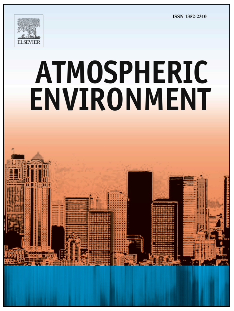

Nitric oxide (NO) and nitrogen dioxide (NO_2): A state-of-knowledge review of their roles in, and consequences for, vegetation and ecosystems

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TITLE:

Nitric oxide (NO) and nitrogen dioxide (NO_2): A state-of-knowledge review of their roles in, and consequences for, vegetation and ecosystems

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ABSTRACT

The atmospheric pollutants nitric oxide (NO) and nitrogen dioxide (NO_2) (collectively referred to as NO_x) remain persistent constituents in the lower atmosphere. Here, we provide a state-of-knowledge overview of their sources, their biochemical and physiological roles in plants, and their consequences for ecosystems, exploring duality in their impacts. Ecosystem exposure to these pollutants is increasing in areas of the globe. Vegetative harm arises from oxidising and acidifying influences on biochemical and metabolic properties following stomatal uptake of NO_x with conflicting information on whether NO and NO_2 act differentially. Emergent general consequences include altered plant physiology, structure and function, with effects on vegetative growth, flowering and community composition e.g. loss of bryophytes and lichens. There is also evidence of negative effects on insect health and behaviour. Yet, recent evidence points to both NO and NO_2 acting as plant signalling molecules and, in some ecosystems, providing a critical source of nutrients to sustain plant growth. The exogenous supply of NO from donor molecules, as well as endogenous NO, can mediate vegetation response to environmental stressors. Ecological responses are modulated by environmental factors (e.g. available nutrients) and other atmospheric constituents such as ozone, carbon dioxide and ammonia. We urgently need studies in realistic environments, including contemporary/future atmospheric conditions, to understand ecosystem consequences arising from atmospheric NO_x exposure. Research needs to consider interactions among endogenous NO production in plants, stomatal uptake of NO_x, and atmospheric NO to NO_2 ratios to estimate risks to vegetation and ecosystems.

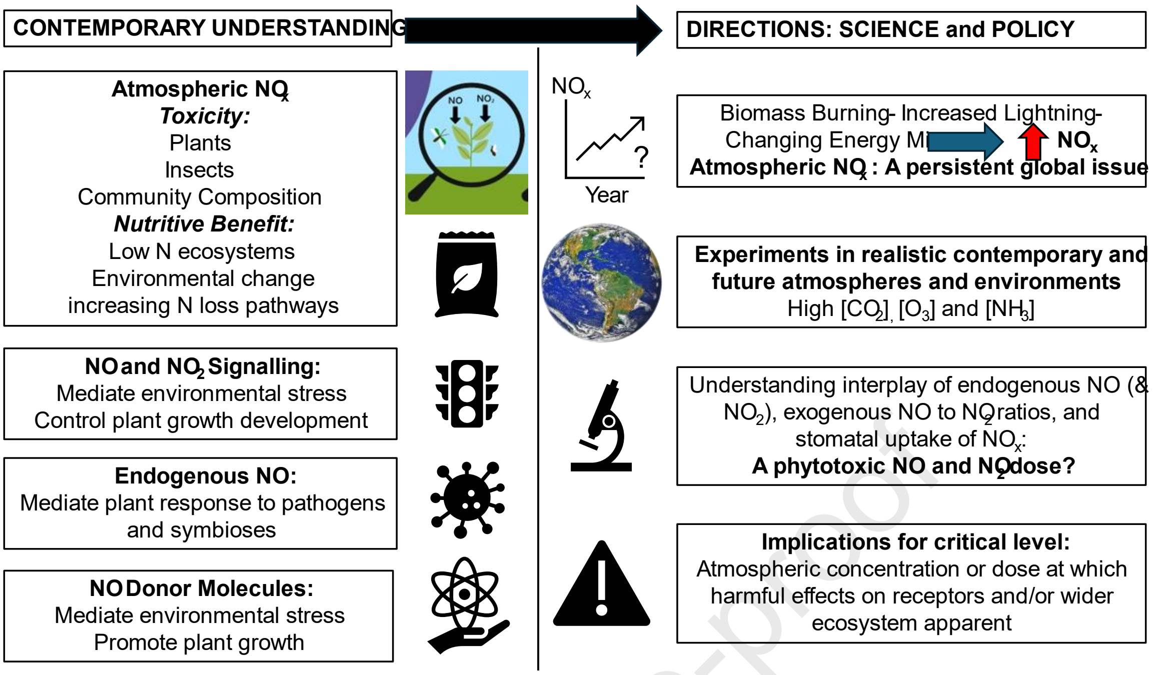
KEYWORDS

air pollution, ammonia, critical level, critical load, NOx, plant, pollination

HIGHLIGHTS

- The pollutants nitric oxide and nitrogen dioxide can play a dual role in plants.
- Negative ecological effects at lower concentrations than existing critical levels.
- Vegetative harm mediated by endogenous and donor molecule nitric oxide production.
- Urgent need for impact studies in contemporary/predicted atmospheric conditions.

GRAPHICAL ABSTRACT



CONTEMPORARY UNDERSTANDING

DIRECTIONS: SCIENCE and POLICY

Atmospheric NO$_x$
Toxicity:
Plants
Insects
Community Composition
Nutritive Benefit:
Low N ecosystems
Environmental change
increasing N loss pathways

NO and NO$_2$ Signalling:
Mediate environmental stress
Control plant growth development

Endogenous NO:
Mediate plant response to pathogens and symbioses

NO Donor Molecules:
Mediate environmental stress
Promote plant growth

Biomass Burning- Increased Lightning-
Changing Energy Mi ↑ **NO$_x$**
Atmospheric NO$_x$: A persistent global issue

Experiments in realistic contemporary and future atmospheres and environments
High [CO$_2$], [O$_3$] and [NH$_3$]

Understanding interplay of endogenous NO (& NO$_2$), exogenous NO to NO$_2$ ratios, and stomatal uptake of NO$_x$:
A phytotoxic NO and NO$_2$ dose?

Implications for critical level:
Atmospheric concentration or dose at which harmful effects on receptors and/or wider ecosystem apparent

1. Introduction

A suite of oxides of nitrogen (NO_y) can be atmospheric pollutants, for instance, nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and peroxyactyl nitrate (PAN; $CH_3C(O)OONO_2$) (Sparks et al., 2001; Sparks et al., 2003; Teklemariam & Sparks, 2004). Of these, two atmospheric oxides of nitrogen (NO and NO_2; often referred to collectively as NO_x but note Wellburn (1990)) have been a particular focus of investigations due to deleterious direct (Anenberg et al., 2022; Faustini et al., 2014) and indirect effects on humans, particularly through harm to vegetation and food supply. Indirect consequences for humanity were traditionally examined through assaying toxic impacts on vegetation when exposed to high concentrations of these pollutants (e.g. Zeevaart, 1976) and led to the setting of critical levels, above which harm was expected to be apparent to vegetation (e.g. ICP Vegetation, 2017).

Since the critical levels for NO_x were initially established, additional information on the effects on vegetation have been published (e.g. Greaver et al., 2023; Lobell et al., 2022). However, the atmospheric conditions have changed considerably over recent decades, including a universal increase in carbon dioxide (CO_2), and, in many areas, declining influence of sulphur dioxide (Aas et al., 2019; Stern, 2005) and increasing ammonia (NH_3) concentrations (e.g. Sutton et al., 2020). These atmospheric changes have subsequent impacts on nitrogen deposition and its influence on ecosystem dynamics through acidification and eutrophication (Bobbink et al., 2022). Plant available nitrogen is a key nutrient that can often be in short supply and can thus limit plant growth (Elser et al., 2007). It may be that certain levels of atmospheric supply of NO_x can help sustain ecosystems and compensate for N loss pathways that may increase with other environmental changes (McCalley & Sparks, 2008). However, direct impacts of elevated NO_x concentrations in the lower atmosphere, which remain high in some areas (Anenberg et al., 2022; Jamali et al., 2020), continue to be of concern in the frame of vegetation and biodiversity of ecosystems. The ecological impact of increased exogenous NO_x supply may depend on levels of other atmospheric pollutants (e.g. Eller et al., 2020) and/or environmental properties (e.g. soil type Caporn, 1992).

Evidence also shows a duality of roles that NO and NO_2 play in plants. As well as vegetative damage, NO and NO_2 affect plant signalling and plant growth dynamics (e.g. Takahashi et al., 2014), with ecosystem level consequences that can extend to plant-herbivore interactions (Campbell & Vallano, 2018) and increased capacity to address stress (e.g. Del Castello et al., 2019). The internal molecular and physiological roles of NO and NO_2 may also be different, potentially causing variation in pathways of impact to be overlooked (Wellburn, 1990). Whether toxicity symptoms are observed will depend upon the magnitude and rate of intake of gaseous compounds into the leaf cells and the capacity to detoxify the gases and associated reaction products. The way the rapidly changing climate and pollutant ‘landscape’ affects vegetation sensitivity to NO_x, potentially different mechanisms of impacts of NO and NO_2, and impacts on ecosystem components other than vegetation, are key knowledge gaps. and may also determine whether the overall role of NO_x is positive or negative.

In synthesizing knowledge on the impacts of NO and NO_2 on vegetation and ecosystems under changing environmental conditions, we aim to address:

- The biochemical, metabolic and physiological processes within plants when exposed to NO and NO_2 and subsequent consequences for growth and other properties e.g. flowering.

- How the effects of NO and NO_2 can extend to other elements of biodiversity, within and across trophic levels. For instance, through increased plant growth from a fertilization effect that leads to loss of other elements of biodiversity, and through direct effects on insect behaviour and signalling.

- How vegetation sensitivity to NO and NO_2 depends on other environmental variables, specifically changed atmospheric conditions (e.g. increased background levels of ozone (O_3)) and climate change, both of which have the potential to alter stomatal regulation of NO and NO_2 uptake.

