOy was NO, as NO + NO_2 accounted for 98% of NO_Y on average. At rural sites where sensitive ecosystems are more likely to be found, more oxidized chemical species such as HNO_3 and PAN become more prevalent, but there are few monitors in these areas.

6. Spatial comparison of NH_3 and NO_2

A meaningful comparison of geographic differences in relative NH3 and NO2 concentrations is not feasible because of sparse network coverage, particularly in parts of the western U.S. Furthermore, concentrations measured at NO2 monitors, which are primarily located in urban areas, are likely much higher than regional NO2 concentrations in rural areas where NH3 monitors are located. Concurrent satellite-based measurements of NO2 and NH3 present a promising alternative to ground-based network measurements and show generally higher NO2 concentrations in the eastern half of the U.S., and in urban and industrial areas more generally, and higher concentrations of NH3 over agricultural areas like the Midwest and the Central Valley of California (Kharol et al., 2018).

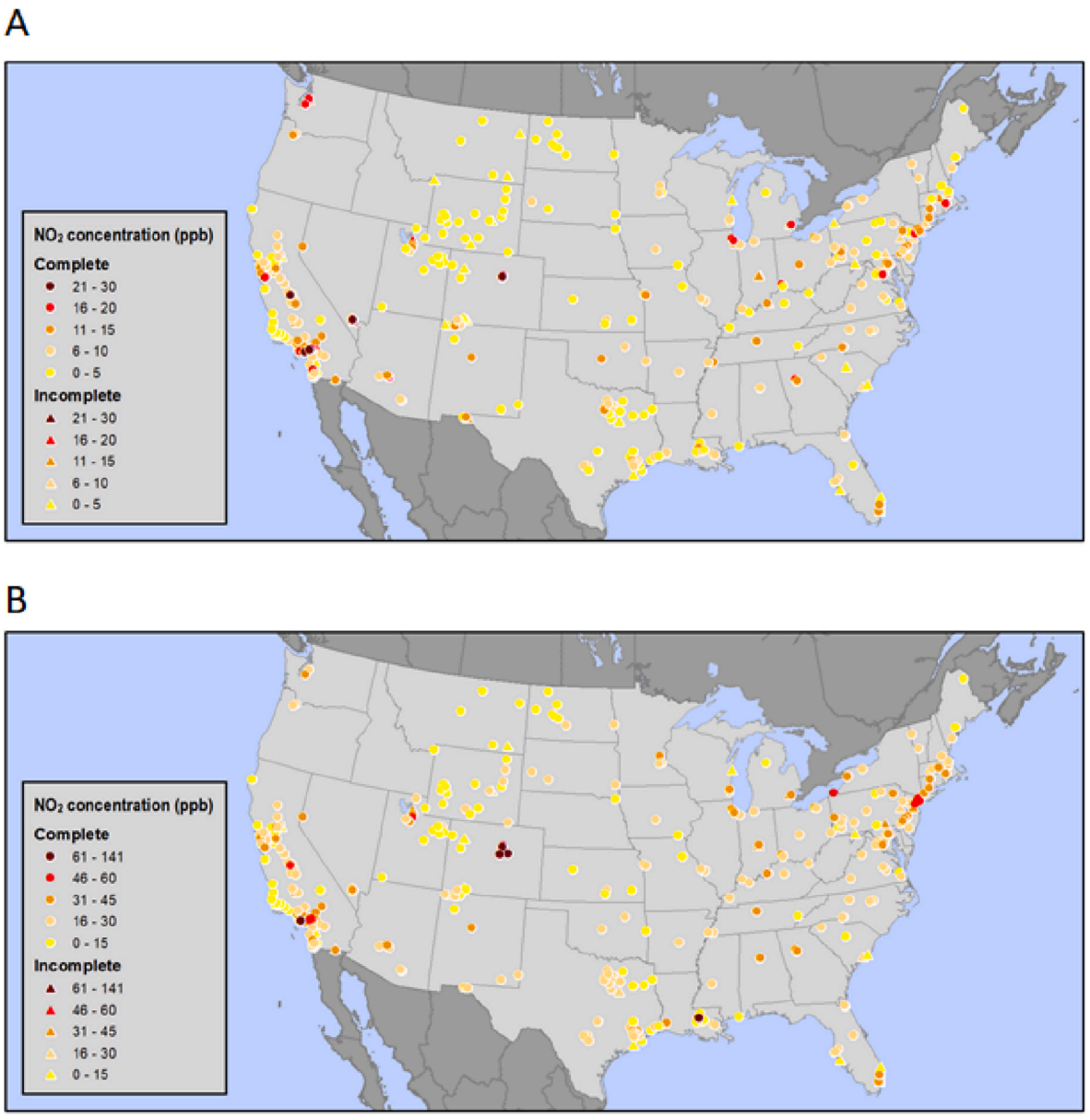

Fig. 2. State and Local Air Monitoring and Clean Air Status and Trends network of A) 2017–2019 3-year average NO_2 and B) 2019 maximum daily average NO_2. Data from: https://aqs.epa.gov/aqsweb/airdata. Monitors with a "complete record" have >75% of observations/records for each year. Sites that met the 75% data capture for of all samples collected for both State and Local Air Monitoring and Clean Air Status and Trends (national) networks are shown with circles and those that are incomplete with triangles.

7. Lichen physiology

Lichen photobionts may be either cyanobacteria, green algae or both. This review focuses on lichens with an algal symbiont, or cholorolichens. A recent review synthesized information on how N generally affects lichens (Carter et al., 2017). In this section we extend that review to compare the effects of NH_3 and NO_2 uptake pathways and effects on physiology (Table 1) published in the peer-reviewed literature through 2020. This synthesis lays the foundation for discussing the mechanisms driving effects on lichen community composition in the following section.

Wet and dry conditions alter how lichens are exposed to NH_3 and NO_2. Since lichens lack stomates to regulate photosynthetic cell exposure to gases from the ambient air, NH_3 and NO_2 typically enter the lichen by diffusing across exterior openings in the mycobiont cortex. In dry conditions NH_3 and NO_2, which are uncharged, may diffuse across the mycobiont cortex to contact the photobionts directly, then cross the algal cell membrane by active and passive transport, as occurs in higher plant cells (Ritchie, 2013). Passive uptake is by diffusion across the cellular bilipid membrane, which occurs until a dynamic equilibrium is reached. The permeability of NH_3 across the lipid bilayers is three orders of magnitude higher than NH_4^+ in plant cells (Howitt and Udvardi, 2000), which is likely the same for lichenized algae. This may be why exposure to NH_3 has been shown to be more toxic than exposure to NH_4^+ (see discussion below). We did not find similar membrane permeability values to compare for NO_2 or NO_3^-, however lipid membranes are not considered significant barriers to NO_2 transport (Signorelli et al., 2011). Lastly, NO_2 is a non-polar molecule and is thus hydrophobic. In comparison, NH_3 carries a partial charge and is hydrophilic. The implications may be that the polar NH_3 molecule dissolves into cytosolic solution more readily than NO_2 once it diffuses across the membrane bilayer, leading to higher cytosolic concentrations in the cell. More research is needed to confirm this.

The form of nitrogen can change the pH of the lichen's external

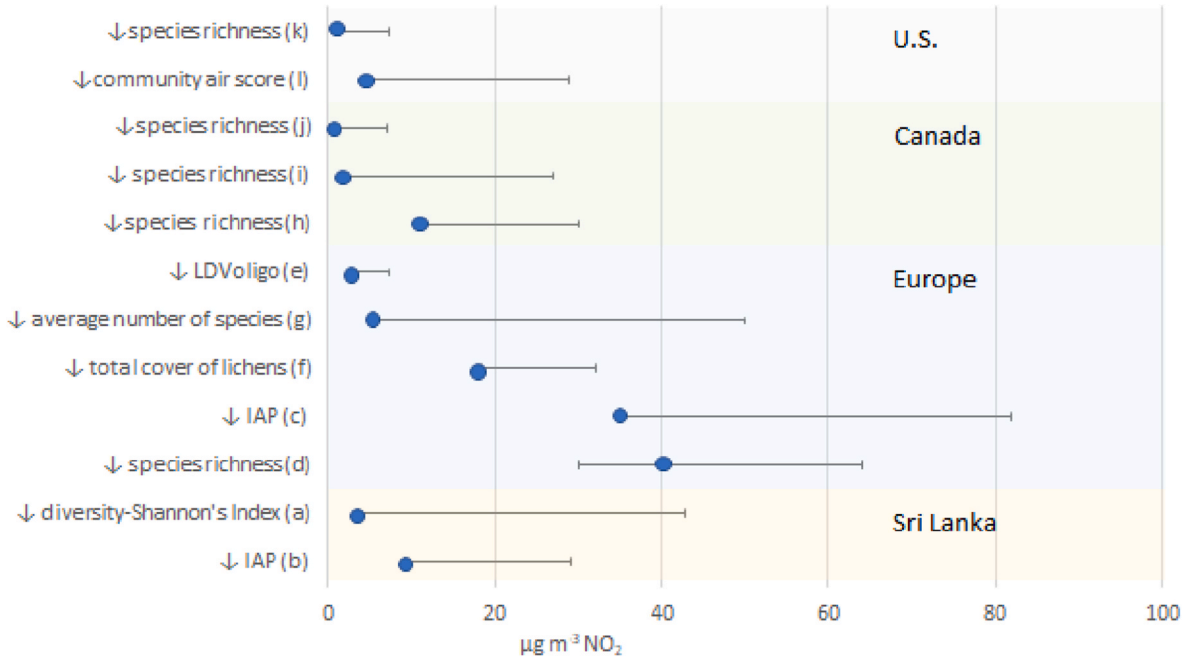

Fig. 3. Studies evaluating the effects of NO_2 on lichen biodiversity. a= (Attanayaka and Wijeyaratne, 2013), b=(Yatawara and Dayananda, 2019), c=(Cepeda Fuentes and Barcia Rowe, 1998), d=(Davies et al., 2007), e=(Pinho et al., 2008), f=(Manninen, 2018), g=(Watmough et al., 2017), h=(Watmough et al., 2014), i=(Gadsdon et al., 2010), j=(Gibson et al., 2013), k=(Perlmutter et al., 2018), l=(Jovan et al., 2012). LOEC levels are indicated by circles, and bars represent the range of NO_2 exposures observed in the study.