2. Sources of Atmospheric Nitrogen Oxides: Global Trends in Emissions, Concentrations and Receptor Exposure

Anthropogenic sources account for approximately two-thirds of total NO_y emissions to the lower atmosphere, and this is primarily from NO production during biomass and fossil-fuel combustion linked to transport and industrial processes, including within agricultural landscapes, and energy production (Jamali et al., 2020; Sparks et al., 2001). A mix of anthropogenic and natural biomass burning, which is increasing in frequency and extent with climate- and land use change (Bowman et al., 2009; Bowman et al., 2020) could lead to 'hotspots' of high NO_x pollutant levels with the relative amount of oxidised and reduced forms depending on burn efficiency (Jaffe & Wigder, 2012). The impacts of biomass burning on NO_x may be compounded through wildfires increasing lightning strike frequency (Zhang et al., 2019). This is because lightning already adds up to 9 Tg N per year to the atmosphere through forming NO_x (e.g. Nault et al., 2017; van der A et al., 2008), representing 10 to 20% of global emissions (Miyazaki et al., 2017; Nguyen et al., 2022). The lightning source alone is likely to increase in the future due to more frequent convective storms (IPCC, 2023), and can lead to local abundances of several ppb (parts per billion) by volume, compared to a typical free tropospheric background of (less than) a 100 parts per trillion by volume (pptv) (Solomon et al., 1999; Val Martin et al., 2008). Most biogenic emissions come through microbial production of NO in the soil (Davidson & Kingerlee, 1997; Sparks et al., 2001). At low atmospheric concentrations of NO (and NO_2) vegetation can also emit these gases with variation among species possibly related to leaf N contents (Sparks et al., 2001). In some dryland systems, abiotic loss of NO (and NO_2 as well as NH_3) from the soil is an important process and may contribute to productivity limitations in conjunction with moisture limitations (McCalley & Sparks, 2008, 2009). The relative importance of these different sources depends on location e.g. lightning is the dominant source in some parts of the tropics but in other tropical and subtropical areas it is biomass burning, while anthropogenic sources dominated much of the tropospheric NO_2 column in the United States of America, Europe and eastern Asia and soil emissions dominated much of the remainder of the terrestrial biosphere, especially non-forested areas (van der A et al., 2008).

Overall, relatively constant estimates of global emissions of NO and NO_2 have been reported: 47.9 Tg N yr^{-1} and 47.5 Tg N yr^{-1} between 2005 and 2014 respectively (Miyazaki et al., 2017) with a large decline, but subsequent bounce back, associated with COVID-19 (Leverett et al., 2025). However, over a 10-year period, the apparent constancy in total global emissions obscured increasing trends in some areas (+29% per decade in India, +26% per decade in China, +20% per decade in the Middle East) and decreases in other regions (-38% per decade in the USA, -8.2% per decade in Southern Africa and -8.8% per decade in western Europe) (Miyazaki et al., 2017).

Once in the atmosphere, NO is rapidly oxidized, in combination with ozone and/or peroxy radicals, to NO_2 (Solomon et al., 1999). There can be subsequent photodissociation to NO and ground state atomic oxygen which can then react with O_2 to form more ozone (O_3) (Sparks et al., 2001). Oxidation of NO by O_2 is also possible but this reaction occurs very slowly at low concentrations of NO while wavelengths of light less than 440nm catalyse the reverse reaction (Wellburn, 1990). Subsequent reactions can form PAN and/or nitric acid (HNO_3) from NO_2, but such reactions take days to weeks, so NO and NO_2 can persist for several days (Solomon et al., 1999).

The pace of these atmospheric reactions and the location of ecosystems in relation to NO_x pollutant sources determines vegetation exposure to these different reactive N species (Figure 1). Close to an emission source, NO_x compounds deposit more readily through stomata than to other surfaces in the environment while further from the pollution source, more of the reactive N is oxidized to forms such as PAN. In regions still further from the reactive N sources, the atmosphere is often dominated by nitric acid, which is highly soluble in water and so tends to deposit to many surfaces faster than it can enter plants through the stomata (see Vallano & Sparks, 2008). These reactions mean that NO_x tends to dominate close to anthropogenic pollution sources (Jamali et al., 2020) while plants will be exposed to other N forms, with an increased dominance of other input pathways (i.e. root uptake mediated by soil processes), further from such pollution sources (Vallano & Sparks, 2008).

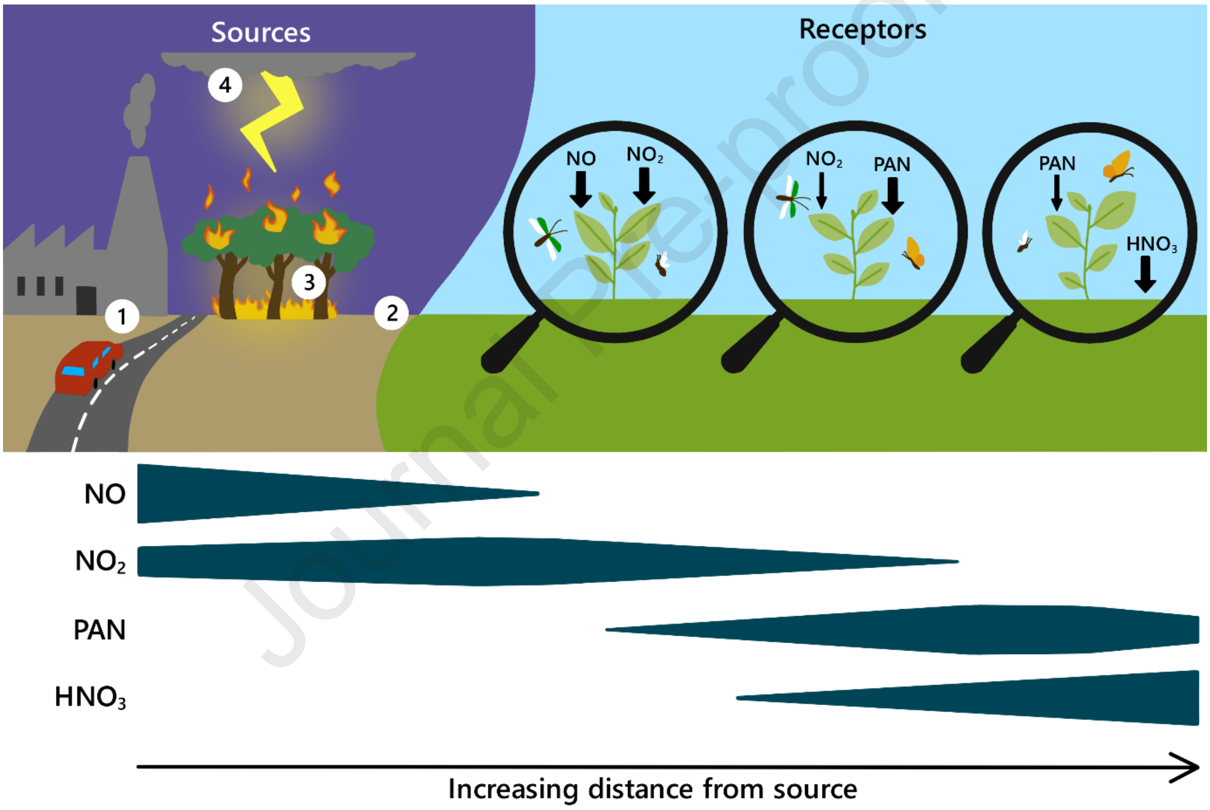


Figure 1: Exposure of plant and insect receptors to different nitrogen oxides changes with distance from source. *Sources of NO include (1) anthropogenic emissions (2) ecosystem emissions, primarily from soil (3) biomass burning and (4) lightning. Relatively rapid reactions with ozone (O_3)/peroxy radicals convert NO to NO_2. Near to sources, stomata dominate deposition pathways of NO_2 and NO. Further from the sources, peroxyactyl nitrate (PAN) dominates deposition to stomata, while at greater distances nitric acid (HNO_3) dominates deposition to surfaces, leading to acidification and eutrophication of ecosystems. As explained in the main text, NO and NO_2 concentrations are neither uniform in space nor time because of variation in location and timing of emissions, atmospheric reactions and chemical transport processes. This also leads to variation in the ratio of NO to NO_2 that plants and other ecosystem components are exposed to. A background level of all these pollutants can be found in the atmosphere and the change in relative amounts is indicative only; reactive forms will likely differ across the landscape depending on air mass movement variability and disassociation of PAN back to NO_2; exposure will also likely differ in urban and rural areas, given the persistence of urban NO. Figure illustration by Els Dhiedt.*

Atmospheric concentrations of NO and NO_2 are neither uniform in time nor space due to variation in the location and timing of NO and NO_2 emissions from various sources, subsequent atmospheric reactions and chemical transport, spatial and temporal dynamics of industrialisation and post-industrialisation, and international policy instruments and the imposition of emissions controls (e.g. Cooper et al., 2022; Nguyen et al., 2022; Stavrakou et al., 2020). Indeed, the atmospheric ratios of NO and NO_2 are affected by NO having weaker water solubility than NO_2 (Klepper, 1979 as cited in Kolbert (2019) and Wellburn (1990)) and may be further changed by rising global temperatures due to an enhanced rate of conversion of NO to NO_2. These processes will affect plant exposure to NO and NO_2 which will be further affected by their interactions with O_3 (e.g. Ryalls et al., 2022).

Annual estimates of NO_2 concentrations can be derived from satellite or ground-based measurements, and there is good agreement between these at the global scale (Jamali et al., 2020). Although much of the world's surface, when considering the oceans as well, is characterised by annual average atmospheric concentrations of 0-1 ppb, there are concentration hotspots, including eastern USA, western Europe, India, China and Japan where values exceeding an annual average of 15 ppb can typically be reached (Anenberg et al., 2022) (Figure 2). There is variation across cities, countries and regions which suggests that even in relatively small geographic areas different interactions between emissions, atmospheric chemistry and meteorology produce variation in annual NO_2 averages (Malley et al., 2018).