environment when it reacts with water or the internal environment when it reacts with water in the cytosol or algal enzymes. Enzyme-mediated assimilation of NO_3^- (i.e. the physiological process to form amino acids-NH_2) includes the reduction of $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$, a reaction that consumes H^+ causing alkalization within the cytosol. During assimilation of NH_4^+, it is reduced by enzymes to release H^+, thus causing acidification within the cytosol. If dry NH_3 reacts with water when it enters the cytosol it dissociates forming NH_4^+, consuming H^+ and releasing an OH^-, alkalizing the cell solution. If dry NO_2 reacts with water in the cytosol it will result in nitric acid (HNO_3), a strong acid which may further dissociate in water to from NO_3^- and release H^+ causing acidification. The changes in pH caused by the reaction between water and NH_3 or NO_2 occur where protonation occurs, therefore either within the lichen or the external habitat. If the above reactions occur with water on tree bark, the pH of tree bark will be altered by the pollution exposure. The pH of tree bark has been identified as an important factor related to epiphytic lichen community composition in areas of Europe with high NH_3 concentrations (van Herk, 2001).

Of the NH_3 and NO_2 transformation products, the cation NH_4^+ is taken up most quickly by the mycobiont (Dahlman et al., 2004; Wang et al., 2018) because of its negative membrane potential (Dahlman et al., 2004). The extracellular cation exchange capacity of the mycobiont varies among species affecting the rate of diffusion of NH_4^+. A lichen species with low extracellular cation exchange capacity means less NH_4^+can bind with the lichen and less exposure is received by the photobiont cells on the interior of the thallus, protecting against the possible toxic effects. Low cation exchange capacity is a trait among N-tolerant species (Gaio-Oliveira et al., 2001).

We found only one study that isolated the effects of NO_2 exposure on lichen physiology in a controlled experiment; NO_2 caused physiological stress, measured as decreasing chlorophyll content, at NO_2 concentrations at 376 µg NO_2 m^{-3} (~200 ppb) and causes consistent stress at 752 µg NO_2 m^{-3} (~400 ppb) after 6 h of exposure (Nash, 1976). Most often NO_2 is considered as part of a pollutant mixture in observational field studies where effects on lichen physiology, such as tissue N concentration, C:N ratio, chlorophyll content, and photosynthesis (von Arb et al., 1990; Watmough et al., 2014; Manninen, 2018) are reported as correlations to the NO_2 concentration. With a lack of physiological effects of NO_2 on lichens documented in controlled experiments, inference may be drawn from the literature on vascular plants.

In general, NO_2 acts as a nutrient in plants exposed to lower concentrations and is well known to cause oxidative stress at higher concentrations. Inference may also be drawn from the effects of NO_3^-, a transformation product of NO_2, on lichen physiology. In general, NO_3^- initially causes nutrient effects such as increased enzymes related to photosynthesis (Munzi et al., 2017), N concentrations, Chl a and photobiont concentrations (Johansson et al., 2010). Exposure to NO_3^- also alters proteomic expression in the lichen fungal partner, mostly affecting proteins related to stress (protein folding) and regulation, while upregulating proteins involved with photosynthesis in the algal partner (Munzi et al., 2017), which the authors suggest may provide more C to the stressed fungal partner. As NO_3^- concentrations increase, inhibitory effects occur, such as cell membrane leakage/damage (Munzi et al., 2009), decreased Fv/Fm (a metric of chlorophyll fluorescence and an indicator of stress), and decreased PI_{ABS} (an index of photosynthetic performance/stress) (Munzi et al., 2012; Munzi et al., 2014; Paoli et al., 2015).

Lichens exposed to NH_3 initially show increased N concentration in the thallus [(Munzi et al., 2019) exposure reported as NH_3 dry deposition]. As NH_3 exposure increases, lichens are damaged and experience stress. Exposures increasing from >1 to 100 µg m^{-3} NH_3 (1.4–142 ppb) caused decreased Fv/Fm (Munzi et al., 2014). A similar result was found when exposure increased from >1 to 14 kg NH_3 ha^{-1} yr^{-1} (Munzi et al., 2019). Exposures from 2 µg m^{-3} NH_3 to 300 µg m^{-3} NH_3 (~2.8–428 ppb) caused decreased PI_{ABS}, which is an indicator of stress combining 3 aspects of photosynthetic activity (light absorption, excitation energy trapping, and conversion of excitation energy to electron transport) (Paoli et al., 2015). It is likely that cell membrane leakage/damage occurs in response to NH_3, as it occurs with exposure to $(NH_4)_2SO_4$ (Munzi et al., 2009), but should be confirmed with a controlled NH_3 exposure experiment. Ammonium toxicity arises as the algal uptake exceeds its assimilation capacity. When the transformation of NH_3 to NH_4^+ occurs in

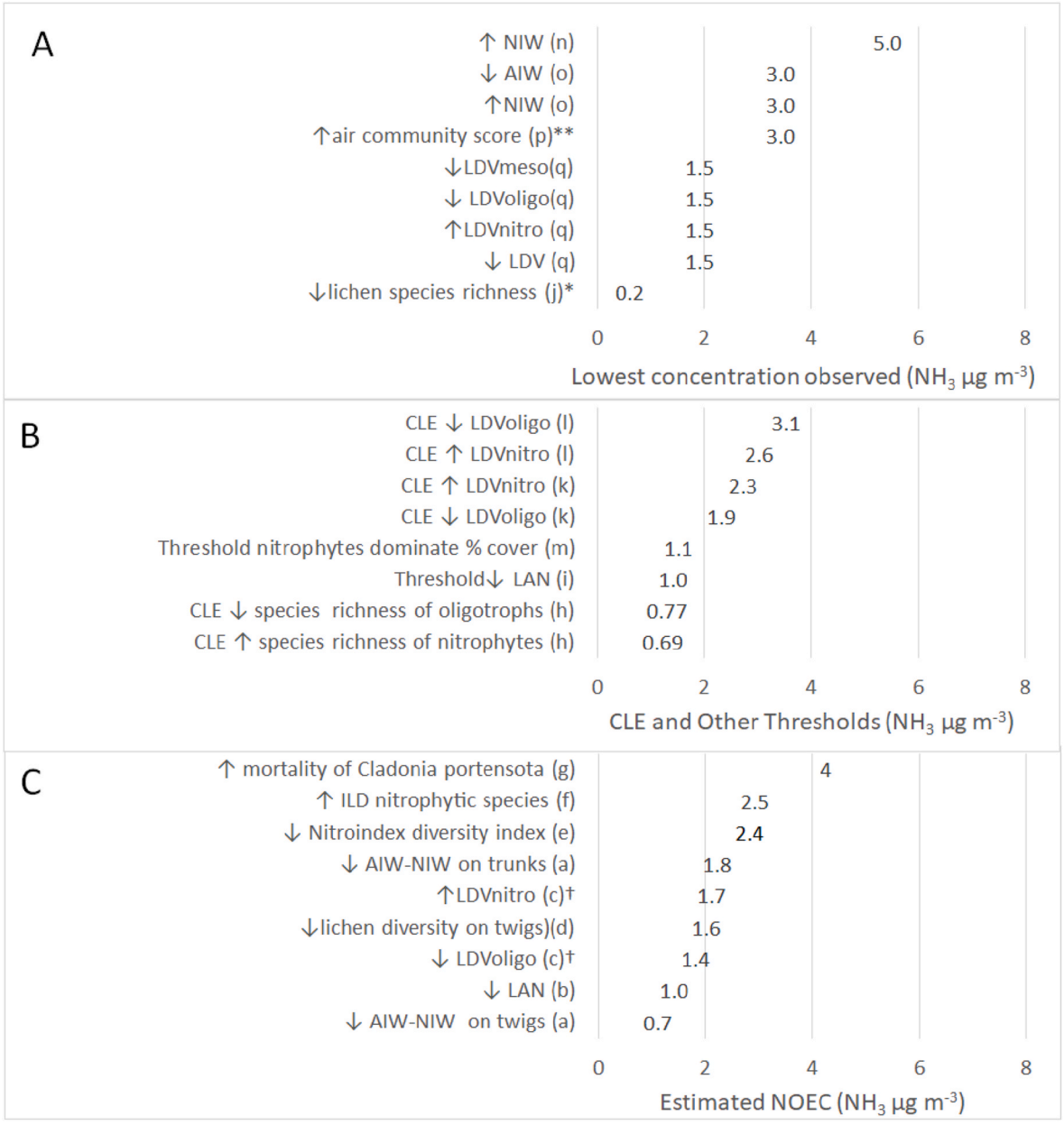

Fig. 4. Studies evaluating the effects of NH_3 on lichen biodiversity. A. Studies that published effects as a correlation or regression across the range of NH_3 exposures observed. B. Studies that published critical level (CLE) C. NOEC levels published by Cape et al., 2009) with analysis of the original publication's data. References are as follows: a= (Pitcairn et al., 2004), b=(Leith et al., 2005), c=(Pinho et al., 2009), d=(Wolseley et al., 2006), e=(Rihm et al., 2009), f=(Frati et al., 2007), g=(Sheppard et al., 2009), h=(Pinho et al., 2014), i=(Wolseley et al., 2010), j=(Watmough et al., 2014), k=(Pinho et al., 2012), l=(Aguillaume et al., 2017), m=(Gadsdon et al., 2010), n=(Sparrius, 2007), o=(van Herk, 2001), p=(Jovan et al., 2012), q=(Pinho et al., 2011). LAN = Lichen Diversity index, LDVnitro = Lichen diversity index nitophytic species, LDVoligo = Lichen diversity index oligotrophic species, *study from Canada, ** study from the United States.†NOEC values are those reported in the original manuscript (Pinho et al., 2009), different NOEC values for this dataset were reported in (Cape et al., 2009).