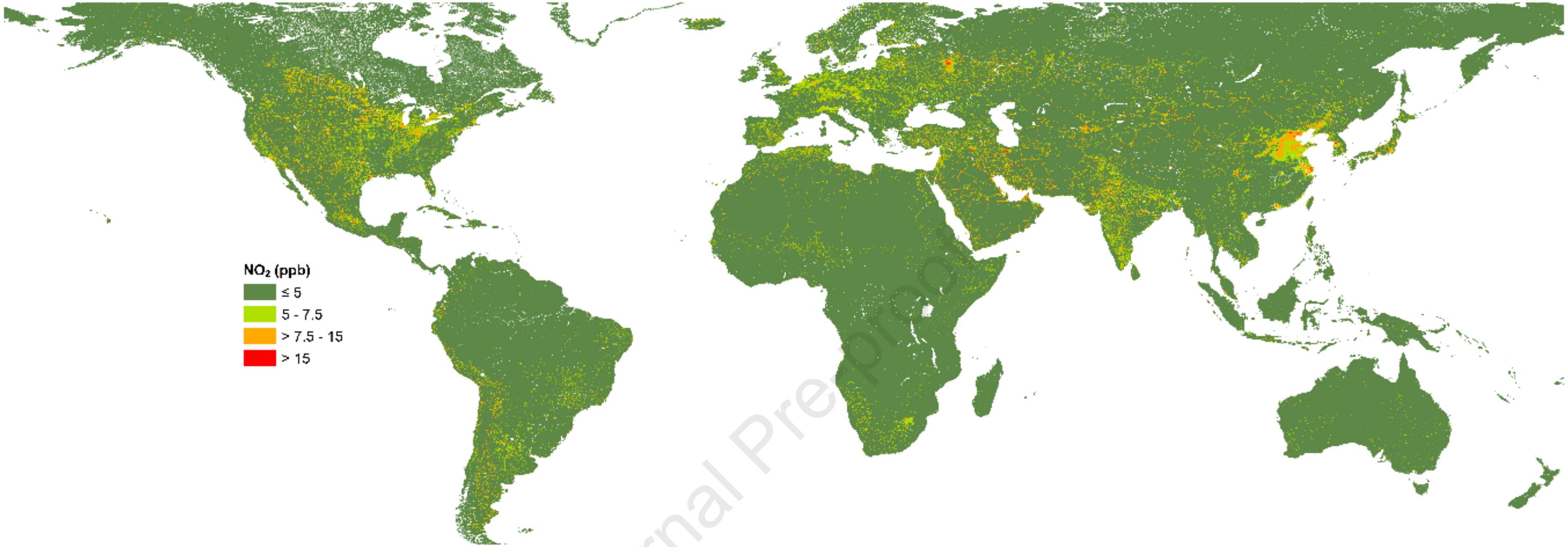


Figure 2: Global estimates of annual average lower atmosphere concentrations of NO_2 adapted from Anenberg et al. 2022 which utilizes a land use regression model that incorporates time varying predictors (e.g. meteorology and satellite NO_2 estimates) and land use characteristics (e.g. road density and emission source). Assuming certain temperature and pressure conditions, 5 ppb translates to the WHO guidelines (World Health Organization, 2021) for direct impact on human health of an annual average of 10 µg m^{-3}, while 15 ppb translates to the current UNECE critical level for vegetation with an annual average of 30 µg m^{-3} (ICP Vegetation, 2017). Evidence compiled in our review suggests this critical level needs assessment, with e.g. effects on lichen community composition at a tenth of this value (Greaver et al., 2023).

As well as annual average variation in NO_2 concentrations across space, there are seasonal (e.g. Hargreaves et al., 2000; van der A et al., 2008) and diurnal (e.g. Edwards et al., 2024) variations in NO_2 that will affect the extent of vegetation exposure. Seasonally, satellite observations confirmed that industrialized regions have maxima in the winter (Dec – February in the northern hemisphere; June to August in the southern hemisphere). In the tropics and subtropics, the seasonal pattern is slightly shifted such that maxima occur in the winter and early spring due to biomass burning. For the Sahel and Ghana in Africa this means that maxima are observed in January and February, July in the tropical rain forest of Central Africa, and in October and November in Southern Africa (Asilevi et al., 2025; van der A et al., 2008). In grassland and more sparsely vegetated regions, the NO_2 peak is observed in summer conditions e.g. January and February for much of Australia, and July and August for the tundra, deserts and steppe areas of the northern hemisphere (van der A et al., 2008).

Local emission sources can obscure seasonal and spatial patterns; for instance, at Rothamsted in the southeast of the UK, proximity to road traffic and dense vegetation increases the mean NO_2 level and virtually eliminates seasonal variation (Hargreaves et al., 2000). In Epping Forest, on the outskirts of London, NO_2 concentrations can be higher in tree canopies rather than at ground level in background sites, whereas the reverse relationship was true of roadway sites (Gadsdon & Power, 2009). Meteorological conditions can also obscure seasonal patterns as observed in Lima, Peru with no obvious winter-summer seasonal variation and with monthly concentrations ranging from 17 to 28 ppb (Tashiro & Taniyama, 2002). Seasonal values in urban areas can sometimes be extreme: very high NO_x nighttime concentrations of approximately 200 ppb, with a maximum of 700 ppb, were estimated in Delhi, India post-monsoon due to a low concentration of oxidants (Nelson et al., 2023).

Diurnal cycles can be determined by the scale of integration and the season of measurement. Regionally, in summertime in northeast Asia, tropospheric NO_2 decreases through the morning hours, reaching a minimum in the early afternoon, and then increases in the late afternoon with little difference between weekdays and weekends (Edwards et al., 2024). In Seoul at the local scale, the summer diurnal variation is less consistent with a late morning maximum in NO_2 followed by a decrease and then small late afternoon increase. However, the range in NO_2 concentrations across the day is much greater than shown at the regional scale and, despite a consistent signature, higher NO_2 values are observed throughout weekdays compared to weekends (Edwards et al., 2024). Regionally and locally overall higher winter NO_2 profiles also increase through daylight hours and are consistently higher on weekdays than weekends (Edwards et al., 2024).

3. Processes of vegetative uptake of NO_x: The emergence of phytotoxicity

There is a potential for transfer through damaged cuticles where NO_2 is in excess (e.g. Gessler et al., 2002) and cuticular wax components are altered (see e.g. Wellburn, 1990). However, uptake through stomata is the predominant entry pathway of gaseous NO_x into plants (e.g. Chaparro-Suarez et al., 2011; Gessler et al., 2000). Even with exposures to NO_2 at atmospheric concentrations of 100µg m^{-3}, *Abies* sp. cuticles had fluxes 1-2 orders of magnitude less than that from stomatal deposition at the same concentrations (as described in Wellburn, 1990).

Stomatal uptake rate is mainly controlled by stomatal conductance to transport of NO_x and the NO_x concentration gradient between the atmosphere and the intercellular air spaces of the leaf (Sparks et al., 2001). The relationship between stomatal conductance and NO_2 uptake is linear for many plants and is considered the primary factor controlling the magnitude of flux into the plant (Sparks, 2009). Other factors that have been observed to influence NO_2 fluxes between leaves and the atmosphere include photon flux density (i.e. light intensity), relative humidity and temperature. For light, this impact appears to be mediated through stomatal aperture (e.g. Neubert et al., 1993; Weber & Rennenberg, 1996), but temperature dependence may relate to decreased solubility of NO_2 under higher temperature in the apoplastic space, while relative humidity may encourage solubilization of NO_2 on the leaf surface rather than uptake occurring through stomata (Weber & Rennenberg, 1996).

Wide variation in uptake rate is observed within plant communities; for instance, a 10-fold variation in uptake rate for sixteen wet tropical forest species, from 153 to 1550 pmol m^{-2} s^{-1} of uptake, at 5 ppb NO_2. Increased uptake was observed at increased heights in the canopy (Sparks et al., 2001). The compensation point - the concentration of atmospheric NO_2 above which leaf uptake occurs rather than emission - was greater at increased leaf N concentrations (Sparks et al., 2001) although laboratory studies on temperate tree species failed to detect a compensation point for NO_2 (Chaparro-Suarez et al., 2011).

Across taxa from different plant communities, more than 600-fold variation in NO_2 uptake capacity has been recorded (Morikawa et al., 1998). Early work showed that for crop species, sunflowers exposed to 0.5 µl l^{-1} (0.5 ppm) NO_2 for 14 days showed absorption rates, on a per unit leaf area basis, four times higher than sorghum (0.55 mg N dm^{-2} day^{-1} vs 0.14 mg N dm^{-2} day^{-1}), with intermediate absorption values being observed for radish (second highest), tomato, tobacco, cucumber, kidney bean and maize (second lowest). There was a clear relationship of greater amount of uptake with larger plants, but sensitivity to the NO_2 appeared to be related to the greater per unit area uptake rates, regardless of total amount absorbed, with sorghum and maize having greater relative tolerance to NO_2 than sunflower and radish (Okano et al., 1988).

In a tropical forest study, the stomatal regulation of NO_2 uptake was only apparent at conductance values lower than 0.25 mol m^{-2} s^{-1}; at conductance rates above 0.25 mol m^{-2} s^{-1}, NO_2 uptake remained constant. The authors suggested that a resistance to NO_2 assimilation exists within the mesophyll tissue with possible internal resistances including the disproportionation reaction of NO_2 in the apoplast and scavenging of NO_2 in the leaf apoplast by ascorbate or other free-radical compounds (Sparks et al., 2001). Some plants also show NO uptake being limited by mesophyll resistance (Neubert et al., 1993). Such resistances do not appear to be the case for all species as the exchange of NO_2 between above ground parts of beech trees and the atmosphere could be exclusively explained by stomatal control (Gessler et al., 2000).

After NO and NO_2 enter the leaf, they dissolve in the leaf apoplast to primarily form nitrous acid (HONO, HNO_2) and nitric acid (HNO_3) that then dissociate to nitrite (NO_2^-) and nitrate (NO_3^-) and protons. This irreversible reaction of NO/NO_2 depends upon the concentration of NO_2^-/NO_3^- in the apoplastic solution (as discussed in Sparks, 2009). Once formed, NO_3^- is rapidly reduced to NO_2^- by nitrate reductase and then NO_2^- is transported into the chloroplast and reduced to ammonium by nitrite reductase before being incorporated into plant proteins (Sparks, 2009). NO can, though, react with many biological targets as it rapidly diffuses through plant cell membranes, including sulfhydryl groups and heme groups. The pool of NO found in plant cells therefore relates to the production process and diffusion, but also processes of storage, scavenging and transport (Del Castello et al., 2019). Thus, reversible reactions with reduced glutathione or thiol groups form compounds such as S-nitroso glutathione (GSNO; an S-nitrosothiol) or dinitrosyl iron complexes (DNICs) that can be stored or transported. Additionally, NO_x compounds can react with organic material such as cell wall components or plasma membranes or undergo secondary chemistry with antioxidant compounds in the cell wall in particular ascorbate (as explained by Eller & Sparks, 2006; Ramge et al., 1993). The ascorbate-oxidant reaction occurs in the cell wall prior to a reactant reaching the living membrane. Plant resistance to damage is dependent upon both the size of the ascorbate pool and the rate at which the pool can be replenished. This replenishment requires the oxidised ascorbate to travel back into the plant cell to be reduced before it can return to the apoplast to react with oxidants (Eller & Sparks, 2006).

The apoplastic reactions of NO_2 can yield nutritive products for the plant through reactions that create nitrate or nitrite when it reacts with water or ascorbate, respectively, which can subsequently form amino acids and proteins (Zeevaart, 1976). The rate of transport of nutritive products into the interior of the cell from the cell wall solution may then influence the steady state flux of oxidant gases into the leaf. The activity of the enzyme nitrate reductase can be an indicator of this transport capacity (e.g. Bender et al., 1991; Eller & Sparks, 2006). Indeed, nitrate reductase activity can influence the magnitude of uptake of foliar NO_2 in tomato but not tobacco (Vallano & Sparks, 2008), with the proportion of N derived from foliar N uptake being greater at lower soil N supply (Vallano & Sparks, 2008).

Taking account of some of the processes that can influence steady-state flux of NO_2 into the leaf, Eller and Sparks (2006) showed 89 % of the variation in uptake by Madagascan periwinkle (*Catharanthus roseus*) was explained by a model incorporating physical resistances (stomatal conductance), reaction between NO_2 and apoplastic ascorbate, and the removal of nitrate from the apoplast. They further demonstrated a direct correlation between nitrate reductase activity and NO_2 flux rate into the leaves (Eller & Sparks, 2006). Although it is unclear whether such a model would be applicable across multiple plant species or functional types (Sparks, 2009), these processes are key controls for whether NO_x causes damage, as the rate at which the pollutant diffuses through the stomata as well as the rate at which they are eliminated in the substomatal cavity will affect the sensitivity of plant leaves (Eller & Sparks, 2006). Indeed, large variation in nitrate reductase activity among plant species may help explain large variation in plant NO_2 uptake (Morikawa et al., 1998; Takahashi et al., 2005) as plants with higher nitrate reductase activities may express higher uptake rates especially at elevated NO_2 concentrations where the cell wall becomes saturated with NO_3^-/NO_2^- (Eller & Sparks, 2006).

Generally, it is considered that at some (high) atmospheric concentrations, NO_x can be phytotoxic while at others it may have beneficial effects through fertilization, at least to the individual plant (Sparks, 2009). Indeed, Wellburn (1990) focussed on the phytotoxicity of gaseous oxides of nitrogen rather than any positive responses, suggesting that the combined stresses of resisting cellular acidification, enhanced levels of nitrite and ammonia and the direct interference of the free radical with critical enzymes, reaction centres and regulatory mechanisms, are thought to be main reason why gaseous oxides of nitrogen inhibit growth (Wellburn, 1990). For instance, the combination of acidity and nitrate may mean cells have greater difficulty in maintaining homeostatic control because the tonoplast pump is strongly inhibited by nitrate (Wellburn, 1990).

The levels at which growth is inhibited may be idiosyncratic between species: there was no difference in biomass between tobacco or tomato individuals in control (0 ppb NO_2) and 40 ppb NO_2 conditions, while at 20 ppb, NO_2 acted like a fertilizer for tobacco and a toxic agent for tomato (Vallano & Sparks, 2008). Even at the phytotoxic levels (4 – 11 ppm) used by Zeevaart (1976), a hundred times higher than now observed in the atmosphere, the nitrite (NO_2^-) content of the leaves was increased, providing the possibility of plant fertilization (Sparks, 2009). Sparks (2009) notes that the concentrations at which injury or decreased performance has been observed are well above the concentrations seen in all but the most polluted environments. At the same time, the plant uptake described above has only been assessed at short time scales, and the potential for chronic influences of NO_x on growth needed further exploration (Sparks, 2009).

4. Exposure to NO_x: Does this capture vegetation consequences of NO and NO_2 uptake?

The atmospheric concentrations of NO and NO_2 at which deleterious consequences for vegetation are apparent may depend on the behaviour of these molecules in plant cells. Where behaviours are different, it may be that a combined expression, considering exposure to concentrations of NO_x, is insufficient to predict vegetation response to these atmospheric pollutants.

Although the reaction of either NO or NO_2 with aqueous solution produces two acids (nitric acid (HNO_3) and nitrous acid (HNO_2)), these acids differ in their chemical activity and cellular pH at which they fully dissociate to protons and nitrate or nitrite respectively. Plants must therefore metabolize one product – nitrite – that is usually not present in appreciable quantities inside cells (Wellburn, 1990). Crucially, the rate at which NO forms both nitrate and nitrite ions in cellular solution appears slower than the rate at which these ions are formed from NO_2, with the appearance of nitrate being particularly slow compared to that of nitrite (Wellburn, 1990). Thus, where plants are exposed to high proportions of NO within the total concentration of NO_x, they could be at significant risk of elevated nitrite concentrations if nitrite reductase is not induced in the chloroplast quickly enough (Wellburn, 1990). This may be a particular issue under elevated levels of soil nitrate supply since ample supplies of nitrate preset the level of shoot nitrite reductase with respect to nitrate (Wellburn, 1990).

Due to a general lack of studies using NO and/or explicitly considering NO to NO_2 ratios, we are not aware of extensive testing of whether there are differences in nitrite production when plants are exposed to either NO or NO_2. However, although nitrite toxicity to plants was classically considered in relation to soil (Oke, 1966), a build-up of nitrite in the cells from exposure to gaseous NO_2 has been shown to be a driver of cell death in *Arabidopsis* in a dose dependent manner. Exposure to 20 ppm NO_2 caused necrotic lesions within 1 hour while 30 ppm NO_2 caused complete leaf collapse (Kasten et al., 2016). Further, NO produced endogenously within the cells promoted this cell death due to nitrite, as shown through assays with mutant varieties (Kasten et al., 2016). Whether or not nitrite builds up after gaseous exposure may be cultivar-specific within species, as well as differing between species. For instance, sweet peppers showed a severe decrease in nitrite reductase activity in response to 1.5 ml l^{-1} (1.5 parts per thousand) of NO or NO_2 for 18 hours, whereas these treatments caused a doubled activity in tomato cultivar Ailsa Craig and no impact in Sonato (Wellburn, 1990). Further, the presence of arbuscular mycorrhizal fungi may mediate any toxic effects from nitrite build up by promoting nitrite reductase activity in the presence of NO_2 (Sun et al., 2020).

Even without understanding the mechanism of response, clear differences in plant physiology and growth measures after exposure to NO or NO_2 have been observed. For instance, glasshouse crops appear to have a limited capacity to utilize N from NO while they can take up N from NO_2 (Mansfield and Murray as cited by Wellburn, 1990). More generally, Wellburn (1990) suggested some species could respond positively, in terms of their growth, in response to atmospheric fumigation with NO_2 but this had not been observed with NO alone. Saxe (1986) showed that NO reduced photosynthesis by approximately 20% across eight cultivars of pot plants while NO_2 rarely had significant effects, with 1 µl l^{-1} (1 ppm) of NO being, on average, four times more inhibitory to photosynthesis than NO_2 (also observed by Hill and Bennett in 1970 (as cited by Wellburn, 1990)).

Clear differences were observed in more recent work where NO and NO_2 have opposite effects on flowering time. Exogenous NO delays the flowering of Arabidopsis Col-0 whereas exogenous NO_2 accelerates flowering time in Col-0 and C24, as well as tomato (Takahashi et al., 2012). Takahashi et al. (2014) suggest that these opposite impacts of NO and NO_2 provide evidence that their interconversion inside and outside cells is limited. Yet, in a companion piece, Takahashi (2014) states that the two nitrogen oxide species [i.e. NO and NO_2] readily interconvert in vivo and in vitro suggesting similarities in their effects on plants. A similarity in consequence is supported for vegetative growth of Arabidopsis, where a similar increase in Arabidopsis shoot biomass was obtained when plants were exposed to NO gas at the same concentration as NO_2 (Takahashi et al., 2014).

The relationships between NO and NO_2 led to the statement from Wellburn (1990) that "*it must have become increasingly obvious to the reader that NO and NO_2, in terms of their responses within plants, differ from each other in their physical, biochemical and physiological effects. For that reason, the convenience of the abbreviation NO_x has been abandoned … because it leads to the assumption of similarity in mode of action between [NO and NO_2], a general neglect of the study of NO in its own right, and an unjustified belief that having clean air controls still contaminated with NO is satisfactory during fumigation studies designed to investigate the effects of other pollutants*".