the cytosol, the resultant NH_4^+, a weak acid, can be sequestered in the algal vacuole, but at high concentrations may collapse the pH gradient of tonoplast vesicles (membrane surrounding the vacuoles) preventing sequestration within the cell. Therefore, at high cellular (cytosolic) concentrations it must be assimilated by the enzyme glutamine synthetase into organic non-toxic forms such as amino acids. Evidence for this conversion to amino acids is documented for both plants (Pearson and Stewart, 1993; Fangmeier et al., 1994; Ludewig et al., 2007) and lichens (Hauck and Wirth, 2010).

Susceptibility to NH_X toxicity could be linked to photosynthetic capacity because, as previously mentioned, lichens often avoid the buildup of NH_X to toxic levels by converting it to amino acids, which relies on carbon from photosynthesis (Hauck and Wirth, 2010). Therefore, decreased photosynthetic capacity in species adapted to low light levels can make them more susceptible to toxicity (Hauck and Wirth, 2010). If photosynthesis increases in response to N additions a positive feedback loop might be created, in which conversion of the NH_X to amino acids could then be used to increase chlorophyll concentration and further increase photosynthetic capacity. A comparison of lichen exposed to NH_3, NH_4^+ and NO_3^-, found exposure to dry deposition of NH_3 caused the most physiological damage, although wet deposition of NH_4^+ had a significant observable physiological impact and there was no significant effect of NO_3^- on chlorophyll *a* fluorescence, implying differential sensitivity to NH_3, NH_4^+ and NO_3^- [(Munzi et al., 2019), exposure reported in units of deposition]

In summary, the scientific literature documents several ways in

Table 1
Comparison of the uptake pathways, physiological effects, and community effects of gas-phase NH_3 and NO_2 on lichens.

Lichen effect	Chemical species	
	NH_3	$N0_2$
Uptake across the mycobiont cortex	In dry conditions, NH_3 diffuses across openings in the mycobiont cortex to contact the photobionts. In wet conditions, NH_3 often reacts with water and is protonated to NH_4^+ of which the rate of uptake is rapid (Dahlman et al., 2004; Wang et al., 2018)	In dry conditions, NO_2 diffuses across openings in the mycobiont cortex to contact the photobionts In wet conditions, NO_2 reacts with water to form HNO_3, NO_3^- or NO
Cell membrane permeability	a polar molecule that is a weak base gas and hydrophyllic crosses the cell membrane by active and passive transport NH_3 permeates across the cell membrane 3x faster than NH_4^+(Howitt and Udvardi, 2000)	a non-polar molecule that is an acidic gas and hydrophobic crosses the membrane by active and passive transport (Signorelli et al., 2011) no information on membrane permeability rates
In algal cell solution	NH_3 often protonates to NH_4^+ in cell solution causing the cell solution to acidify (Munzi et al., 2017)	NO_2 reacts with water in cell solution to create the acid HNO_3, which dissociates to NO_3^-, a conjugate base, thereby causing alkalization, and nitrite (NO_2^-), a free radical (Munzi et al., 2017) NO_3^- and NO_2^- which both may be reduced to NH_4^+ via nitrate reductase (NR) and nitrite reductase (NiR), respectively energy is required to reduce NO_3^-
Storage in tissue	Toxic, may be stored in the vacuole as NH_4^+, or converted to amino acids to detoxify (Hauck and Wirth, 2010)	
Contributes to tissue nitrogen	Yes, exposure measured as 1. NH_3 dry deposition (Munzi et al., 2019), and 2. Site with agricultural sources only, but no exposure concentration reported (Gaio-Oliveira et al., 2001)	No studies available for NO_2 exposure, inference available from studies on 1. NO_3^- exposure (Johansson et al., 2010) and 2. Sites with NO_x as the main source (Gaio-Oliveira et al., 2001)
Physiological stress	Yes (Munzi et al., 2014; Paoli et al., 2015)	Yes (Nash, 1976)
Biodiversity-lichens	↓ N sensitive species ↑ Abundance N tolerant species (Fig. 4).	↓ N sensitive species ↑ Abundance N tolerant species (Fig. 3) until a threshold is reached causing decline

which NH_3 and NO_2 have similar pathways through the mycobiont cortex, differing rates of membrane diffusion into the algae, different molecular polarity that affects diffusion into the cytosol, different storage within the cell and different consequences on internal and external pH (Table 1), with potentially important consequences for algal photosynthesis. Together, there is very little information quantifying exposure response relationships, which could be used to identify CLEs or similar thresholds associated with impacts to photosynthesis. For NO_2 we identified just one study using controlled chambers (Nash, 1976), causing us to rely on studies focusing on NO_3^- for insight. Likewise, besides the one study relating NH_3 reported as air concentrations to physiological effects [Fv/Fm (Munzi et al., 2014),], we had to include studies about NH_3 reported as deposition or solutions of reduced nitrogen. To better understand quantitative dose-response relationships, more experiments with controlled exposures relevant to current ambient air concentrations currently are needed for both NH_3 and NO_2 exposure.

8. Lichen diversity effects

While we can't establish exposure response or exposure thresholds for the physiological effects of NH_3 and NO_2, the mechanisms discussed in the previous section likely lead to reduced reproduction and survival that in turn alter the composition of lichens communities. Lichen community composition may be quantified by several metrics that typically including measures of species abundance and richness (Kricke & Loppi; Leblanc and Desloover, 1970; Asta et al., 2002; Jovan et al., 2012; Herzig et al., 2020). Indices aimed at characterizing community-level N effects vary in design but usually classify lichen species as oligotrophs (syn. acidophytes; N-sensitive and requiring low substrate pH), mesotrophs (syn. neutrophytes; moderately N-tolerant), or eutrophs (syn. nitrophytes; "N-loving'' and requiring a high-pH substrate) originally developed by van Herk (1999). These indices are especially effective when calibrated to the pollutant mixture where they are applied (Herzig et al., 2020). Here we synthesize evidence on lichen community response to exposures below approximately 100 μg NO_2 m^{-3} (53 ppb) and 8 μg NH_3 m^{-3} (11ppb) to be relevant to current concentrations measured in the U.S.

9. NO_2

We identified peer-reviewed publications that quantify the relationship between NO_2 concentrations and lichen biodiversity; studies that did not identify the effects of NO_2 from an air pollution mixture were not included. Thirteen studies were identified (Table 2 and Fig. 3). Studies from Sri Lanka (n = 2), Europe (n = 6), Canada (n = 3) and the U.S (n = 2) all show effects occurring below the current 3-yr annual average concentrations of NO_2 for some monitoring sites in the US (30 NO_2 ppb ~56.4 μg NO_2 m^{-3}, Table 2 and Fig. 2). The studies were conducted in ecosystems from a range of climates zones (Köppen climate classification) including Tropical, Temperate, and Continental (Table 2) demonstrating the effect of NO_2 on lichen diversity is widespread and the data from sites in varying climates is coherent. Despite this, most sub-climates in the U.S. are underrepresented in the literature, including areas where lichens occur and lichen community composition is documented to respond to nitrogen (as total N deposition) (Geiser et al., 2021).

All NO_2 studies we identified were an observational design, where NO_2 concentrations are measured proximal to the lichen sampling site and typically correlation or regression is used to statistically evaluate the relationship between NO_2 exposure and lichen diversity. These methods indicated that effects on diversity were related over the range of exposures. When studies report a correlation or regression, we report the lowest NO_2 concentration observed as the LOEC, however the true value initiating an effect at a given site may lie between the first and second lowest NO_2 concentration. In the studies included in our synthesis there is a relationship between the LOEC and the max NH_3 concentration observed in a study ($R^2 = 0.64$, $p = 0.001$), indicating that studies with more polluted sites have higher LOEC values. This could be because more sensitive species have already been lost. When studies reported a threshold instead of or in addition to a correlation or regression, we report the threshold value they identified (Table 2). We did not identify any papers that calculated a CLE value for NO_2 based on lichen diversity. The United Nations Economic Commission for Europe (UN/ECE) has developed an NO_2 CLE for Europe and the U.S. has developed a NO_2 Secondary National Ambient Air Quality Standard, both the CLE and Secondary NAAQS are based on effects to vascular plants (see discussion below).