5. The changing understanding of the production and role(s) of NO and NO_2 within plants

Nitric oxide (NO) has been found to be endogenously produced (e.g. He et al., 2004). In land plants, a reductive process involving nitrate- and/or nitrite-reductase is thought to be the most common production pathway under normal cell conditions (Kolbert et al., 2019; Santolini et al., 2017). Subsequently, both NO and NO_2 have been implicated in plant signalling pathways (Delledonne, 2005; Santolini et al., 2017; Sharma et al., 2024; Takahashi et al., 2014; Takahashi & Morikawa, 2014). Some have suggested that NO_2's primary role, at low concentrations, may be as a signalling molecule (Takahashi et al., 2014). For NO, plant signalling can be mediated by GSNO which, in turn, can affect plant health (Kolbert et al., 2019). Overexpression of the enzyme that controls GSNO content can enhance broad-spectrum disease resistance in plants although loss of function mutations in the enzyme can also compromise multiple modes of resistance (Johnson et al. 2008, Kolbert et al., 2019). More generally, laboratory studies have shown NO can have a role in plant susceptibility to pathogens through influencing signalling pathways (Delledonne et al., 1998), and in combination with reactive oxygen species (ROS), by triggering hypersensitive cell death and thus preventing pathogen spread (Agurla et al., 2014; Delledonne, 2005). Symbiotic relationships may be facilitated by the presence of NO as shown in the nodule fixation zone of the *Medicago trucatula* – *Sinorhizobium meliloti* symbiosis. NO presence was not due to denitrification or N-fixation processes but rather an NO-synthase type enzyme suggesting a role for NO beyond defence and hypersensitive programmed cell death (Baudouin et al., 2006). Both NO and NO_2 have, arguably, been considered akin to plant hormones, while less controversially as positive regulators of plant development through regulating organ growth (e.g. Kolbert et al., 2019; Shapiro, 2005; Takahashi et al., 2014).

Nitric oxide plays a role in stomatal opening/closure, which could affect atmospheric NO_x uptake. In beans (*Vicia faba*), cytokinins decrease the level of NO in sodium nitroprusside-treated guard cells, facilitating stomatal opening in light and dark (Sami et al., 2018) while in stomatal guard cells, NO accumulation permits ABA-induced stomatal closure (as reviewed in Kolbert et al., 2019). An interaction between NO and ABA helps mitigate water stress and UV-B radiation damage in maize (Sami et al., 2018). Additionally, stomatal closure induced by NO may assist in plant immunity response against pathogens (Agurla et al., 2014).

Scavenging reactions with NO can influence homeostatic plant levels (Del Castello et al., 2019). In particular, the Phytoglobin-NO cycle may be very important for sustaining the energy supply to plants under hypoxic conditions (Kolbert et al., 2019). Upregulation of phytoglobins with a high affinity for oxygen, such as Phytogb1, can be induced by NO under hypoxic, low ATP and/or low nitrate conditions. Subsequent reactions convert NO to nitrate which then converts to nitrite to then become a substrate, in the mitochondria, for further NO production. This chain of reactions provides energy through ATP generation, helps with re-oxidation of accumulated NAD(P)H under hypoxia, and aids the maintenance of various physiologically important ratios e.g. NADH/NAD+ (Kolbert et al., 2019).

Overall, NO can be considered a 'do-it-all' molecule playing crucial roles during the entire lifespan of a plant (Delledonne, 2005; Shapiro, 2005). These roles have emergent properties that affect responses to environmental conditions. For instance, NO induces endogenous auxin concentrations to facilitate adventitious root development in cucumber (*Cucumis sativus*), improves root branching in sunflower (*Helianthus annuus*), helps mediate arbuscular mycorrhizal colonization in tomato plants through overexpression of Phytogb1, delays gibberellin-induced programmed cell death in the aleurone layers of barley (*Hordeum vulgare*) and contributes to lignification of vascular tissues (Corti Monzón et al., 2014; Martínez-Medina et al., 2019; Procházková & Wilhelmová, 2011; Sami et al., 2018). The application of NO donor compounds (such as sodium nitroprusside (SNP), GSNO and S-nitroso-N-acetylpenicillamine (SNAP)) applied externally to the plant point to an array of consequences including delay and/or control of flowering time (Corti Monzón et al., 2014; He et al., 2004; Procházková & Wilhelmová, 2011); modulation of stress response to, *inter alia*, drought, UV-B radiation, salinity, hypoxia and heavy metals (with reviews in e.g. Del Castello et al., 2019; Sahay & Gupta, 2017; Sami et al., 2018); protection against pathogens (e.g. resistance in pearl millet to downy mildew Manjunatha et al., 2008); and, protection of fruit from senescence (especially when combined with nanoparticles (da Veiga et al., 2024a,b)) (see also Kolbert et al., 2019). However, the extent to which these donors mimic the impacts of NO (endogenous or atmospheric) needs careful consideration (Floryszak-Wieczorek et al., 2006). For instance, the commonly used SNP also raises levels of cyanide and iron, causing difficulty in deciphering the role of NO in the response (Keisham et al., 2019).

Despite this wide array of roles for NO (and NO_2) in plants, much remains unclear regarding consequences of stomatal uptake of atmospheric NO and NO_2 influencing these processes. Furthermore, much of the highlighted work involves pharmacological studies with NO scavengers and enzyme inhibitors which makes it difficult to discriminate physiologically relevant effects from pharmacological ones (Delledonne, 2005).

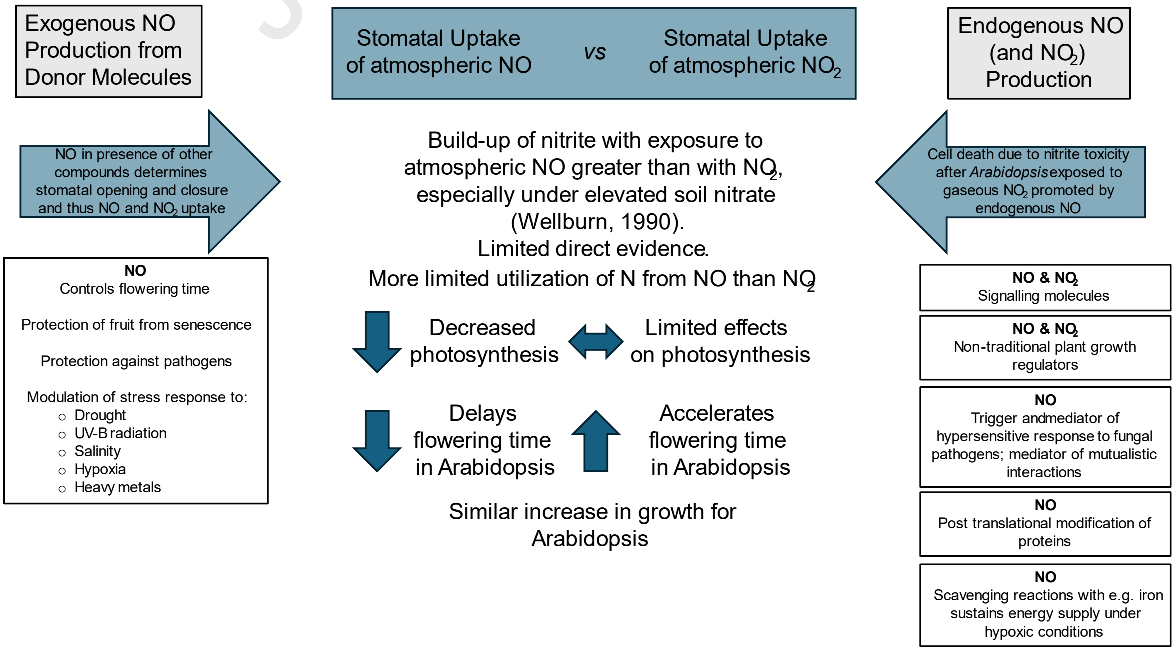


Figure 3*: The roles and some consequences of NO and NO_2 within plants. Depending on whether NO is produced endogenously, exogenously from donor molecules, or taken in through stomata after atmospheric exposure, there are a range of positive and negative roles for the molecules. Importantly, the presence of NO within the plant can affect the capacity to take in gaseous pollutants, while also regulating response to other environmental conditions e.g. hypoxia. The consequences of stomatal uptake of atmospheric NO and NO_2 can also differ between the two molecules, depending on the considered plant response (see examples for Arabidopsis e.g. Takahashi et al., 2014; Takahashi et al., 2012). Differences in response between NO and NO_2 and how to consider endogenous levels of these molecules raise questions as to the use of a combined atmospheric metric of exposure (NO_x) when considering harm to vegetation and other receptors.*

6. Physiology, growth, flowering, yield and condition impacts for vegetation after intake of atmospheric NO and NO_2

Experimental approaches

A range of biochemical and metabolic responses have been documented for plant species in response to experimental exposure to NO_x, relating to rates of photosynthesis and respiration, growth and senescence dynamics, flowering and yield. Many early studies exposed plants to acute levels of pollutants over relatively short time periods in experimental settings (World Health Organization, 2000a). More recent work (

Table 1) has tended to use lower concentrations over longer time periods and with a greater focus on physiological processes. These have shown both inhibitory and stimulatory effects of NO_2 which may relate to the experimental conditions. For instance, poplar clones (*Populus alba x Populus berolinensis*) exposed to NO_2 at 4 µl l^{-1} (4 ppm) for 48 hours showed a significant reduction in net photosynthetic rate and reduced dark respiration rates compared to control (<0.1 µl l^{-1}, <0.1 ppm) conditions and compared to leaves exposed for 14 hours (Hu et al., 2015). According to Hu et al. (2015) stimulatory effects in plants appear associated with concentrations of 80 to 135 nl l^{-1} (80 – 135 ppb) which may even explain variable responses within the same species such as *Glycine max*. However, in the longer term, such exposures may prove to be deleterious for season-integrated responses. Thus, exposure of 12 herbaceous plant species to diesel fumes comprising 77 nl l^{-1} to 98 nl l^{-1} mean NO_x (77 – 98 ppb; with ratio of 1.4 to 2.2 $NO:NO_2$) led to consistent patterns of accelerated senescence and delayed flowering, as well as changes in surface wax structure (Honour et al., 2009). As noted earlier, idiosyncratic responses can be observed among species across gradients of exposure e.g. toxic impacts for tomato at 20 ppb NO2 but fertilization effects for tobacco, while 40 ppb NO2 led to no differences compared to control conditions in either species (Vallano & Sparks, 2008).

New evidence exists for deleterious consequences at lower concentrations of NO_2 in a single pollutant exposure. Laboratory experiments have shown that pollen viability declined by between 3 and 5 % in both hazel (*Corylus avellana*) and oak (*Quercus robur*) at between 0.05 – 0.06 ppm NO_2, even when exposed to pollutants for just 6 hours, while viability declines of between 7 and 13% were observed at 0.10 – 0.11 ppm NO_2 in hazel, oak, *Betula pendula* and *Acer negundo* (Pereira et al., 2021).

Pollutant gradients and remote sensing approaches

Studies along pollution gradients and through remote sensing may complement experimental findings. Such gradient/correlational studies need to be interpreted with care, as isolating the effects of direct gaseous NO_x exposure and controlling for additional impacts, such as from soil acidification and eutrophication and/or co-occurring atmospheric pollutants, can be difficult.

Epidemiological studies, for instance long term cohort investigations, have proved useful in identifying the effects of other gaseous pollutants such as ozone (O_3). For instance, researchers have identified growth reductions due to O_3 in Norway spruce in southern Sweden (Karlsson et al. 2006) and both spruce and European beech in Switzerland (Braun et al. 2017). Further, more recent work in Swiss beech and spruce forests has allowed contrasts with experimental findings used to inform O_3 critical levels (Braun et al. 2022) as well as associating Norway spruce mortality with drought and nitrogen deposition (e.g. Tresch et al. 2023). Insight may be aided by bringing together studies from multiple locations where the actions of NO_x can be reasonably disentangled from other conditions e.g. high or low temperatures (in the context of resurveys and global change, see arguments in Verheyen et al. (2017)).

Studies could also be conducted where there are clear sources of NO_x without other atmospheric pollutants, but such scenarios may be rare. Instead, for informing policy, it may be more representative to quantify the real-world impact of NO_x in conjunction with co-occurring pollutants, without necessarily elucidating a clear mechanism. Overall, such studies offer the potential to understand realistic chronic consequences of pollutant exposure for growth, biodiversity and community composition, as emphasized by Sparks (2009). For instance, a remote sensing investigation recently suggested that direct NO_2 damage, sometimes in conjunction with O_3, contributes to crop yield losses of between 10 and 25 % in different regions of the globe (Lobell et al., 2022).

Many of the gradient – community composition studies have focused on lichens and bryophytes. Akin to vascular plants, as exposure concentrations rise, NO_2 can first act as a nutrient and then cause physiological stress and mortality with implications for community composition (see also for vascular plants Bignal et al., 2007; as explained for lichens by Greaver et al., 2023). In urban areas, there are marked influences from air pollution on lichen and bryophyte assemblages. For instance, in London, diversity declined where NO_x exceeded 70 µg m^{-3} and NO_2 exceeded 40 µg m^{-3}. There was also a significant positive relationship between NO_x and lichen abundance because of ubiquitous distribution of pollution tolerant species mainly associated with eutrophication (Davies et al., 2007). New records and rare species were generally confined to areas of low NO_x where the ratio of NO to NO_x was lowest (Davies et al., 2007). Larsen et al. (2007) showed that out of sixty-eight lichen and bryophyte species, nineteen had distributions that correlated with nitrogen oxides, while 23% of the lichens and one bryophyte species could only be found where average NO_x was below 56 µg m^{-3}. By controlling for edge effects as well as distance from roadways, NO_2 was the most significant and positively correlated variable explaining the proportion of lichens considered to be nitrophytes while it was negatively correlated with total lichen cover, with a range of NO_2 between 18.4 and 30.0 µg m^{-3} (see Table 1 in Gadsdon et al., 2010). Such relationships were not clear when examining Italian roadside lichen communities, but this was attributed to very low NO_2 concentrations of between 7.3 and 16.6 µg m^{-3} (Frati et al., 2006) and may relate to the rural site location.

In a synthesis of lichen response to NO_2, in rural and urban areas, Greaver et al. (2023) suggested that lichen community composition can be altered at <1 to 3 µg m^{-3}, based on a 'no effect or lowest effect concentrations' approach. In boreal forests, and from a combination of open-top chamber and gradient approaches, Manninen (2018) and Manninen & Huttunen (2000) proposed a critical level for NO_2 of 5 µg m^{-3}, based on lichen responses and 10-15 µg m^{-3} based on coniferous tree species. Bryophyte species transplanted at different distances from a roadway also exhibited one or more of increased growth, membrane leakage, N concentration and chlorophyll content with the effects being consistent with the NO_2 profile away from the road, including to a background concentration of 15 ppb at 100m (Bignal et al., 2008). Growth increases were only observed in those transplants in open moorland areas, while transplants within a woodland setting exhibited no growth increases despite increased N and pigment concentrations in the short-term (3 months) but not the longer (7 month) term (Bignal et al., 2008).

Interactions with other trophic levels can affect plant responses to NO_2. Correlative studies have shown poorer crown condition and increased defoliation and damage on trees closer to motorways, with a clear link between the distance over which damage was observed and NO_2 profiles (Bignal et al., 2007).

Table 1*: Example recent studies showing different methodological approaches and take-home messages from NO_2 impacts on vegetation. Note the caveats that, for some studies, make it difficult to understand causation. Units from the source literature are quoted in the body of the table; 1 µl l^{-1} is equivalent to 1 ppm and 1 nl l^{-1} is equivalent to 1 ppb. Due to the need to understand atmospheric pressure and temperature conditions, we do not convert µg m^{-3} to ppb.*

Approach	Vegetation Type	Main Take Home Message	Caveats	Reference
Review	Lichens	Monitoring in US does not accurately represent exposure of systems to NO_2 in rural areas. Lichen community composition altered at current levels of exposure with no effect or lowest effect concentrations from <1 to 3 µg m^{-3} NO_2	Authors identified that there is very little information quantifying exposure – response relationships which could be used to identify critical levels…causing a reliance on studies focusing on NO_3^- for insight. They recommend that “more experiments with controlled exposures relevant to current ambient air concentrations are needed for both NH_3 and NO_2 exposure”	Greaver et al., 2023
Chamber	4 temperate tree species	At or above the current critical level led to declines in pollen viability but for two species (hazel and oak) half the critical level led to declines in viability.	Only 6 hour exposures but highlighted species-specific differences	Pereira et al., 2021
Solardome	12 Herbaceous plant species	77 nl l^{-1} to 98 nl l^{-1} mean NO_x (with ratio of 1.4 to 2.2 NO:NO_2) generally led to accelerated senescence and delayed flowering.	Diesel exhaust so not solely NO and NO_2. Species specific responses which may also relate to different exposure lengths and season	Honour et al. 2009
OTC and pot experiment	Trees – hybrid poplar clones	4 µl l^{-1} NO_2 has significant negative influence on stomata-related physiological processes	Short term exposure (48 hours)	Hu et al. 2015
Survey	Lichens and bryophytes on 145 oak trees around London	Three zones including two central regions with few lichens and no bryophytes, surrounding region with high cover of nitrophytes, and an outer region with species absent from central London and acidophytes	Correlative distribution study with multiple air pollutants	Larsen et al. 2007

Transplant experiment	6 bryophytes transplanted to woodland/moorland adjacent to motorway	Strongest effects on growth, membrane leakage, chlorophyll concentration and nitrogen concentration found in first 50 to 100 m, consistent with NO_2 profile	Seven months of monitoring from autumn to spring. Other pollutants present and not all profiles characterised.	Bignal et al. 2008
Survey	>3000 epiphytes on 334 Fraxinus excelsior trees around London including 74 lichen, 14 moss, 7 fungal and 3 algal species	Diversity declined where NO_x exceeded 70 µg m^{-3} and NO_2 exceeded 40 µg m^{-3} but a positive relationship between NO_x and lichen abundance	Positive relationship between NO_x and lichen abundance due to ubiquitous distribution of pollution tolerant species. Observational survey with multiple pollutants.	Davies et al. 2007
Survey	Lichen diversity at distance from highway in Central Italy	No association between NO_2 concentrations and the diversity of epiphytic lichens.	Only low NO_2 values measured which likely explains lack of response. Transplanted thalli of one species showed reduction in chlorophyll a, b and total carotenoids as well as accumulation of N but NO_2 was not responsible.	Frati et al. 2006
Survey	Lichens growing on boreal conifer tree trunks	Species specific responses depending on tolerance to pollutants, with relationship to elevated atmospheric NO_2 and particulate matter containing N. A critical level of 5 µg m^{-3} for NO_2 is proposed.	Survey approach. Measurements of throughfall of various N fractions in urban forest ecosystems are required along temperature and precipitation gradients to verify the proposed critical levels and loads	Manninen 2018
Open Top Chamber (plus field investigation)	Scots pine and Spruce trees	Based on combination of approaches, and S and N concentrations in needles, recommended that to protect against N deposition, the critical level for NO_2 should be 10-15 µg m^{-3}	No NO_2 treatment alone – treatments either with O_3 or SO_2 or both.	Manninen and Huttunen, 2000

7. NO and NO_2 effects on biodiversity other than vegetation

NO and NO_2 can affect other parts of the ecosystem in addition to direct effects on vegetation. This can be a direct impact on the organisms, or it could be indirectly through pollutant influences on the vegetation. In the context of high doses of diesel exhaust (with NO at 19.8 ppm and NO_2 at 17.5 ppm), pollinators were observed to decline through direct effects on their health (Reitmayer et al., 2019). This may be associated with cognitive behaviour decline, as acute exposure to diesel exhaust fumes can impair olfactory learning and memory in honeybees, although other key air pollutants such as particulate matter, carbon monoxide and total volatile organic compounds (VOCs) also varied compromising the ability to isolate the impacts of NO_x (Leonard et al., 2019). In laboratory behaviour studies and/or atmospheric modelling, pollinators suffer from indirect effects, due to reduced foraging efficiency as odours degrade (Girling et al., 2013) (for other pollutants see also Fuentes et al., 2016). Indeed, Girling et al. (2013) showed that at environmentally relevant levels (100 ppb NO, 10 ppb NO_2), the nitrogen oxide fraction of the exhaust gases was a key facilitator of odour degradation of floral volatiles, given odour degradation also occurred under varying ratios and concentrations of NO and NO_2 in the absence of other diesel exhaust components.