Increasing NO_2 was correlated to decreases in several diversity metrics, including lichen species richness (Davies et al., 2007; Gibson et al., 2013; Watmough et al., 2014; Watmough et al., 2017; Perlmutter et al., 2018), Shannon's diversity index (Attanayaka and Wijeyaratne, 2013) and the lichen diversity value (LDV) for oligotrophs (LDVoligo) (Pinho et al., 2008), although 2 of the 5 studies on species richness do

Table 2
Nitrogen dioxide (NO_2) Effects on Lichen Biodiversity from studies published after (or not included) in Cape et al. (2009). Abbreviations are Index of Air Pollution (IAP), Lichen Diversity Value (LDV), Lichen Diversity Value of nitrophytic lichens (LDVnitro), Lichen Diversity Value of oligotrophic lichens (LDVoligo), Lowest Observed Effect Concentration (LOEC), concentrations converted from ppb reported in the original paper at 25 °C (A).

Reference	Climate	Location	Ecosystem	Observed effect	LOEC (μg NO2 ·m-3)	Threshold (μg NO2 ·m-3)
(Jovan et al., 2012)	Temperate: Hot and warm summer Mediterranean (Csa and Csb)	Southern California, USA	mixed conifer-black oak forest	Community air score increased with NO_2 (r^2 0.42, p = 0.03)	4.0	NR
(Perlmutter et al., 2018)	Temperate: Humid-subtropical (Cfa)	Wake County, NC, USA	Roadside trees (103 lichen species)	species richness decreased with increasing NO_2 (bole: r2 = 0.71, p < 0.001; base r^2 = 0.75, p < 0.001)	0.94 [A]	NR
(Watmough et al., 2014)	Continental warm summer and subarctic (Dfb and Dfc)	sites with varying road densities Ontario, Canada	Forest dominated by sugar maple (10 lichen species)	species richness decreased with increasing NO_2 (R^2 = −0.38, p < 0.001), correlation matrix	1.3	20, only one species left
Gibson et al., 2013)	Continental: warm summer (Dfb)	Cape Breton, Canada	plateau is dominated by coniferous boreal and taiga vegetation and the lowlands by deciduous forest (17 lichen species)	species richness decreased with increasing NO_2 (R^2 = 0.44), correlation matrix, p-value not reported	0.18[A]	NR
(Watmough et al., 2017)	Continental: warm summer (Dfb)	Ontario, Canada	Roadside (4 lichen species)	species richness declined by 50% 22 μg NO_2 m^{-3} (100m from the roadside)-no statistics reported	11	22, 50% decline in species
(Manninen, 2018)	Temperate: Hot summer continental (Dfa)	Helsinki metropolitan area, Finland	(12 indicator species)	Average number of species declined with increasing NO_2 (r = −0.36, p ≤ 0.5), Pearson's correlation	5	NR
(Gadsdon et al., 2010)	Temperate: Oceanic (Cfb)	north-east of London, UK	Epping Forest (16 lichen species)	Nitrophyte cover increased with increasing NO_2 (r^2 = 0.48, p < 0.001) and total lichen cover decrease with increasing NO_2 (r^2 = 0.40, p < 0.001)	18	26, cover of nitrophytes >50%
(Pinho et al., 2008)	Temperate: Hot summer Mediterranean (Csa)	SW Portugal	Lichens growing on Quercus suber L. trees	LDVoligo decreased with increasing concentrations of NO 2 (r^2 = 0.40, p < 0.001) LDVnitro no significant relationship with NO_2	2.9	NR
(Cepeda Fuentes and Barcia Rowe, 1998)	Temperate: Hot summer Mediterranean (Csa)	Seville, Spain	Lichens growing on tree species Melia azedarach L. (23 lichen species)	IAP decreased with increasing NO_2 (R^2 = 0.88, P < 0.05) Correlation; (r^2 = 0.77, p = 0.01) cluster analysis	35	NR
(Davies et al., 2007)	Temperate: Oceanic (Cfb)	London, UK	(74 lichen species)	Species richness decrease with increasing NO_2 (r = 0.96, p < 0.01, n = 5)	30	40 onset of decreasing # of lichen species
(Yatawara and Dayananda, 2019)	Tropical Rainforest (Af)	Kegalle District, Sri Lanka	Lichens growing on two tree species: Mangifera indica and Cocos nucifera (89 lichen species)	IAP decreased with increasing NO_2 (R^2 = 0.64 p < 0.05) correlation	9.3	NR
(Attanayaka and Wijeyaratne, 2013)	Tropical Rainforest (Af)	Colombo, Sri Lanka	Lichens growing on three tree species	Shannon's Diversity index decreased with increasing NO_2 (−0.35, p < 0.05)	3.6	NR
Frati et al., 2006	Temperate: Hot summer Mediterranean (Csa)	Italy	(32 species)	No significant relationship between NO_2 and IAP	n.s.	n/a

not report the p-value (Gibson et al., 2013; Watmough et al., 2017). Results from the study examining lichen cover show decreasing total lichen cover (Gadsdon et al., 2010) was offset by increasing cover of eutrophs. It is important to note that declines in species richness are likely due to a decline in oligotrophic species and may be partially offset by gains in eutrophic species, however the one study that evaluated species richness of eutrophs showed no significant effect of NO_2 (Pinho et al., 2008). Community shifts were documented for more complex biodiversity indices, like community air scores derived from gradient analysis (Jovan et al., 2012), and the Index of Atmospheric Purity (IAP), which is an equation that relates species richness, frequency, abundance and a 'sensitivity score' to quantify composition changes in lichen communities (Cepeda Fuentes and Barcia Rowe, 1998; Yatawara and Dayananda, 2019). No relationship between the IAP and NO_2 was found in only one case (Frati et al., 2006), which the authors attributed to low levels of air pollution at their site.

Collectively, this body of evidence supports that increasing NO_2 is significantly related to decreases in lichen biodiversity, most especially oligotroph diversity, and that the threshold initiating effects could be quite low (<1 μg NO_2 $\cdot m^{-3}$). Due to the varied locations and approaches of reviewed studies, however, it's impossible to compare their results more directly. Furthermore, relatively few studies investigate NO_2, and it's unclear to what extent other co-occurring N species may affect biodiversity indices. More quantitative data on the relationship between NO_2 exposure and lichen diversity responses across the U.S. and globally would strengthen confidence that the NO_2 levels that alter biodiversity response documented in this paper are broadly applicable.

10. NH_3

We identified peer-reviewed publications that quantify the relationship between NH_3 concentrations and lichen diversity; studies that did not identify the effects of NH_3 from an air pollution mixture were not included. In 2009, a review of NH_3 on lichens was published (Cape et al., 2009) which estimated NOECs using datasets from 7 other publications from sites in European countries including Scotland (n = 2), England (n = 2), Switzerland (n = 1), Portugal (n = 1), and Italy (n = 1) (Table S1). We identified 10 studies published since or not included in Cape et al. (2009) that were mostly from sites in European countries including the Netherlands (n = 2), Portugal (n = 3), Spain (n = 1), and the U.K. (n = 2)

with two studies from North America (Canada n = 1 and the U.S. n = 1) (Table 3). These studies show effects occurring below the 2017–2019 3-yr annual average concentrations of NH_3 for some monitoring sites in the US (6 μg NH_3 m^{-3}~ 9 NH_3 ppb, Table 3 and Fig. 1). Altogether, these 17 studies occurred in Temperate or Continental climates (Köppen climate classification; Table 3 and Table S1), and several subgroups within those larger climate categories. Continental ecosystems in the U. S. are under-represented, particularly the hot summer Continental climate, which occurs in much of the central eastern U.S., an area where lichens occur, and lichen community composition is documented to respond to nitrogen deposition (Geiser et al., 2021).

Like the NO_2 studies in the prior section, almost all NH_3 studies used an observational design where NH_3 was measured near the lichen sampling sites, except Sheppard et al. (2009), which used experimentally controlled field additions of NH_3. The additional studies we review here define continuous relationships that inform LOEC values (Fig. 4A) or identify thresholds/CLEs (Fig. 4B) while Cape et al. (2009) reports NOEC values (Fig. 4C). It is important to note Cape et al. (2009) estimated NOECs using a statistical procedure to identify the point at which an effect is statistically significantly different from that observed at the lowest concentration observed. This approach is required to define NOECs because for most studies true background concentrations of NH_3 are not known. For studies presenting correlations or regressions, we used the same rules as used for NO_2 (i.e., the LOEC is equal to the lowest NH_3 concentration observed).

The lowest estimated NOEC from Cape et al. (2009) (0.7 μg NH_3 m^{-3}~1.0 ppb) is based on the onset of community composition shifting from acidophytes/oligotrophs to nitrophytes/eutrophs along a gradient of sites with increasing distance from an agricultural point source in Scotland (Pitcairn et al., 2004; Cape et al., 2009), while the highest estimated NOEC (4.0 μg NH_3 m^{-3}–5.7 ppb at 25 °C) is based on mortality of the lichen *Cladonia portentosa* (Cape et al., 2009; Sheppard et al., 2009). Studies published since Cape et al. (2009) indicate a similar range of NH_3 concentrations for CLEs and other thresholds (Fig. 4B) as well as LOEC values (Fig. 4C). One LOEC value is lower (0.2 μg NH_3 m^{-3}~0.28 ppb at 25 °C) (Watmough et al., 2014) than the range of estimated NOECs reported by Cape et al., 2009). The study is based on 67 sites in Ontario, Canada for which lichen richness was negatively correlated to increasing NH_3 ($r^2 = -0.71$, $p < 0.001$) (Watmough et al., 2014). There were ten species of lichens identified in total and only one species remained at 1.4 μg NH_3 m^{-3} (Watmough et al., 2014)

Compared to NO_2, more studies investigate NH_3 effects on lichen diversity and include many of the same metrics. Likewise, these studies suggest the same kind of community shifts occur with increasing NH_3 as with NO_2. However, there is more evidence that eutrophic/nitrophyte lichen diversity and abundance increase with increasing NH_3. This relationship is documented by studies using several different metrics including the 'Nitrofiele Indicatie Waarde' (NIW, index of nitrophyte lichen abundance)(van Herk, 2001; Pitcairn et al., 2004; Wolseley et al., 2006; Sparrius, 2007; Gadsdon et al., 2010), LDVnitro (Pinho et al., 2009; Pinho et al., 2011; Pinho et al., 2012; Aguillaume et al., 2017), Index of Lichen Diversity for strictly nitrophyte species (IDLsn)(Frati et al., 2007), proportion of nitrophytes (Gadsdon et al., 2010), and richness of nitrophyte species (Pinho et al., 2014). There was only one case where an index (percent cover of eutrophic lichens) was not significantly correlated with NH_3 measurements (Jovan et al., 2012), which the authors attributed to site-specific conditions, including much higher air concentrations of oxidized versus reduced nitrogen pollutants.

A corresponding decline in oligotrophic/acidophyte lichens with increasing NH_3 is demonstrated by several metrics including the 'Acidofiele Indicatie Waarde' (AIW, an index of acidophyte lichen abundance)(van Herk, 2001; Pitcairn et al., 2004; Wolseley et al., 2006), LDVoligo (Pinho et al., 2009; Pinho et al., 2011; Pinho et al., 2012), and richness of oligotrophic species (Pinho et al., 2014). The L_{AN} index, which integrates oligotroph and eutroph abundance, decreased with increasing NH_3 indicating a shift in community to dominance by nitrophytes (Wolseley et al., 2010), similarly AIW minus NIW values also indicate this shift (Pitcairn et al., 2004). In some studies, the changes in functional group diversity results in an overall decrease in diversity of total lichens as measured by LDV (Pinho et al., 2011) and species richness (Watmough et al., 2014). However, in other sites the increase in eutrophs offsets the decrease in oligotrophs resulting in no net change of total lichen species diversity, as measured by LDV (Pitcairn et al., 2004; Pinho et al., 2014; Aguillaume et al., 2017) and species richness (Aguillaume et al., 2017).

Collectively, this body of evidence supports that increasing NH_3 significantly alters biodiversity and lichen community composition. When the diversity metrics we reviewed are grouped by outcome categories (i.e., changes to the oligotrophs, eutrophs, the relationship between them, or total biodiversity; Supplemental Fig. 2), we see the NH_3 concentrations for NOEC, LOEC and other thresholds were similar among groups. This coherency indicates the ranges are broadly applicable. As discussed previously for NO_2, however, we'd need better standardization of methods across studies in order to compare outcomes and thresholds more directly. Finally, more quantitative data on the relationship between NH_3 exposure and lichen diversity responses, most especially from unrepresented climates the U.S. (e.g., Continental hot summer) and globally (e.g., tropics), would help to strengthen confidence that the NH_3 levels that alter biodiversity documented in this paper are broadly applicable.

11. Comparing studies on NO_2 and NH_3 lichen diversity

In general, changes in lichen community composition appear to be similar for NO_2 and NH_3 in the studies we identified. Making further comparisons, however, is fraught with several major challenges. For instance, the exposure concentrations of pollutants reported in the studies are measured for different periods of time, which varies from a few days to a year, and introduces uncertainty into how well the studies characterize the exposure. Besides methodological inconsistencies between studies, one especially critical question is whether co-occurring pollutants may have affected the observed outcomes. Co-occurring pollutant exposures are rarely reported in studies, and current and past co-occurring pollutant exposure (e.g. nitric acid and SO_2) can affect lichen biodiversity in similar ways (Nash, 1973; Riddell et al., 2008)

There is a lack of controlled experimental studies for both NO_2 and NH_3 exposure effects on lichen diversity, with only one study reporting findings from a field addition of NH_3 (Sheppard et al., 2009), making it difficult to isolate relationships between lichen diversity metrics and specific pollutants. On the other hand, executing controlled experiments at scale to observe shifts in biodiversity metrics is itself a difficult undertaking. While not controlled release, conducting more studies near agricultural point sources that create a gradient of NH_3 exposure could help better define NH_3 specific lichen responses (Pitcairn et al., 2004; Leith et al., 2005; Wolseley et al., 2006; Frati et al., 2007; Pinho et al., 2009; Pinho et al., 2011; Aguillaume et al., 2017) assuming other pollutants stay constant across the gradient. Perhaps studies from roadsides (Watmough et al., 2017; Perlmutter et al., 2018) or correlations with road density (Watmough et al., 2014) could inform on NO_2 effects although many other pollutants likely co-occur along a gradient from roadsides.

If we consider our earlier synthesis of what's currently known about the physiological impacts of NO_2 and NH_3, there are several compelling reasons to suspect that they or their transformation products could ultimately lead to different outcomes in survivorship, and by extension, community composition. If we take our review of biodiversity indices at face value and consider only indices that don't distinguish between functional groups, there did seem to be a more consistent overall lichen diversity in response to NO_2 (Davies et al., 2007; Watmough et al., 2014; Perlmutter et al., 2018) while for NH_3, studies indicate mixed results, where two studies found evidence for declines as measured by LDV (Pinho et al., 2011) and species richness (Watmough et al., 2014), while

Table 3
Ammonia (NH_3) Effects on Lichen Biodiversity from studies published after (or not included) in Cape et al. (2009). Abbreviations are: Acidofiele Indicatie Waarde (AIW), Nitrofiele Indicatie Waarde'(NIW), index of nitrophyte lichen abundance, Lichen Diversity Value (LDV), Lichen Diversity Value of nitrophytic lichens (LDVnitro), Lichen Diversity Value of oligotrophic lichens (LDVoligo), L_{AN} value (N-sensitive species scores minus N-tolerant species scores), Critical level (CLE), Lowest Observed Effect Concentration (LOEC).

Reference	Climate	Location	Ecosystem	Observed effect	LOEC (μg $NH_3 \cdot m^{-3}$)	Threshold or CLE (μg $NH_3 \cdot m^{-3}$)
(Pinho et al., 2012)	Temperate: Hot summer Mediterranean (Csa)	Lisbon, Portugal	Semi-natural cork-oak woodland	LDVnitro increased with increasing NH_3 ($R^2 = 0.89$ $p < 0.0001$) Linear regression	n/a	CLE = 2.3
(Pinho et al., 2012)	Temperate: Hot summer Mediterranean (Csa)	outside of Lisbon, Portugal	Semi-natural cork-oak woodland	LDVoligo decreased with increasing NH_3 ($R^2 = 0.89$, $P < 0.0001$) Linear regression	n/a	CLE <1.9
(Aguillaume et al., 2017)	Temperate: Warm-Summer Mediterranean (Csb)	NE Spain	holm-oak (Quercus ilex) forest, transect from an agricultural point source	n.s. relationship between LDV and species richness with NH_3	n.s	n/a
(Aguillaume et al., 2017)	Temperate: Warm-Summer Mediterranean (Csb)	NE Spain	holm-oak (Quercus ilex) forest, transect from an agricultural point source	LDVoligo decreased with increasing NH_3 ($R^2 = 0.76$ and $p < 0.0001$), Linear regression	n/a	CLE <3.1
(Aguillaume et al., 2017)	Temperate: Warm-Summer Mediterranean (Csb)	NE Spain	holm-oak (Quercus ilex) forest, transect from an agricultural point source	LDVnitro increased with increasing NH_3 ($R^2 = 0.87$, $p < 0.0001$), Linear regression	n/a	CLE <2.6
(Watmough et al., 2014)	Continental: warm summer and sub-artic (Dfb and Dfc)	Ontario, Canada	sites with different road densities, mostly dominated by *Acer saccharum*	lichen richness negatively correlated to NH_3 ($r^2 = -0.37$, $p < 0.001$) correlation matrix value	0.2	1.5 = only one species found
(Pinho et al., 2014)	Temperate: Hot summer Mediterranean (Csa)	Alentejo Litoral region, Portugal	Mediterranean evergreen woodlands *low pollution area	Total species richness and LDV n.s. with NH_3	n.s	n/a
(Pinho et al., 2014)	Temperate: Hot summer Mediterranean (Csa)	Alentejo Litoral region, Portugal	Mediterranean evergreen woodlands *low pollution area	increasing richness of nitrophyte species with increasing NH_3 ($R = +0.65$ and $p = 0.01$)	n/a	CLE = 0.69
(Pinho et al., 2014)	Temperate: Hot summer Mediterranean (Csa)	Alentejo Litoral region, Portugal	Mediterranean evergreen woodlands	decreasing richness of oligotrophic species with increasing NH_3 ($R = -0.63$ and $p = 0.01$)	n/a	CLE = 0.77
(Wolseley et al., 2010)	Temperate: Oceanic (Cfb)	U.K.	Samples taken from 9 tree species	L_{AN} value was negatively related to NH_3 concentrations on trunks ($R^2 = 0.51$) and twigs ($R^2 = 0.36$), no p-value reported	n/a	<1.0
(Gadsdon et al., 2010)	Temperate: Oceanic (Cfb)	NE of London, UK	Epping Forest	Proportion nitrophytes ($r^2 = 0.19$), lichen cover ($r^2 = 0.18$) an NIW score ($r^2 = 0.14$), p-value not reported	n/a	1.1 nitrophytes >50% lichen cover
(Pinho et al., 2011)	Temperate: Hot summer Mediterranean (Csa)	Lisbon, Portugal	Cork-oak (*Quercus suber*) woodland, proximal to agricultural source	decreasing LDV with increasing NH_3 concentrations ($R^2 = 0.33$, $p = 0.011$), logarithmic relationship	1.5	not reported
(Pinho et al., 2011)	Temperate: Hot summer Mediterranean (Csa)	Lisbon, Portugal	Cork-oak (*Quercus suber*) woodland, proximal to agricultural source	decreasing LDVoligo with increasing NH_3 (R^2 0.89, $p < 0.0001$)	1.5	not reported
(Pinho et al., 2011)	Temperate: Hot summer Mediterranean (Csa)	Lisbon, Portugal	Cork-oak (*Quercus suber*) woodland, proximal to agricultural source	decreasing LDVmeso with increasing NH_3 ($R^2 = 0.77$, $p < 0.0001$)	1.5	not reported
(Pinho et al., 2011)	Temperate: Hot summer Mediterranean (Csa)	Lisbon, Portugal	Cork-oak (*Quercus suber*) woodland, proximal to agricultural source	increasing LDVnitro with increasing NH_3 ($R^2 = 0.90$, $p < 0.0001$)	1.5	not reported
(Jovan et al., 2012)	Temperate: Hot and warm summer Mediterranean (Csa and Csb)	Southern California	mixed conifer–black oak forest,	n.s. relationship between eutrophic index and NH_3 ($r^2 = 0.27$, $P = 0.099$)	n.s	n/a
(Jovan et al., 2012)	Temperate: Hot and warm summer Mediterranean (Csa and Csb)	Southern California	mixed conifer–black oak forest (26 species of lichens)	Community air score increased with increasing NH_3 ($r^2 = 0.48$, $p < 0.02$)	3	not reported
(van Herk, 2001)	Temperate: Oceanic (Cfb)	The Netherlands	*Quercus robur* trees that occurred in mixed managed, non-managed and urban areas	decreasing abundance of AIW with increasing NH_3 concentrations, curve ($r^2 = 0.58$, $n = 104$) data fit to a 3rd order polynomial regression	3	35 μg NH_3 m^{-3} all acidophytic species disappeared
(van Herk, 2001)	Temperate: Oceanic (Cfb) and Continental: warm summer (Dfb)	The Netherlands	*Quercus robur* trees that occurred in mixed managed, non-managed and urban areas	Increasing NIW with increasing NH_3 concentration,all sites together ($r^2 = 0.59$, $n = 104$),NIW values were aggregated to an average per square of 5 × 5 km ($r^2 = 0.90$, $n = 21$), Linear regression	3	not reported
(Sparrius, 2007)	Temperate: Oceanic (Cfb)	Friesland, northern Netherlands	*Quercus robur* trees	NIW increases with increasing NH_3, the correlation was stronger in 1996 ($R^2 = 0.90$, $p = 0.004$) than in 2003 ($R^2 = 0.67$ $p = 0.046$), after NH_3 concentrations in the study sites declined	5	not reported