For herbivores, short term, high concentration fumigation studies showed positive effects on aphid colony growth (Dohmen et al., 1984) while susceptibility or resistance of a given plant genotype to insect herbivory can be altered under pollutant stress (Masters & McNeill, 1996). On the other hand, recent experiments have shown that direct foliar assimilation of NO_2 increased levels of nitrogen-based defensive metabolites (leaf alkaloids) in tobacco (*Nicotiana tabacum*) leaves and reduced herbivore consumption and growth (of its natural leaf feeding herbivore, *Manduca sexta*) in chambers of 40 ppb NO_2 compared to controls (0 ppb NO_2) (Campbell & Vallano, 2018). Here, the indirect impact of foliar N uptake on insects was demonstrated, as there was no direct effect of the NO_2 on feeding behaviour when insects were allowed access to the same artificial diet in the different chambers (Campbell & Vallano, 2018).

It was noteworthy that these NO_2 effects on consumers occurred regardless of whether plants were grown on moderate or low root-available nitrate (500 mM vs 50 mM respectively), suggesting that the effect of NO_2 uptake on N-based defences was not based on overall N availability. Campbell and Vallano (2018) argue that dissolved NO_2 in the apoplast may represent a mobile N pool available for transport to the site of alkaloid biosynthesis, which is the roots. In contrast, C-based defensive compounds (phenols, terpenes) were reduced under higher root N, consistent with theories on plant defence which predict reduced C-based defences in high nutrient environments (Campbell & Vallano, 2018). Overall, they suggest that plant defences will be uniquely sensitive to N derived from foliar uptake with the potential to affect a wide range of organisms that interact with a plant's secondary metabolome, including herbivores, pollinators and microbes (Campbell & Vallano, 2018).

A free-air fumigation study (NO at ± 38.5 ppb, NO_2 at ± 21.2 ppb relative to controls (NO ≈ 2 ppb and NO_2 ≈ 5 ppb) from Figure 1 in Ryalls et al. (2022)) showed that elevating NO_x pollution levels from diesel exhaust reduced counts of locally-occurring wild and managed insect pollinators (by 69 % on average) and flower visits by 89 %. These declines in insects were not universal: although all bees (honeybees, solitary bees, bumblebees), all flies (hoverflies, other flies), butterflies and moths declined in abundance, beetles (the majority of which were pollen beetles), true bugs and parasitic wasps were not significantly affected by pollution treatments. The study focussed on pollinators but has wider-reaching implications as VOCs are used ubiquitously by plants and insects for communication and perception of their environment (Ryalls et al., 2022). Some experimental plots had ozone applied in combination with the diesel exhaust; a similar decline in pollinator numbers

(70%) and flower visitation (90%) in comparison to the diesel treatment alone was observed (Ryalls et al., 2022).

8. Modifying factors: The potential influences of current and future atmospheres on vegetation responses to NO_x

Early air pollution research was focussed on acidifying deposition and often concentrated on extreme pollution episodes associated with sulphur dioxide (SO_2) and nitrogen oxides. Investigations showed that while individual gases may be non-toxic in some circumstances, their combined influence, at the same concentrations, could lead to toxicity symptoms whether supplied sequentially or concurrently (e.g. Bender et al., 1991; Freer-Smith, 1984; Goodyear & Ormrod, 1988; Runeckles & Palmer, 1987). Thus, the critical level for NO_x for vegetation was set in the context of the presence of SO_2 and ozone (ICP Vegetation, 2017). However, atmospheric SO_2 emissions have markedly declined in many areas (Aas et al., 2019; Stern, 2005), while chronic levels of O_3 continue to pose threats to vegetation (Unger et al., 2020). In addition, there is an ongoing alkalinization of the atmosphere as NH_3 levels continue to increase in relation to agricultural intensification (Sutton et al., 2020), and, in urban areas and near to roadways, from catalytic converter modifications leading to NH_3 emissions (Cape et al., 2004). Understanding how these atmospheric dynamics, and the general rise in carbon dioxide (CO_2) concentrations, may influence NO_x impacts on vegetation and other ecosystem components has been a focus of some research.

Inconsistent results between years in open-top chamber investigations of multiple pollutants (NO_x, ozone, and SO_2), across an array of crop plants (including wheat, barley, spring rape, bush bean) has been attributed to an interaction between pollutants and climatic variables (Adaros et al., 1991a, 1991b). Impacts may also depend upon the growth stage and/or age of the plants although this may not be consistent among species. For instance, higher impacts were found for reproductive structures rather than total biomass for spring rape (Adaros et al., 1991b) and ozone and NO_2 had a greater than additive impact on pollen tube growth in lilies (Masaru et al. 1976 as cited in Goodyear & Ormrod, 1988). On the other hand, bush beans sequentially exposed to 50 - 60 nl l^{-1} (50 – 60 ppb) of ozone and 30-40 nl l^{-1} (30 – 40 ppb) NO_2 were unaffected in terms of yield, as estimated from pod weight, but leaf dry weight and leaf area were lowest under such exposure (Bender et al., 1991). Reductions in photosynthesis, of 37%, were observed in 1-year old spruce needles, but not current year needles, when exposed to both ozone and NO_2 in a daily cycle, and with continuous NO_2 exposure (Küppers & Klumpp, 1988). The maintenance of photosynthesis in younger needles under combined application of ozone and NO_2 may relate to increased enzymatic activities (nitrate reductase, superoxide dismutase) in younger but not older needles (Klumpp et al., 1989).

In a plant community-focussed investigation, using open top chambers in a beech forest understorey in Germany, combined exposure to NO_2 and O_3 (and SO_2) at high concentrations showed that growth and aboveground development was dependent on species (Steubing et al., 1989). For instance, *Hedera helix* (ivy) was insensitive to exposure while *Allium ursinum* (broad leaved garlic) and *Arum maculatum* (arum lily) were very sensitive. For those species that were sensitive, the combined pollutant exposure caused early senescence, together with higher wettability of leaf surfaces due to epicuticular waxes being degraded and leaching of ions (Steubing et al., 1989). Steubing et al. (1989) also showed impacts beyond the plant community, with a decreased bacteria to fungal ratio in all treatments despite a lack of change in pH, with the greatest reductions in bacteria and greatest increases in fungi occurring in the plots exposed to all pollutants.

The increased contribution of ammonia (NH_3) to atmospheric conditions may influence vegetation response to NO and NO_2 as both reduced and oxidized molecules can be absorbed through stomata.

Since both forms can have toxic outcomes at the plant level (World Health Organization, 2000b), their combined presence in the atmosphere around a receptor could lead to deleterious impacts below the level at which such effects are observed singly, but few studies have assessed these interactions. The current year shoots' net carbon assimilation (i.e. P_{max}) in two-year old Douglas fir plants was higher under NH_3 (at 66 µg m^{-3}) and a combined treatment with both NH_3 and NO_2 (at 52 µg m^{-3} and 82 µg m^{-3} respectively), but not NO_2 alone (at 95 µg m^{-3}). An increase in photosynthetic units, based on chlorophyll *a* and *b* content, counteracted declines in J_{max} (van Hove et al., 1992). Shoots exposed to NO_2 alone had a lower water use efficiency, a finding that was not observed in the combined pollutant treatment, despite NH_3 also affecting stomatal closure, at least based on transpiration rate in the dark (van Hove et al., 1992). This study avoided any indirect acidification or eutrophication effects through the soil by introducing a barrier between the gases and the soil surface, although their use of charcoal filtered air permitted relatively high levels of pollutants in the control chamber (an average NH_3: 15 µg m^{-3}; NO: 15 µg m^{-3}; NO_2: 5 µg m^{-3}); the authors also cautioned that there was no replication (of chambers, or through a repeat experiment) so results should be interpreted with care (van Hove et al., 1992).

Gradient studies in the context of road environments have highlighted relationships between NH_3 and NO_2 and biodiversity responses (e.g. Manninen et al., 2023). In Ontario, epiphytic foliose lichen richness decreased with increasing concentrations of both gases, while vascular plant richness, and percentage of non-native species, was positively related. Above a concentration of 20 µg m^{-3} NO_2 and 1.4 µg m^{-3} NH_3, only one epiphytic lichen species was found (*Phaeophyscia rubropulchra*). Results could be related to road density and suggested a background influence of traffic despite sites being located away from local sources of contamination (Watmough et al., 2014). However, isolating the causal factors underlying observed relationships is difficult, and other environmental gradients may influence responses, especially vascular plant richness. At the regional scale, temporal change in epiphytic communities may relate more to air quality recovery (in SO_2 and O_3 as well as NO_2) rather than climate change, although current climate conditions may better explain contemporary spatial variation (Hutsemékers et al., 2023).