several studies found no effect on the LDV (Pitcairn et al., 2004; Pinho et al., 2014; Aguillaume et al., 2017) and species richness (Aguillaume et al., 2017). Why would NO_2 more consistently cause declines in total diversity than NH_3 when NH_3 is thought to be more toxic than NO_2? If the finding is real, it could be because exposure concentrations of NO_2 were higher than NH_3; for instance, the median max exposure included in our syntheses is 11.6 μg NH_3 m^{-3} and 29 μg NO_2 m^{-3} (~16.6 NH_3 ppb and 15.4 NO_2 ppb). But, again, we run into the problem of there being uncontrolled factors we aren't aware of, like the issue of co-occurring pollutants. For example industrial combustion emits oxidized N and S gases (EPA, 2021) leading to co-linear atmospheric concentration of NO_2 and SO_2 (Attanayaka and Wijeyaratne, 2013), as well as N and sulfur deposition (Horn et al., 2018) in many sites.

12. U.S. National Ambient Air Quality Standards

The concentrations levels of NO_2 that indicate reduced lichen biodiversity occur well below the current NO_2 NAAQS standard (Table 4, 100 μg NO_2 m^{-3}–53 ppb). The NO_2 standard was set to protect against injury to vegetation (Table 4) and has been not revised since it was initially set in 1971. Additionally, the science assessment for the ongoing secondary NO_2 NAAQS review (EPA, 2020) does not include information on effects of NO_2 on lichens, although these effects are within the scope of the science assessment and should be included in future reviews. It is important to note the U.S. Environmental Protection Agency (EPA) reviews the secondary NAAQS for ecological effects which are considered in the category of "public welfare" (primary NAAQS are for human health), defined in section 302(h)of the Clean Air Act (CAA). The CAA states the NAAQS should be reviewed every 5 years, and each review includes a comprehensive scientific assessment that accurately reflects the latest scientific knowledge of air pollutant effects. The NAAQS are based on "judgement of the [EPA] administrator" to "protect public welfare from any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air." The term "adverse" is subject to interpretation as administrative law and is not necessarily the no effects concentration (NOEC).

In comparison to the U.S. secondary NAAQS, CLEs are also developed to determine ambient air concentrations limits and associated ecological effects. CLEs are developed by the United Nations Economic Commission for Europe (UN/ECE) and are currently set with annual average of 30 μg NO_2 m^{-3} (~15.9 ppb), which is also well above exposure levels associated with NO_2 effects on lichen biodiversity in this synthesis. CLEs are defined differently than NAAQS, which explains, in part, why the values for CLEs and NAAQS differ. CLEs are 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). The CLE values are based on a no observable effects concentration (NOEC) and represent a recommended level that countries may then choose to interpret into policy that regulates the pollutants. It has been over a decade since the CLEs for NO_2 were reviewed, therefore the information synthesized in this paper indicate a lower NOEC of NO_2 than currently represented by the NO_2 CLE.

Table 4
NAAQS standards in the US and CLEs in Europe for nitrogen dioxide and ammonia.

Biological Effects	Group of pollutants	Chemical indicator	Averaging Time	UNECE (CLE)	USEPA (NAAQS)
Foliar injury	NOx	NO_2	24-h	75 μg m^{-3}[a]	n/a[b]
		NO_2	Annual mean	30 μg m^{-3}[a]	53 ppb (~100 μg m^{-3})[c]
Lichen diversity	NHx	NH_3	Annual mean	1 μg m^{-3}[d]	n/a
Higher plants	NHx	NH_3	Annual mean	3 μg m^{-3}[d]	n/a

[a] Proposed in 1987, revised in 1988 and 1992; retained in WHO 2000
[b] While there are no standards for non-human biota, in 2010 a primary NAAQS (human health effects) was set at 100 ppb (~188 μg m^{-3}[b]) 24-hr average.
[c] Set in 1971.
[d] Proposed in 1988, revised in 2007.

The effects on biodiversity associated with NH_3 concentrations from studies identified in this synthesis occur at NH_3 concentrations below the current 3-yr annual average concentrations of NH_3 for some sites in the U.S. measured at routine monitoring network sites (Fig. 2) and well below the spikes of NH_3 recorded proximal to CAFOs in the U.S. In the U.S., NH_3 is not directly regulated as a NAAQS pollutant. In Europe, CLEs of NH_3 differ among taxonomic groups and the CLE with an annual averaging time was most recently revised in 2007 (Cape et al., 2009; Sutton et al., 2009b) to 1 μg NH_3 m^{-3} for ecosystems where sensitive lichens and bryophytes are an important part of ecosystem integrity. Studies used to determine the 2007 CLE (Supplemental Table S1) and those studies published since the most recent CLE review (Table 3) are in Fig 4. There are two new studies in the peer-reviewed literature below estimated NOEC of 1 μg NH_3 m^{-3} that may be considered in the next review of the NH_3 CLE.

13. Conclusion

Understanding lichen vulnerability to NO_2 and NH_3 exposure requires quantification of the ambient exposures experienced in the environment and the pollution concentrations that cause adverse effects on physiology and diversity. Our knowledge of ambient exposures in the U.S. is limited by the spatial coverage of current monitoring of NH_3 and NO_2 ambient air concentrations, which likely does not accurately represent exposures of NO_2 to ecosystems in rural areas and likely does not capture spikes of NH_3 concentrations proximal to intensive agriculture. In addition, there are several research gaps and uncertainties that cloud the relationship between NH_3 emission and atmospheric concentration. Improvement of these measurements will improve understanding of NO_2 and NH_3 exposures experienced by lichens.

While the physiological effects on lichens that result from NH_3 exposures are generally well characterized, there is relatively little information from controlled experiments. It is unclear if lichen uptake is more sensitive to NO_2 or NO_3^-, a transformation product of NO_2, than NO_2 itself. There is currently not enough information on either NO_2 or NH_3 at concentrations relevant to current ambient concentrations to characterize exposure response relationships or to set meaningful thresholds of exposure based on lichen physiology. Despite this research gap, know physiological effects provide the mechanisms that lead to changes in lichen community composition and diversity. There are observational studies that link NO_2 and NH_3 to lichen diversity and characterize thresholds, such as estimated NOECs, LOECs and CLEs, although some ecosystems (based on climate classification) are currently not represented in the evidence base. For both NO_2 and NH_3, when the lichen community is grouped into functional groups based on N-sensitivity, there is a shift in species composition of the community from N-sensitive (acidophyte/oligotrophic) to N-tolerant (nitrophyte/eutrophic) species. There is more evidence that NO_2 concentrations, at the levels reported, cause decreases in total lichen diversity, than NH_3 concentrations. To facilitate comparisons of the level of pollution exposures that causes effects on lichens among studies, inconsistency among studies in the time periods measured to reflect pollutant exposures need to be more standardized as well as documentation of co-occurring atmospheric pollutants (or other stressors).

Air quality policy in the U.S. and Europe includes information on lichens to different extents. In Europe, NH_3 CLEs include evaluation of effects on lichens from results published through 2007 (Cape et al., 2009; Sutton et al., 2009a). The studies published since 2007 synthesized in our study support a NOEC of 1 μg NH_3m^3 (~1.4 NH_3 ppb) for

lichens, with one paper suggesting a slightly lower value (Pinho et al., 2014). Evidence from the recent peer-reviewed literature supports those effects occur at NH_3 concentrations below the 2017–2019 3- year annual average concentration in the U.S. measured at routine monitoring network sites (generally range up to about 6 μg NH_3 m^3 ~ 9 NH_3 ppb) and well below the two-week max values (40 μg NH_3 m^3 ~ 9 NH_3 ppb) and shorter-term spikes of NH_3 recorded proximal to CAFOs 700 μg NH_3 m^{-3} (~1000 ppb). Our study identifies that the NO_2 NAAQS (EPA, 2020) in the U.S. and the CLEs for Europe have not yet included the recent evidence that NO_2 decreases lichen biodiversity. Inclusion of these effects in a scientific assessment that supports air pollution policy is necessary to more fully describe the effects experienced in the ecosystems for which lichens play an important role.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

This paper is a synthesis of primary data collected in other peer-reviewed publications

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Disclaimer: The views expressed in this article are those of the author [s] and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

Appendix A. Supplementary data

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References

Aguillaume, L., Avila, A., Pinho, P., Matos, P., Llop, E., Branquinho, C., 2017. The critical levels of atmospheric ammonia in a mediterranean holm-oak forest in north-eastern Spain. Water, Air, Soil Pollut. 228, 93.

Asta, J., Erhardt, W., Ferretti, M., 2002. Mapping lichen diversity as an indicator of environmental quality. In: Nimis, P.L., Scheidegger, C., Wolseley, P.A. (Eds.), Monitoring with Lichens—Monitoring Lichens. Kluwer Academic Publisher The Netherlands., pp. 273–279

Attanayaka, A., Wijeyaratne, S.C., 2013. Corticolous lichen diversity, a potential indicator for monitoring air pollution in tropics. J. Natl. Sci. Found. Sri Lanka 41, 131–140.

Behera, S., Sharma, M., Aneja, V., Balasubramanian, R., 2013. Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environ. Sci. Pollut. Control Ser. 20, 8092–8131.

Cape, J.N., van der Eerden, L.J., Sheppard, L.J., Leith, I.D., Sutton, M.A., 2009. Evidence for changing the critical level for ammonia. Environ. Pollut. 157, 1033–1037.

Carter, T.S., Clark, C.M., Fenn, M.E., Jovan, S., Perakis, S.S., Riddell, J., et al., 2017. Mechanisms of nitrogen deposition effects on temperate forest lichens and trees. Ecosphere 8.

Cepeda Fuentes, J.M., Barcia Rowe, J., 1998. The effect of air pollution from nitrogen dioxide (N02) on epiphytic lichens in Seville, Spain. Aerobiologia 14, 241–247.

Dahlman, L., Persson, J., Palmqvist, K., Nasholm, T., 2004. Organic and inorganic nitrogen uptake in lichens. Planta 219, 459–467.

Davies, L., Bates, J.W., Bell, J.N.B., James, P.W., Purvis, O.W., 2007. Diversity and sensitivity of epiphytes to oxides of nitrogen in London. Environ. Pollut. 146, 299–310.

EPA, U.S., 2020. Integrated Science Assessment for Oxides of Nitrogen, Oxides of Sulfur, and Particulate Matter-Ecological Criteria. US Environmental Protection Agency, Washington, D.C.

Fangmeier, A., Hadwigerfangmeier, A., Vandereerden, L., Jager, H.J., 1994. Effects of atmospheric ammonia on vegetation - a review. Environ. Pollut. 86, 43–82.

Frati, L., Caprasecca, E., Santoni, S., Gaggi, C., Guttova, A., Gaudino, S., et al., 2006. Effects of NO2 and NH3 from road traffic on epiphytic lichens. Environ. Pollut. 142, 58–64.

Frati, L., Santoni, S., Nicolardi, V., Gaggi, C., Brunialti, G., Guttova, A., et al., 2007. Lichen biomonitoring of ammonia emission and nitrogen deposition around a pig stockfarm. Environ. Pollut. 146, 311–316.

Gadsdon, S.R., Dagley, J.R., Wolseley, P.A., Power, S.A., 2010. Relationships between lichen community composition and concentrations of NO2 and NH3. Environ. Pollut. 158, 2553–2560.

Gaio-Oliveira, G., Branquinho, C., Maguas, C., Martins-Loucao, M.A., 2001. The concentration of nitrogen in nitrophilous and non-nitrophilous lichen species. Symbiosis 31, 187–199.

Geiser, L.H., Root, H., Smith, R.J., Jovan, S.E., St Clair, L., Dillman, K.L., 2021. Lichen-based critical loads for deposition of nitrogen and sulfur in US forests. Environ. Pollut. 291.

Gibson, M.D., Heal, M.R., Li, Z., Kuchta, J., King, G.H., Hayes, A., et al., 2013. The spatial and seasonal variation of nitrogen dioxide and sulfur dioxide in Cape Breton Highlands National Park, Canada, and the association with lichen abundance. Atmos. Environ. 64, 303–311.

Golston, L.M., Pan, D., Sun, K., Tao, L., Zondlo, M.A., Eilerman, S.J., et al., 2020. Variability of ammonia and methane emissions from animal feeding operations in northeastern Colorado. Environ. Sci. Technol. 54, 11015–11024.

Guo, X.H., Wang, R., Pan, D., Zondlo, M.A., Clarisse, L., Van Damme, M., et al., 2021. Validation of IASI satellite ammonia observations at the pixel scale using in situ vertical profiles. J. Geophys. Res. Atmos. 126.

Hauck, M., Wirth, V., 2010. Preference of lichens for shady habitats is correlated with intolerance to high nitrogen levels. Lichenol. 42, 475–484.

Herzig, R., Schindler, C., Urech, M., Rihm, B., Lotscher, H., Thomann, G., 2020. Recalibration and validation of the Swiss lichen bioindication methods for air quality assessment. Environ. Sci. Pollut. Control Ser. 27, 28795–28810.

Hiranuma, N., Brooks, S., Thornton, D., Auvermann, B., 2012. Atmospheric ammonia mixing rations at an open-air cattle feeding facility. J. Air Waste Manag. Assoc. 60, 210–218.

Hoesly, R., Smith, S., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., et al., 2018. Historical (1750-2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS). Geosci. Model Dev. (GMD) 11, 369–408.

Horn, K.J., Thomas, R.Q., Clark, C.M., Pardo, L.H., Fenn, M.E., Lawrence, G.B., et al., 2018. Growth and survival relationships of 71 tree species with nitrogen and sulfur deposition across the conterminous U.S. PLoS One 13.

Howitt, S.M., Udvardi, M.K., 2000. Structure, function and regulation of ammonium transporters in plants. Biochim. Biophys. Acta 1465, 152–170.

Johansson, O., Nordin, A., Olofsson, J., Palmqvist, K., 2010. Responses of epiphytic lichens to an experimental whole-tree nitrogen-deposition gradient. New Phytol. 188, 1075–1084.

Jovan, S., 2008. Lichen Bioindication of Biodiversity, Air Quality, and Climate: Baseline Results from Monitoring in Washington, Oregon, and California. U.S. Department of Agriculture, Forest Service, Pacific Northwest Research Station Portland, OR, p. 115.

Jovan, S., Riddell, J., Padgett, P.E., Nash, T.H., 2012. Eutrophic lichens respond to multiple forms of N: implications for critical levels and critical loads research. Ecol. Appl. 22, 1910–1922.

Kricke, R. & Loppi, S. Bioindication: the IAP approach. In: Monitoring with Lichens – Monitoring Lichens (eds. Nimis, PL, Scheidegger, C & Wolseley, P). Kluwer Netherlands, pp. 21-37.

Leblanc, F., Desloover, J., 1970. Relation between industrilization and distribution and growth of epiphytic lichens and mosses in montreal. Can. J. Bot. 48, 1485 (+).

Leith, I.D., van Dijk, N., Pitcairn, C.E.R., Wolseley, P.A., Whitfield, C.P., Sutton, M.A., 2005. Biomonitoring Methods for Assessing the Impacts of Nitrogen Pollution: Refinement and Testing. JNCC Peterborough.

Ludewig, U., Neuhauser, B., Dynaowski, M., 2007. Molecular mechanisms of ammonium transport and accumulation in plants. FEBS (Fed. Eur. Biochem. Soc.) Lett. 581, 2301–2308.

Manninen, S., 2018. Deriving nitrogen critical levels and loads based on the responses of acidophytic lichen communities on boreal urban Pinus sylvestris trunks. Sci. Total Environ. 613–614, 751–762.

Munzi, S., Branquinho, C., Cruz, C., Maguas, C., Leith, I.D., Sheppard, L.J., et al., 2019. Delta N-15 of lichens reflects the isotopic signature of ammonia source. Sci. Total Environ. 653, 698–704.

Munzi, S., Cruz, C., Branquinho, C., Pinho, P., Leith, I.D., Sheppard, L.J., 2014. Can ammonia tolerance amongst lichen functional groups be explained by physiological responses? Environ. Pollut. 187, 206–209.

Munzi, S., Paoli, L., Fiorini, E., Loppi, S., 2012. Physiological response of the epiphytic lichen Evernia prunastri (L.) Ach. to ecologically relevant nitrogen concentrations. Environ. Pollut. 171, 25–29.

Munzi, S., Pisani, T., Loppi, S., 2009. The integrity of lichen cell membrane as a suitable parameter for monitoring biological effects of acute nitrogen pollution. Ecotoxicol. Environ. Saf. 72, 2009–2012.

Munzi, S., Sheppard, L.J., Leith, I.D., Cruz, C., Branquinho, C., Bini, L., et al., 2017. The cost of surviving nitrogen excess: energy and protein demand in the lichen Cladonia portentosa as revealed by proteomic analysis. Planta 245, 819–833.

Nash, T.H., 1973. Sensitivity of lichens to sulfur dioxide. Bryol. 76, 333–339.

Nash, T.H., 1976. Sensitivity of lichens to nitrogen dioxide fumigations. Bryologist 79, 103–106.

Nash, T.H., 2008. Lichen sensitivity to air pollution. In: Nash, T.H.) (Ed.), Lichen Biology. Cambridge University Press, Cambridge, pp. 301–316.

Paoli, L., Maslanakova, I., Grassi, A., Backor, M., Loppi, S., 2015. Effects of acute NH3 air pollution on N-sensitive and N-tolerant lichen species. Ecotoxicol. Environ. Saf. 122, 377–383.
Pardo, L.H., Fenn, M.E., Goodale, C.L., Geiser, L.H., Driscoll, C.T., Allen, E.B., et al., 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. Ecol. Appl. 21, 3049–3082.
Pearson, J., Stewart, R.G., 1993. Atmospheric ammonia deposition and its effects on plants. Tansley Review No. 56. New Phytol. 125, 283–305.
Perlmutter, G.B., Blank, G.B., Wentworth, T.R., Lowman, M.D., Neufeld, H.S., Plata, E.R., 2018. Highway pollution effects on microhabitat community structure of corticolous lichens. Bryol. 121, 1–13, 13.
Pinho, P., Augusto, S., Martins-Loução, M.A., Pereira, M.J., Soares, A., Máguas, C., et al., 2008. Causes of change in nitrophytic and oligotrophic lichen species in a Mediterranean climate: impact of land cover and atmospheric pollutants. Environ. Pollut. 154, 380–389.
Pinho, P., Branquinho, C., Cruz, C., Tang, Y.S., Dias, T., Rosa, A.P., et al., 2009. Assessment of critical levels of atmospheric ammonia for lichen diversity in cork-oak woodland, Portugal. In: Sutton, M.A., Reis, S., Baker, S.M.H. (Eds.), Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts. Springer Netherlands, Dordrecht, pp. 109–119.
Pinho, P., Dias, T., Cruz, C., Sim Tang, Y., Sutton, M.A., Martins-Loução, M.-A., et al., 2011. Using lichen functional diversity to assess the effects of atmospheric ammonia in Mediterranean woodlands. J. Appl. Ecol. 48, 1107–1116.
Pinho, P., Llop, E., Ribeiro, M.C., Cruz, C., Soares, A., Pereira, M.J., et al., 2014. Tools for determining critical levels of atmospheric ammonia under the influence of multiple disturbances. Environ. Pollut. 188, 88–93.
Pinho, P., Theobald, M.R., Dias, T., Tang, Y.S., Cruz, C., Martins-Loução, M.A., et al., 2012. Critical loads of nitrogen deposition and critical levels of atmospheric ammonia for semi-natural Mediterranean evergreen woodlands. Biogeosciences 9, 1205–1215.
Pitcairn, C.E.R., Leith, I.D., Sheppard, L.J., van Dijk, N., Tang, Y.S., Wolseley, P.A., et al., 2004. Field intercomparison of different bio-indicator methods to assess the effects of atmospheric nitrogen deposition. In: Sutton, M.A., Pitcairn, C.E.R., Whitfield, C.P. (Eds.), Bioindicator and Biomonitoring Methods for Assessing the Effects of Atmospheric Nitrogen on Statutory Nature Conservation Sites. JNCC, pp. 168–177.
Posthumus, A.C., 1988. Critical levels for effects of ammonia and ammonium. In: Proceedings of the Bad Harzburg Workshop. UBA Berlin, pp. 117–127, 1988.
Riddell, J., Nash, T.H., Padgett, P., 2008. The effect of HNO3 gas on the lichen Ramalina menziesii. Flora 203, 47–54.
Rihm, B., Urech, M., Peter, K., 2009. Mapping ammonia emissions and concentrations for Switzerland — effects on lichen vegetation. In: Sutton, M.A., Reis, S., Baker, S.M.H. (Eds.), Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts. Springer Netherlands, Dordrecht, pp. 87–92.
Ritchie, R.J., 2013. The ammonia transport, retention and futile cycling problem in cyanobacteria. Microb. Ecol. 65, 180–196.
Schwede, D.B., Lear, G.G., 2014. A novel hybrid approach for estimating total deposition in the United States. Atmos. Environ. 92, 207–220.
Sheppard, L.J., Leith, I.D., Crossley, A., van Dijk, N., Cape, J.N., Fowler, D., et al., 2009. Long-term cumulative exposure exacerbates the effects of atmospheric ammonia on an ombrotrophic bog: implications for critical levels. In: Sutton, M.A., Reis, S., Baker, S.M.H. (Eds.), Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts. Springer Netherlands, Dordrecht, pp. 49–58.
Signorelli, S., Moller, M.N., Coitino, E.L., Denicola, A., 2011. Nitrogen dioxide solubility and permeation in lipid membranes. Arch. Biochem. Biophys. 512, 190–196.
Sparrius, L.B., 2007. Response of epiphytic lichen communities to decreasing ammonia air concentrations in a moderately polluted area of The Netherlands. Environ. Pollut. 146, 375–379.
Sutton, M.A., Reis, S., Baker, S.M., 2009a. Atmospheric Ammonia-Detecting Emission Changes and Environmental Impacts. Springer, Berlin.
Sutton, M.A., Wolseley, P.A., Leith, I.D., van Dijk, N., Tang, Y.S., James, P.W., et al., 2009b. Estimation of the ammonia critical level for epiphytic lichens based on observations at farm, landscape and national scales. In: Sutton, M.A., Reis, S., Baker, S.M.H. (Eds.), Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts. Springer Netherlands, Dordrecht, pp. 71–86.
Van Dobben, H.F., Ter Braak, C.J.F., 1998. Effects of atmospheric NH3 on epiphytic lichens in The Netherlands: the pitfalls of biological monitoring. Atmos. Environ. 32, 551–557.
van Herk, C.M., 1999. Mapping of ammonia pollution with epiphytic lichens in The Netherlands. Lichenol. 31, 9–20.
van Herk, C.M., 2001. Bark pH and susceptibility to toxic air pollutants as independent causes of changes in epiphytic lichen composition in space and time. Lichenol. 33, 419–441.
von Arb, C., Mueller, C., Ammann, K., Brunold, C., 1990. Lichen physiology and air-pollution .2. Statistical-analysis of the correlation between So2, No2, No and O-3, and chlorophyll content, net photosynthesis, sulfate uptake and protein-synthesis of parmelia-sulcata taylor. New Phytol. 115, 431–437.
Walker, J., Robarge, W., Wu, Y., Meyers, T., 2006. Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio techniques. Agric. For. Meteorol. 138, 54–68.
Wang, C.H., Wang, M., Jia, R.Z., Guo, H., 2018. Thalli growth, propagule survival, and integrated physiological response to nitrogen stress of ramalina calicaris var. japonica in shennongjia mountain (China). Front. Plant Sci. 9.
Warner, J., Dickerson, R., Wei, Z., Strow, L., Y, W., Liang, Q., 2017. Increased atmospheric ammonia over the world's major agricultural areas detected from space. Geophys. Res. Lett. 44, 2875–2884.
Watmough, S.A., McDonough, A.M., Raney, S.M., 2014. Characterizing the influence of highways on springtime NO2 and NH3 concentrations in regional forest monitoring plots. Environ. Pollut. 190, 150–158.
Watmough, S.A., Rabinowitz, T., Baker, S., 2017. The impact of pollutants from a major northern highway on an adjacent hardwood forest. Sci. Total Environ. 579, 409–419.
Wilson, S., Serre, M., 2007. Examination of atmopsheric ammonia levels near hog CAFOs, homes, and schools in Eastern North Carolina. Atmos. Environ. 41, 4977–4987.
Wolseley, P., Sutton, M., Leith, I., van Dijk, N., 2010. Epiphytic lichens as indicators of ammonia concentrations across the UK. Bibl. Lichenol. 105, 75–85.
Wolseley, P.A., James, P.W., Theobald, M.R., Sutton, M.A., 2006. Detecting changes in epiphytic lichen communities at sites affected by atmospheric ammonia from agricultural sources. Lichenol. 38, 161–176.
Yatawara, M., Dayananda, N., 2019. Use of corticolous lichens for the assessment of ambient air quality along rural–urban ecosystems of tropics: a study in Sri Lanka. Environ. Monit. Assess. 191, 179.
EPA, U.S. (2021), 2017 National Emissions Inventory Data, https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data , (last accessed Oct. 4, 2022).