The atmosphere has a much higher concentration of CO_2 than when the critical level for NO_x was first set. Elevated carbon dioxide has influences on stomatal dynamics (Liang et al., 2023) that may affect the magnitude and rate of pollutant uptake. Indeed, Sparks (2009) suggests increases in available N from gaseous uptake at the leaf may drive additional C gain in otherwise N-limited sites. A recent, fully factorial open top chamber study investigated the impact of elevated CO_2 in conjunction with elevated ozone and nitrogen dioxide on *Arabidopsis thaliana* since it had previously been noted that CO_2 had inconsistent impacts on flowering time that may relate to interactions with other pollutants (Eller et al., 2020). Interactions between elevated ozone, nitrogen dioxide and soil nitrate availability caused the strongest phenological delays in *Arabidopsis* but these were dampened when CO_2 was also elevated. We are not aware of other investigations with contemporary levels of CO_2 being conducted on ecosystems, but earlier work did show the importance of CO_2 and NO_x interactions in glasshouse settings (e.g. Caporn, 1989), suggesting further work on these impacts is warranted.

9. Modifying factors: Environmental influences on vegetation responses to NO and NO_2

Environmental conditions, beyond other atmospheric gases, might be expected to modulate plant responses to NO and NO_2, especially those that affect stomatal responses and/or physiological process rates (e.g. light, relative humidity, soil moisture, temperature). For instance, environmental conditions that allow more rapid uptake of pollutants could lead to greater likelihood of toxic impacts depending on the innate detoxification capacity of the receptors and transport rates.

Detoxification capacity and/or potential nutritive impacts of gaseous N supply may further depend on soil nitrate supply to the vegetation, which regulates the induction of nitrate reductase (Wellburn, 1990). As nitrogen available to roots is lowered, the contribution of NO_2 to the N budget of the plant can increase; for instance, barley grown at 0.1 mM nitrate accumulates 85% more nitrate than controls when exposed to 0.3 µl l^{-1} (0.3 ppm) NO_2 for 9 days, while at 10 mM nitrate, fumigated seedlings have 25% less nitrate than controls (Rowland et al., 1987). In 3-month old spruce seedlings, pre-treated with no nitrogen source or nutrient solutions containing nitrate and ammonium or nitrate only, fumigation with 100 mm^3 m^{-3} (100 ppb) NO_2 led to an increased capacity for nitrate uptake in the absence of ammonium but the absence of both ions caused a decrease in plant N concentration, while root nitrate uptake was decreased under fumigation when ammonium ions were part of the supply (Muller et al., 1996).

Noted in Caporn (1992) was that the calcareous or acid nature of the soil could affect the response of vegetation to NO_x based on the response of bryophytes. Morgan et al. (1992) found that exposure to NO_x (at 35 nl l^{-1} (35 ppb) NO or 35 nl l^{-1} (35 ppb) NO_2) disrupted the activity of nitrate reductase to a greater extent in calcifuge species than calcicoles – which may have reflected a greater availability of nitrate in calcareous sites.

10. Future Directions: Assessing the Continued Risk to Biodiversity and Ecosystems from NO and NO_2 Pollution

Although NO_x emissions in some regions are declining, elsewhere (e.g. China, India) they have rapidly increased, and there are concerns that there could be significant increases in NO_x emissions associated with shifts to hydrogen-based renewable fuels and/or ammonia, including in shipping (Leverett et al., 2025). This suggests that NO_x will remain an important constituent in the lower atmosphere and continue to pose a direct risk to vegetation and ecosystems. Further, these pollutants may pose negative impacts through acidification and eutrophication given their contribution to total N deposition to an ecosystem. However, when assessing the risk posed by these pollutants it is also important to bear in mind the positive influences that NO and NO_2 can have on vegetation and the wider system e.g. sustaining productivity in some circumstances and/or providing protection against other environmental harms.

Conflicting results i.e. positive or negative responses to NO and NO_2 can be understood in relation to difficulties in distinguishing impacts of the two compounds, to biochemical pathways and the potential for interconversion within plants, species-specific (and likely individual) differences in metabolism and detoxification capacity, as well as from study artefacts such as its design (e.g. duration of exposure, exposure concentration, single and/or mixed pollutants) and the specific response variable measured (e.g. photosynthesis, flowering time, biomass).

These factors provide a framework within which the following key questions need addressing to understand sensitivity of vegetation and ecosystems to these pollutants in an era of rapid environmental change:

(i) Under what environmental contexts does gaseous NO_x supply help maintain the biodiversity of ecosystems through supporting vegetation, especially when other environmental changes may enhance N loss pathways (e.g. McCalley & Sparks, 2008)?

(ii) To what extent does the sensitivity of vegetation response to NO_x, and crucially different gaseous supply ratios of NO and NO_2, depend on the context of the contemporary atmosphere and other environmental conditions e.g. climate, as well as the receptors themselves?

(iii) Can the positive roles of NO and NO_2, and the quantities involved, be related to atmospheric exposure to NO and NO_2?

(iv) Can findings from isolated effects of foliar uptake based on short-term studies be related to long-term chronic impacts?

These questions need answering through laboratory studies as well as field-based tests of ecosystem response at atmospherically relevant concentrations, preferably with single and combined exposures to pollutants. Field-based tests are challenging given interconversions among the different chemical pollutants in the atmosphere. Understanding may be complemented with well-designed surveys and epidemiological studies that can aid elucidation of causal inference. In interpreting results in the frame of continued risk to vegetation and ecosystems, it is beneficial to have a clear definition of what constitutes harm to system components in an era of environmental change.

11. Conclusions: Appraising Critical Levels for NO and NO_2

Understanding of NO and NO_2 dynamics and their influence on vegetation and ecosystems has moved on since critical levels were first set in the US (in 1971, at an annual average of 100 µg NO_2 m^{-3}) and Europe (in 1988 and 1992, at an annual average of 30 µg NO_2 m^{-3}). Although the toxic and beneficial character of these molecules for vegetation was acknowledged, the evidence we have summarized suggests that deleterious impacts can sometimes be observed at much lower levels than previously thought, particularly for epiphytic lichens and bryophytes (e.g. Greaver et al., 2023) and for other ecosystem components (e.g. Ryalls et al., 2022). Yet, understanding of the positive roles of these compounds throughout the plant lifecycle has expanded, including of the physiological and biochemical processes arising from endogenous production.

The atmospheric conditions are markedly altered since the NO_x thresholds for vegetative harm were set. The few experiments in these changed conditions makes it difficult to assess the veracity of existing critical level(s) in the context of the contemporary environment. That NO and NO_2 uptake into plants is clearly related to stomatal conductance and the subsequent ability of plants to transport and/or detoxify reaction products supports adopting an approach to critical levels based on a phytotoxic dose through stomatal uptake. Such a pathway is used for tropospheric ozone pollution (ICP Vegetation, 2017) and could take account of changed environmental conditions, including sensitivity to climate change, and vegetative ability to address harm. However, there can be practical challenges associated with establishing such dose(s) for different vegetation types, including: application of NO and NO_2 in the absence of interconversion, especially in field conditions; resourcing sufficient experimental investigations in different conditions to provide a robust evidence base; reaching agreement on a level that accounts for detoxification capacity; and, establishing a method that protects the most sensitive species which does not get unduly influenced by data extremes, which may be associated with concerns around robustness and reliability.

Another approach to setting critical level(s) may be informed by sensitive species since evidence exists for deleterious responses at different thresholds depending on whether lichens and bryophytes or vascular plants are considered. This may advocate for adopting a critical level approach like ammonia, where different thresholds of harm are defined depending on whether lichens and bryophytes are considered integral to an ecosystem’s structure and function (ICP Vegetation, 2017). This approach is somewhat similar to critical loads where thresholds are set to minimise and/or avoid damage to the most sensitive environmental receptor, with the critical load being defined as the amount of substance added to a system below which there is no apparent harm (Bobbink et al. 2022). Adopting any new approach to defining and/or quantifying critical level(s) for NO_x, expressed as NO_2 or otherwise, could require significant additional research and consensual decisions to be reached in relevant bodies e.g. through the Working Group on Effects within the Convention on Long Range Transboundary Air Pollution.

In developing the evidence base around critical level(s) for NO_x we recommend that further consideration be given to:

(i) The interplay between internal roles for NO and NO_2 and their gaseous entry into the plant, especially whether findings from studies that exogenously apply NO donor molecules can be related to atmospheric (pollutant) intake;

(ii) Direct or indirect effects of atmospherically relevant concentrations on ecosystem components other than vegetation;

(iii) How the proportion of NO_2 within NO_x affects ecosystem responses. This may be particularly relevant for vegetation in urban ecosystems, where NO can remain a significant part of the atmospheric mix (Davies et al., 2007);

(iv) Any relationships between critical levels for nitrogen compounds and critical loads for nitrogen. Indeed, given recent revisions to empirical critical loads for nitrogen (Bobbink et al., 2022) typical deposition velocities may suggest that concentration-based critical levels would need to be lower to remain within N deposition limits for sensitive systems – but the quantification of deposition velocities themselves need addressing in changed atmospheric conditions.

Overall, the persistence of elevated NO and NO_2 concentrations in the lower atmosphere remains concerning in the frame of vegetation and biodiversity of ecosystems, now and into the future. In addition, these compounds can have further indirect impacts on human wellbeing through exacerbating climate change; through the formation of acid rain, nitrate, particulate matter and ozone; and, through altering local radiative forcing (e.g. Crutzen, 1979; Edwards et al., 2024; Otero et al., 2021; Solomon et al., 1999; Sparks et al., 2001). Together with changes associated with energy transitions (Leverett et al., 2025), this underscores the urgency to (i) maintain a continued focus on NO_x, (ii) understand their wider consequences for the earth system and (iii) find methods to mitigate harm.

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13. Data Statement

No new data were collected in the compilation of this article.

14. CReDIT Taxonomy

MPP: Conceptualization, Visualization, Writing – original draft, Writing – review and editing **LJ:** Conceptualization, Writing – review and editing **KS:** Conceptualization, Visualization **FH**: Conceptualization, Writing – review and editing.

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HIGHLIGHTS

- The pollutants nitric oxide and nitrogen dioxide can play a dual role in plants.
- Negative ecological effects at lower concentrations than existing critical levels.
- Vegetative harm mediated by endogenous and donor molecule nitric oxide production.
- Urgent need for impact studies in contemporary/predicted atmospheric conditions.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: