Biomonitors of atmospheric nitrogen deposition: potential uses and limitations

Edison A. Díaz-Álvarez1,2, Roberto Lindig-Cisneros2 and Erick de la Barrera2,*

1Posgrado en Ciencias Biológicas, Universidad Nacional Autónoma de México, Av. Universidad 3000, C.U., Mexico City 04510, Mexico
2Instituto de Investigaciones en Ecosistemas y Sustentabilidad, Universidad Nacional Autónoma de México, Ant. Ctra. a Pátzcuaro 8701, Morelia, Michoacán 58190, Mexico

*Corresponding author: Instituto de Investigaciones en Ecosistemas y Sustentabilidad, Universidad Nacional Autónoma de México, Antigua Carretera a Pátzcuaro 8701, Morelia, Michoacán 58190, México. Tel: +52 (443) 322-3810.Email: delabarrera@unam.mx

Atmospheric nitrogen deposition is the third largest cause of global biodiversity loss, with rates that have more than doubled over the past century. This is especially threatening for tropical regions where the deposition may soon exceed 25 kg of N ha$^{-1}$ year$^{-1}$, well above the threshold for physiological damage of 12–20 kg of N ha$^{-1}$ year$^{-1}$, depending on plant species and nitrogenous compound. It is thus urgent to monitor these regions where the most diverse biotas occur. However, most studies have been conducted in Europe, the USA and recently in China. This review presents the case for the potential use of biological organisms to monitor nitrogen deposition, with emphasis on tropical plants. We first present an overview of atmospheric chemistry and the nitrogen metabolism of potential biomonitors, followed by a framework for monitoring nitrogen deposition based on the simultaneous use of various functional groups. In particular, the tissue nitrogen content responds to the rate of deposition, especially for mosses, whose nitrogen content increases by 1‰ per kilogram of N ha$^{-1}$ year$^{-1}$. The isotopic signature, $\delta^{15}N$, is a useful indicator of the nitrogen source, as the slightly negative values (e.g. 5‰) of plants from natural environments can become very negative (−11.2‰) in sites with agricultural and husbandry activities, but very positive (13.3‰) in urban environments with high vehicular activity. Mosses are good biomonitors for wet deposition and atmospheric epiphytes for dry deposition. In turn, the nitrogen saturation of ecosystems can be monitored with trees whose isotopic values increase with saturation. Although given ecophysiological limitations of different organisms, particular studies should be conducted in each area of interest to determine the most suitable biomonitors. Overall, biomonitors can provide an integrative approach for characterizing nitrogen deposition in regions where the deployment of automated instruments or passive monitoring is not feasible or can be complementary.

Key words: Atmospheric monitoring, ecosystem saturation, environmental pollution, epiphytic plants, nitrogen content, stable isotopes

Editor: Kevin Hultine

Received 6 May 2017; Revised 13 February 2018; Editorial Decision 16 February 2018; accepted 20 February 2018

Cite as: Díaz-Álvarez EA, Lindig-Cisneros R, de la Barrera E (2018) Biomonitors of atmospheric nitrogen deposition: potential uses and limitations. Conserv Physiol 6(1): coy011; doi:10.1093/conphys/coy011.

Introduction

Nitrogen is one of the essential elements for life and the most abundant in the terrestrial atmosphere, 80% of which is composed of N$_2$ (Soderlund, 1976). Due to the high chemical stability derived from its strong triple bond, this molecule can only be divided by processes involving large quantities of energy or through the action of specialized nitrogen-fixing microorganisms (Galloway et al., 2003). For this reason, in the pre-industrial age, more than 99% of the atmospheric...
nitrogen was unavailable for the great majority of organisms, which lack the enzyme nitrogenase required for fixing N2 (White et al., 2012). However, as a result of our growing human population and its associated demand for food and energy, the biologically available nitrogen has more than doubled in the atmosphere over the last century. Agriculture, industry and the use of automobiles are the main sources of a complex of chemical species known as reactive nitrogen (Nr), originated from the splitting of N2 (Galloway et al., 2008).

Such an increased deposition of atmospheric nitrogen has adverse effects on biodiversity. Indeed, this form of atmospheric pollution is considered to be the third largest threat to global biodiversity, following only changes in land use and climate (Sala et al., 2000; Payne et al., 2017). In particular, a deposition rate of 10 Kg of N ha−1 year−1, which has already been recorded for some ecosystems, is sufficient to cause physiological damage in plants (Fenn et al., 2003; Bobbink et al., 2010; Simkin et al., 2016; Payne et al., 2017). Global projections of nitrogen deposition are especially threatening for tropical regions, where it could exceed 25 Kg of N ha−1 year−1 during the present century (Galloway et al., 2004, 2008; Phoenix et al., 2006).

Implementation of monitoring programs that enable evaluation of the status of this phenomenon and its effects on different ecosystems is thus necessary, especially in the tropics where the most diverse biotas occur. However, the deployment and operational costs of automated air quality monitoring networks may exceed the financial capacity of developing countries. One economical alternative is the use of passive collectors, which are effective in tracking pollution over large areas. Another potential alternative for tracking the nitrogen that enters ecosystems is the use of biomonitor organisms, whose spontaneous occurrence in sites of interest allows an integrative assessment of nitrogen deposition even with a single collection event, as could be during an exploratory field campaign, or in extensive exploration efforts such as national forest surveys. A biomonitor, ‘is an organism that contains information on the quantitative aspects of the quality of the environment’ (Markert et al., 2003). The particular species to be selected in each region of interest (i) should have an ample ecological and geographic distribution, (ii) should be abundant and available throughout the year and (iii) there should be a clear relationship between the variable of interest and the response of the bioindicators (Conti and Cecchetti, 2001).

This paper presents the case for the potential utility of direct measurements of the nitrogen content and isotopic signature of plant tissue for characterizing nitrogen deposition. We start by showing how reactive nitrogen is formed and released to the atmosphere through anthropic activities and discuss the isotopic variation of these chemical species. Next, we explore the advantages and disadvantages of using different types of bio-monitors such as mosses and vascular plants, as well as their particular responses to the different forms of nitrogen.

**Reactive species of nitrogen in the atmosphere**

Agriculture releases reactive nitrogen through the volatilization and leaching of nitrogenated fertilizers (Fig. 1; Cameron et al., 2013). In turn, husbandry contributes to such reactive nitrogen through volatilized ammonia gas (NH3; Fowler et al., 2013). Industrial activity and motor vehicles also release reactive nitrogen to the atmosphere through the combustion of fossil fuels and other processes that consume large quantities of energy, which break the triple bond of N2 and form nitrogen oxides (NOx, i.e. NO and NO2; Fig. 1; Galloway et al., 2008).

Such nitrogen oxides and ammonia emitted to the atmosphere are subject to different chemical reactions that lead, for example, to the formation of water-dissolved compounds and gases (NO3−, NH4+, HNO3), and aerosols [(NH4)2SO4 and NH4NO3] (Anejia, 2001). These compounds are subsequently transferred to the surface of the earth either as dry deposition, in which the atmospheric gases or aerosols deposit by gravity, or as wet deposition, in which the nitrogen ions are deposited in fog, snow or precipitation (Fig. 1; Anderson and Downing, 2006; Decina et al., 2017).

**Isotopic composition of atmospheric reactive nitrogen**

The isotopic values of reactive nitrogen in the atmosphere have a direct relationship with the source of emission (Box 1). For instance, biogenic emissions of the soil have very negative δ15N values between −50%o and −20%o (Felix et al., 2013; Felix and Elliott, 2014). Such an ample range of values for gaseous nitrogen species leads to differences in the δ15N of the nitrogenous compounds that dissolve in atmospheric water. In particular, the isotopic values of NH3 from volatilization of ammonia in the soil and animal wastes, tend to be low, as negative as −40%o (Freyer, 1978, 1991; Kendall et al., 2007; Felix et al., 2014, 2017). In turn, the δ15N for NO3− and for NH4+ range from −15%o to 15%o, where NO3− is usually less negative than NH4+ (Hoering, 1957; Heaton, 1990; Liu et al., 2012a). In this respect, the negative values observed for the NH4+ are the result of the very negative NH3 reacting in the atmosphere (Felix et al., 2014, 2017). In addition, land use influences the δ15N of NH4+ from wet deposition are less negative in rural areas, ranging from −7%o to 1%o, than in urban zones where they range from −16%o to −5%o (Ammann et al., 1999; Stewart et al., 2002; Xiao and Liu, 2002; Garten, 2006; Liu et al., 2012a; Xiao et al., 2012; Harmens et al., 2014; Sheng et al., 2014).

With respect to dry deposition, the isotopic signature of atmospheric NOx is the result of the synergy of various factors. For example, in gasoline and diesel vehicles, both the isotopic composition (positive or negative) and the nitrogen
concentration in the fuel interact with the amount of isotopic fractionation during combustion following the mixing of N$_2$ with O$_2$, which depends on the operation of the engine (Moore, 1977; Felix et al., 2013). The burning of coal and trash can also result in an ample range of δ$_{15}$N values, depending on various factors, including the isotopic composition of the material burned, temperature, pressure and time of the reaction that influence fractionation (Box 1; Moore, 1977; Liu et al., 2012a; Felix et al., 2012, 2013; Felix and Elliott, 2014). For instance, the NOx emitted by electrical energy plants (stationary source) through the combustion of coal and trash can also result in an ample range of δ$_{15}$N values, depending on various factors, including the isotopic composition of the material burned, temperature, pressure and time of the reaction that influence fractionation (Box 1; Moore, 1977; Liu et al., 2012a; Felix et al., 2012, 2013; Felix and Elliott, 2014). For instance, the NOx emitted by electrical energy plants (stationary source) through the combustion of coal has δ$_{15}$N values between 6‰ and 13‰ in South Africa and between 5‰ and 26‰ in China (Heaton, 1990; Li and Wang, 2008). Similarly, the δ$_{15}$N of the combustion of gasoline, diesel, natural gas and the incineration of trash in France yield values of 4.6–7.7‰ (Widory, 2007). In turn, studies of roadside vehicular emissions have δ$_{15}$N of 3.7–15.0‰ (Moore, 1977). In contrast, the combustion of coal and fuel oil in the European country range from −7.5‰ to −5.3‰ (Widory, 2007). And the NOx from the combustion of gasoline in vehicles (mobile source) in South Africa reach isotopic values of between −13‰ and −2‰ (Widory, 2007).

**A framework for biomonitoring atmospheric nitrogen deposition**

The use of biomonitors can provide an integrative assessment of ecosystem responses to nitrogenous pollution with consideration of the physiological, ecological and atmospheric conditions of the region of interest (Fig. 1; Sutton...
Box 1: Stable isotopes and the δ notation

Isotopes are atoms of an element that have the same number of protons and electrons, but a different number of neutrons; i.e. they are of different atomic mass. Of the known elements, there are at least 300 stable isotopes. Some elements, such as tin, have up to ten, while 21 elements are known to only have one isotope (Sulzman, 2007).

For the case of nitrogen, there are two stable isotopes. 14N is the most common and the lightest, with an abundance on Earth of 99.63%. In turn, the heaviest isotope is 15N, with a terrestrial abundance of a mere 0.37% (Rosman and Taylor, 1997; Sulzman, 2007). A stable isotope is one that remains energetically stable over time; i.e. it neither emits energy nor decays, as it occurs with radioactive isotopes that gradually mutate towards a more stable state. The better known is the radioactive isotope of carbon, 14C, which is widely used in archaeological studies (Sulzman, 2007).

Differences in the isotopic composition of some materials are so small that they are reported in parts per thousand (‰), relative to an international standard. The standard used for the isotopic analyses of nitrogen is the N2 of the air.

The isotopic abundance of a material is determined using the following formula:

\[ \delta^{15}N(\%) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000, \]

where \( \delta^{15}N \) is the isotopic proportion of the sample relative to the standard, \( R \) is the proportion between the heavy isotope and the light isotope, so that \( R_{\text{sample}} \) is the proportion in the sample and \( R_{\text{standard}} \) is the proportion in the standard (Evans, 2001).

In chemical reactions, the differences in the \( \delta^{15}N \) of the substrate and the product result from a process known as isotopic fractionation through which the lighter isotope is favoured over its heavier counterpart. This process is described by \( \Delta \)

\[ \Delta = \delta^{15}N_s - \delta^{15}N_p, \]

where \( \delta^{15}N_s \) is the isotopic composition of the substrate and \( \delta^{15}N_p \) is the isotopic composition of the product (Evans, 2001). One tissue will be more enriched than another when it has a greater proportion of 15N, and depleted in the opposite case. For the case of biological reactions, accumulated fractionation is known as isotopic discrimination.

Almost all chemical processes are subject to some degree of isotopic fractionation, in consequence relative abundances of an isotope can reveal the nature of the process from which it comes. Biological organisms are not the exception, all their metabolic reactions reveal their interaction with the environment, allowing track biogeochemical processes. In this case, stable isotopes, particularly of nitrogen, become an excellent integrative tool for understand the organism-environment interactions.

The total nitrogen content indicates the rate of nitrogen deposition

The total nitrogen content of biomonitor can help estimate the rate of atmospheric deposition in an ecosystem. In this case, epiphytic and litophytic mosses are the best potential biomonitors because their tissue nitrogen content is determined by the prevailing atmospheric deposition. Mosses growing on the forest floor are also suitable biomonitors but to a lesser extent, given that the soil can contribute up to 37% of their tissue nitrogen content (Liu et al., 2012a).

Estimation of atmospheric deposition is thus possible from the nitrogen content of tissues, which increases by ca. 1% (dry weight) for each 10 Kg N ha\(^{-1}\) year\(^{-1}\) of deposition (Pitcairn et al., 1998; Liu et al., 2008c). This can be observed in natural areas of Europe, where the nitrogen content of mosses ranges between 0.5% and 0.7% and can double in polluted sites (Harmens et al., 2011). However, the nitrogen content of mosses only increases linearly up to a threshold of 20 Kg N ha\(^{-1}\) year\(^{-1}\), after which it decreases progressively.
Moreover, when the main form of nitrogen in deposition is NH$_4^+$ such a saturation is reached when this ion exceeds only 12 Kg N ha$^{-1}$ year$^{-1}$ (Pitcairn et al., 1998; Wiedermann et al., 2009). For instance, the nitrogen content of mosses decreases along pollution gradients in China, from 3.0% to 0.9% in urban areas and from 2.3% to 1.6% as pollution increases in rural areas (Liu et al., 2008a,b; Xiao et al., 2010). Given that the inherent nitrogen content of mosses varies amply among species, ranging from 0.1% to 0.5% for different species of pleurocarpus mosses (Pitcairn et al., 1998; Wiedermann et al., 2009; Harmens et al., 2014), it is important to determine dose-response curves for the particular candidate biomonitors in each region of interest.

An important environmental factor that influences the relationship between nitrogen content of the mosses is precipitation. Indeed, the nitrogen content is better correlated with the rate of nitrogen deposition when the annual precipitation is above 1000 mm (with the rate of nitrogen deposition when the annual precipitation. Indeed, the nitrogen content is better correlated with the rate of nitrogen deposition when the annual precipitation is above 1000 mm (Zeichmeister et al., 2008). The type of atmospheric deposition (wet or dry) also influences the nitrogen content of mosses. While wet deposition can cause a 0.01% increase in nitrogen content, dry deposition can lead to an increase of nitrogen content between 0.04% and 0.07% for each 1 Kg N ha$^{-1}$ year$^{-1}$, reaching up to 4% in sites with high rates of dry deposition of ammonia, but just up to 1.6% in sites with wet deposition (Hicks et al., 2000; Solga et al., 2005; Pitcairn et al., 2006; Liu et al., 2013a; Harmens et al., 2014).

Vascular plants can also be utilized as biomonitors of the rate of nitrogen deposition, although care must be taken in their consideration as their responses are not linear. For example, the nitrogen content of the epiphytic orchid Laelia speciosa (Kunth) Schltr., 1914, amounts to 1.2% (dry mass) under a deposition of 10 Kg N ha$^{-1}$ year$^{-1}$, but 80 Kg N ha$^{-1}$ year$^{-1}$ are required to double the nitrogen content (Díaz-Álvarez et al., 2015). This response has also been observed for seedlings of the tree species Cryptomeria japonica (Thunb. Ex Lf.) and Pinus densiflora (Siebold & Zucc.) and for adult individuals of Pinus resinosa Aiton. and Schima superba (Reinw. ex Blume) (Nakaji et al., 2001; Zhang et al., 2013). In this respect, an increased nitrogen availability often leads to the development of new tissue in vascular plants, rather than to increased levels in the existing cells, thus diluting what otherwise could amount to luxury nitrogen (Taiz and Zeiger, 2002).

Vascular plants can be an excellent complement to mosses for biomonitoring nitrogen deposition. Vascular plants prevail in environments that can be extreme for mosses to prosper, such is the case for urban heat island and arid regions. Additionally, given that vascular plants conform most of the plant cover, they are ideal for using other technologies such as remote sensing which can provide information about biomass and chlorophyll content variations as a result of alterations on atmospheric deposition (Schmidtlein et al., 2012).

The isotopic composition discerns among natural, agricultural and urban nitrogen sources

The δ$_{15}$N of plants depends on multiple factors, including mycorrhizal associations, form of nitrogen used, soil depth accessed, but most importantly atmospheric sources (Fig. 1; Table 1). Indeed, epiphytic and lithophytic plants growing in natural sites without exposure to nitrogenous pollution have δ$_{15}$N that are negative but very close to zero (Wania et al., 2002). In contrast, volatilization and leaching from agricultural and husbandry activities alters the isotopic composition of the vegetation, making it very negative (Craine et al., 2015).

In urban environments the isotopic composition of plants can be positive or negative, depending on the dominant species of reactive nitrogen in the atmosphere (Fig. 1). For instance, in cities where the predominant nitrogen species are gaseous NH$_3$ and rain bound NH$_4^+$, the δ$_{15}$N tend to be very negative (Xiao et al., 2010; Liu et al., 2012b; Felix et al., 2013, 2017). This has been documented for urban mosses in China (Liu et al., 2008a,b,c, 2012a,b, 2013b; Xiao et al., 2010) and for urban plants in the vicinity of a fertilizer factory in Brazil, whose δ$_{15}$N reaches ~41% (Stewart et al. 2002; Heaton et al., 2004).

In contrast, the isotopic signature of urban plants from various functional types is positive when NOx is the main source of nitrogen (Fig. 1). This has been documented for different mosses, including Bryum argenteum (Hedw.) and Grimmia pulvinata (Hedw) in London and Braunia sp. and Grimmia sp. in Mexico City (Pearson et al., 2000; Díaz-Álvarez and de la Barrera, 2017). Such positive values of δ$_{15}$N have also been measured for grasses in the megalopolis of Los Angeles (Wang and Pataki, 2009). The vicinity of roads, where NOx from motor vehicles are emitted, can also determine the isotopic signature in otherwise natural environments, as positive δ$_{15}$N have been measured for the needles of the conifers Picea abies (L.) H. Karst. from Norwegian forests (Ammann et al., 1999) and Pinus edulis (Engelm) within the Grand Canyon National Park in the USA (Kenkel et al., 2016). A similar response to NOx from motor vehicles has been documented for vascular epiphytes from west-central Mexico such as the orchid Laelia speciosa and the bromeliad Tillandsia recurvata (L.) (Díaz-Álvarez et al., 2016; Díaz-Álvarez and de la Barrera, 2017).

A group with special potential for biomonitoring nitrogenous pollution in tropical regions is the so called atmospheric plants, a group that includes those epiphytes and lithophytes whose nutrition relies almost exclusive on deposited nutrients. Indeed, given their cosmopolitan distribution atmospheric mosses are widely utilized biomonitors (Markert et al., 2003). Moreover, they are particularly adequate for tropical regions, where they reach their maximum diversity (Cárdenas and...
Delgadillo, 2009). However, mosses depend on the availability of water for sustaining metabolic activity, thus their monitoring potential is limited to the rainy season. In contrast, succulent epiphytes, especially those with CAM photosynthesis, can be metabolically active throughout the year, thus providing a continuous record of atmospheric deposition regardless of seasonal weather variations (Amann et al., 1999; Andrade et al., 2007; Zotz et al., 2010). Orchids, for instance, can be found in multiple ecosystems throughout the tropics from sea level up to the subalpine forest above 3500 m (Ernshaw et al., 1987). Atmospheric plants thus, allow a relatively accurate determination of both the source and the magnitude of atmospheric deposition with a very low or null isotopic discrimination given a direct water flux into the cells of mosses (Liu et al., 2012a). In this case, nitrogen is subject to foliar uptake, either by direct influx of gaseous or aqueous nitrogen, i.e. NO, NO2, NH3 and HNO3, directly from the atmosphere during gas exchange or when nitrogen particles are deposited on the plant and dissolved in rain or fog allowing the absorption of the ions NO3− and NH4+ (Hietz et al., 2002; Vallano and Sparks, 2008; Padgett et al., 2009).

Although, atmospheric plants can pick up the isotopic signal of atmospheric deposition, care must be taken when, developing atmospheric biomonitor given the occasional presence of functional roots can obscure the isotopic signal measured from plant tissues (Hietz et al., 2002; Reyes-García and Griffiths, 2009; Liu et al., 2012a). Indeed, epiphytic plants that root in the canopy soil tend to be enriched in 15N compared with those that grow on thinner branches, where no substrate accumulation occurs, because the decomposition of the accumulated organic matter produces nitrogenous compounds with δ15N close to zero (Wania et al., 2002). Such a canopy soil originated from debris of the phorophyte is depleted in 15N relative to the forest soil which tend to accumulate 15N as the volatilization and biological uptake of the lighter isotope is favoured (Wania et al., 2002; Liu et al., 2012a; Craine et al., 2015).

**Trees indicate ecosystem nitrogen saturation**

The δ15N of trees is a good indicator of the state of saturation of atmospheric nitrogen in an ecosystem. The leaves and roots of the trees of N-saturated ecosystems tend to have positive δ15N, because saturation increases soil nitrification, a process that involves high rates of isotopic fractionation (Fig. 1; Box 1). In general, plants of ecosystems exposed to low rates of atmospheric deposition tend to present δ15N that are negative but close to zero (Craine et al., 2015). However, saturation leads to increased rates of nitrate leaching, which in turn causes saturated soils to become enriched with 15N, thus their δ15N can become positive. Saturation also makes the relation between foliar δ15N and nitrification closer than that between foliar δ15N and the δ15N of the nitrogen deposition (Ollinger et al., 2002; Pardo et al., 2006; Emmett, 2007). The opposite occurs for translocated nitrogen as a series of isotopic fractionations occurs as it moves from the roots to the branches to the leaves, because a series of enzymes such as nitrate reductase, nitrite reductase and glutamine synthetase are involved in nitrogen transformation, and each one has its own amount of discrimination (Evans, 2001).

Associations with mycorrhizal fungi also influence the δ15N of the plants, and trees in particular, having the

**Table 1: Isotopic values for different plants from contrasting environments**

| Life form | Species | Rural δ15N | Urban δ15N | Reference |
|-----------|---------|------------|------------|-----------|
| Moss      | *Braunia* sp. | −3.4‰ | 3.3‰ | Díaz-Álvarez et al. (2016) |
| Mosses    | 8 species | −12‰ | 6.0‰ | Pearson et al. (2000) |
| Mosses    | 4 species | −1.4‰ | −12.5‰ | Liu et al. (2008a) |
| Moss      | *Haplocladium microphyllum* (Hedw.) | −1.3‰ | −6.5‰ | Liu et al. (2008b) |
| Mosses    | 4 species | −7.9‰ | −3.9‰ | Liu et al. (2012a) |
| Annual C3 grasses | 4 species | −4.2‰ | 13.3‰ | Wang and Pataki (2009) |
| Herb     | *Impatiens* sp. | −1.2‰ | −6.1‰ | Stewart et al. (2002) |
| Herb     | *Calluna vulgaris* (L.) | −8.6‰ | 0.2‰ | Power and Collins (2010) |
| Vascular epiphytes | 8 species | −3.0‰ | −10.9‰ | Stewart et al. (2002) |
| Epiphytic bromeliad | *Tillandsia recurvata* | −6.0‰ | 3.0‰ | Zambrano et al. (2009) |
| Epiphytic bromeliad | *Tillandsia usneoides* | −11.2‰ | −2.2‰ | Felix et al. (2016) |
| Epiphytic orchid | *Laelia speciosa* | −3.1‰ | 5.6‰ | Díaz-Álvarez et al. (2016) |
| Tree     | *Eriotheca* sp. | −1.6‰ | −5.1‰ | Stewart et al. (2002) |
| Tree     | *Picea abies* | −3.0‰ | 2.0‰ | Ammann et al. (1999) |
potential to alter both the nitrogen relations of the plants and the isotopic signature of the assimilated nitrogen (Craine et al., 2009, 2015). Under natural conditions (lower rates of atmospheric deposition), mycorrhizae supply their hosts with nitrogen that is depleted in $^{15}\text{N}$ (Emmett et al., 1998). However, saturation can induce species turnover within the mycorrhizal community, from species with high amounts of isotopic discrimination against $^{15}\text{N}$ to species with low discrimination, contributing to the isotopic enrichment of the plants and the homogenization of the isotopic signature of the ecosystem (Emmett et al., 1998; Craine et al., 2009; Sheng et al., 2014).

### Metabolic limitations of biomonitors

Biomonitors can become useful tools for detecting nitrogenous pollution over wide areas of terrestrial ecosystems. However, organismal responses are constrained by enzymatic processes. For brevity, this discussion is restricted to the metabolic limitations of mosses, which assimilate NH$_4^+$ to a greater extent when supplied simultaneously with NO$_3^-$. Likewise, these organisms preferentially assimilate organic compounds such as amino acids. For example, under simultaneous application of glycine with NH$_4^+$ and NO$_3^-$, assimilation of this amino acid is up to two times greater than that of the nitrate (Wanek and Pörtl, 2008; Wiedermann et al., 2009). The main reason for this is the high energetic cost of assimilation of NO$_3^-$, which requires two consecutive reactions. In the first, NO$_3^-$ is reduced to NO$_2^-$ by the enzyme nitrate reductase, consuming two electrons in the process. In the second, NO$_2^-$ is reduced to NH$_4^+$ by nitrite reductase, using six electrons (Heldt and Piechulla, 2011).

Nitrification reductase can be inhibited by assimilation of NH$_4^+$ from atmospheric deposition when the ratio between NH$_4^+$ and NO$_3^-$ is high (Liu et al., 2012a). Furthermore, high rates of atmospheric deposition can reduce or even completely inhibit nitrate reductase activity, whether it is due to the strong relationship between NH$_4^+$ and NO$_3^-$, or to the increased concentration of NO$_3^-$ in the deposition of nitrogen. Indeed, while certain concentrations of NO$_3^-$ are necessary to stimulate nitrate reductase synthesis and activity, an excessive amount of the ion exerts a negative feedback on the enzyme (Heldt and Piechulla, 2011). For this reason, when atmospheric deposition reaches 10 Kg N ha$^{-1}$ year$^{-1}$, a significant reduction is observed in the assimilation of NO$_3^-$ and, on exceeding 30 Kg N ha$^{-1}$ year$^{-1}$, the nitrate reductase in the mosses is totally suppressed (Gordon et al., 2002; Forsum et al., 2006; Liu et al., 2012a,b). High concentrations of atmospheric NOx (greater than 63 nL L$^{-1}$) cause suppression of nitrate reductase in mosses of different anthropic environments. Exposure to NO causes nitrate reductase activity to decrease within 24 h, while exposure to NO$_2$ causes such an activity reduction over 21 days leading to the complete loss of inducibility of nitrate reductase even when NO$_3^-$ is available (Morgan et al., 1992; Forsum et al., 2006; Liu et al., 2012a,b).

Reduced assimilation of nitrate forces the mosses to assimilate other nitrogenated compounds in the atmospheric deposition, the different isotopic values of which are presented in Table 1. As a consequence, inhibition of nitrate reductase can cause variation in the isotopic values of moss tissues and can make determination of the source of the nitrogen observed in the tissue differ from the true source by up to 21% (Liu et al., 2012a,b).

Thus, inhibition of nitrate reductase can cause a discrepancy between the nitrogen content of the mosses and the rate of atmospheric deposition on the site they inhabit. This can occur because nitrate that is deposited on the mosses can be partially assimilated or may not be assimilated at all. This will depend on the degree of inhibition of nitrate reductase. Consequently, part of the deposition (which contains the nitrate) will not be accurately recorded. In this case, estimation of atmospheric deposition could be more accurate in mosses when the ratio between NH$_4^+$ and NO$_3^-$ is higher than in deposition with low NH$_4^+$ and NO$_3^-$ ratios (Liu et al., 2012a). It has been observed that the nitrogen content of mosses is lower under wet than under dry deposition (Pitcairn et al., 2006; Liu et al., 2012a,b). Because mosses lack an epidermal cuticle, the inhibition of nitrate reductase may contribute to the leaching of a fraction of the deposited nitrate instead of being stored in the tissues of these organisms. In contrast, the leaching of unassimilated nitrogen during excessive wet deposition is greatly prevented by the cuticle for vascular plants (Pitcairn et al., 2006; Liu et al., 2012a,b).

Monitoring nitrogen deposition by means of different organisms can be a useful tool for estimating the rate of nitrogen deposition in many regions. However, caution must be taken because the inhibition of the nitrate reductase above a species-specific threshold can lead to underestimations of actual deposition rate.

### Perspectives

The nitrogen content and isotopic values of biomonitors can be suitable to inform environmental policy design for reducing the emissions of nitrogenous compounds, thus contributing to the mitigation of the adverse effects that atmospheric nitrogen deposition may have on priority ecosystems. Mosses can be especially useful because their nitrogen content responds directly to the rate of atmospheric deposition and their isotopic signature to the source. This is true up to certain deposition rate above which N accumulation decreases as a result of nitrate reductase inhibition. With the simultaneous use of different types of biomonitors, a multidimensional evaluation can be carried out regarding the state of ecosystems in the tropics. This could involve biomonitors that indicate the state of saturation, such as trees and shrubs, and those that indicate the source, such as vascular epiphytes with which it is possible to estimate the rate of atmospheric deposition using mosses. Further research
should consider the ‘calibration’ and development of potential biomonitors suitable for each region of interest. For the case of tropical regions, atmospheric plants may prove particularly adequate. In any case, caution must be exercised given that biomonitors cannot provide the exact magnitude of atmospheric deposition, but a semiquantitative approximation, including characterizing the nitrogen source. In this case, the simultaneous use of an ensemble of various species can be of great utility in identifying areas subject to pollution by atmospheric nitrogen, especially in regions where nitrogen saturation has not occurred.

Acknowledgments

We thank Keith MacMillan, who translated and revised the first English version of the manuscript, Oldemar, who illustrated Fig. 1, and useful discussions with Dr E.A. Yepez. An earlier version of this work was defended by E.A.D.A. as a requirement of the Posgrado en Ciencias Biológicas, UNAM, to advance to candidacy. This manuscript was greatly improved by thorough and generous comments by Dr K. Hultine and an anonymous reviewer, and its publication was possible thanks to the administrative skill of Dr L. Stader.

Funding

This work was funded by theDirección General de Asuntos del Personal Académico, Universidad Nacional Autónoma de México (Programa de Apoyo a Proyectos de Investigación e Innovación Tecnológica (PAPIIT) IN205616). E.A.D.-A. held a generous graduate research fellowship from the Consejo Nacional de Ciencia y Tecnología, México.

References

Ammann M, Siegwolf R, Pichlmayer F, Suter M, Saurer M, Brunold C (2009) Musgos del Valle de México: Cuadernos 40. Instituto de Biología, Universidad Nacional Autónoma de México, México, D.F., pp 9–12.

Conti ME, Cecchetti G (2001) Biological monitoring: lichens as bioindicators of air pollution assessment—a review. Environ Pollut 114: 471–492.

Craine JM, Brookshire ENJ, Cramer MD, Hasselquist NJ, Koba K, Marin-Spiota E, Wang L (2015) Ecological interpretations of nitrogen isotope ratios of terrestrial plants and soils. Plant Soil 396: 1–26.

Craine JM, Elmore AJ, Aidar MP, Bustamante M, Dawson TE, Hobbie EA, Kahmen A, Mack MC, McLauchlan KK, Michelsen A, et al. (2009) Global patterns of foliar nitrogen isotopes and their relationships with climate, mycorrhizal fungi, foliar nutrient concentrations, and nitrogen availability. New Phytol 183: 980–992.

Decina SM, Templier PH, Hutrya LR, Gately CK, Rao P (2017) Variability, drivers, and effects of atmospheric nitrogen inputs across an urban area: emerging patterns among human activities, the atmosphere, and soils. Sci Total Environ 609: 1524–1534.

Díaz-Álvarez EA, de la Barrera E (2017) Mapping pollution in a megapolis: the case for atmospheric biomonitors of nitrogen deposition. BioReiv, 118257. doi:10.1101/118257

Díaz-Álvarez EA, Lindig-Cisneros R, de la Barrera E (2015) Responses to simulated nitrogen deposition by the neotropical epiphytic orchid Laelia speciosa. PeerJ 3: e1021.

Díaz-Álvarez EA, Reyes-García C, de la Barrera E (2016) A δ15N assessment of nitrogen deposition for the endangered epiphytic orchid Laelia speciosa from a city and an oak forest in Mexico. J Plant Res 129: 863–872.

Emshaw MJ, Winter K, Ziegler H, Stichler W, Cruttwell NE, Kerenga K, Cribb PJ, Wood J, Croft JR, Carver KA, et al. (1987) Altitudinal changes in the incidence of crassulacean acid metabolism in vernal ephemeral and related life forms in Papua New Guinea. Oecologia 73: 566–572.

Emmott BA (2007) Nitrogen saturation of terrestrial ecosystems: some recent findings and their implications for our conceptual framework. Water Air Soil Pollut Focus 7: 99–109.

Emmott BA, Kjønaas OJ, Gundersen P, Koopmans C, Tietema A, Sleep D (1998) Natural abundance of 15N in forests across a nitrogen deposition gradient. For Ecol Manage 101: 9–18.

Evans R (2001) Physiological mechanisms influencing plant nitrogen isotope composition. Trends Plant Sci 6: 121–126.

Felix JD, Avery GB, Mead RN, Kieber RJ, Willey JD (2016) Nitrogen content and isotopic composition of Spanish Moss ( Tillandsia usneoides L.): reactive nitrogen variations and source implications across an urban coastal air shed. Environ Process 3: 711–722.

Felix JD, Elliott EM (2014) Isotopic composition of passively collected nitrogen dioxide emissions: vehicle, soil and livestock source signatures. Atmos Environ 92: 359–366.
Felix JD, Elliot EM, Gay DA (2017) Spatial and temporal patterns of nitrogen isotopic composition of ammonia at U.S. ammonia monitoring network sites. Atmos Environ 150: 434–442.

Felix JD, Elliot EM, Gish T, Maghirang R, Cambal L, Clougherty J (2014) Examining the transport of ammonia emissions across landscapes using nitrogen isotopes ratios. Atmos Environ 95: 563–570.

Felix JD, Elliott ME, Shaw SL (2012) Nitrogen isotopic composition of coal-fired power plant NOx: influence of emission controls and implications for global emission inventories. Environ Sci Technol 46: 3528–3535.

Felix JD, Elliott EM, Timothy TJ, McConnell LL, Shaw SL (2013) Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach. Rapid Commun Mass Spectrom 27: 2239–2246.

Fenn ME, Baron JS, Allen EB, Rueth HM, Nydick KR, Geiser L, Bowman WD, Sickman JO, Meixner T, Johnson DW, et al. (2003) Ecological effects of nitrogen deposition in the Western United States. BioScience 53: 404–420.

Forsum Å, Dahlman L, Näsholm T, Nordin A (2006) Nitrogen utilization by Hylocomium splendens in a boreal forest fertilization experiment. Funct Ecol 20: 421–426.

Fowler D, Pyle JA, Raven JA, Sutton MA (2013) The global nitrogen cycle in the twenty-first century: introduction. Philos Trans R Soc B 368: 20130165.

Freyer HD (1978) Seasonal trends of NH3 and NOx nitrogen isotope composition in rain collected at Jiillich, Germany. Tellus 30: 83–92.

Freyer HD (1991) Seasonal variation of 15N/14N ratios in atmospheric nitrate species. Tellus B 43: 30–44.

Galloway JN, Detener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA, et al. (2004) Nitrogen cycles: past, present, and future. Biogeochemistry 70: 153–226.

Galloway JN, John D, Aber JD, Erisman JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby BJ (2003) The nitrogen cascade. Bioscience 53: 341–356.

Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai Z, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA (2008) Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320: 889–892.

Garten CT Jr (2006) Nitrogen isotope composition of ammonium and nitrate in bulk precipitation and forest throughfall. Int J Environ Anal Chem 47: 33–45.

Gordon C, Wynn JM, Woodin SJ (2002) Impacts of increased nitrogen supply on high Arctic heath: the importance of bryophytes and phosphorus availability. New Phytol 149: 461–471.

Harmens H, Schnyder E, Thöni L, Cooper DM, Mills G, Leblond S, Mohr K, Poikolainen J, Santamaria J, Skudnik M, et al. (2014) Relationship between site-specific nitrogen concentrations in mosses and measured wet bulk atmospheric nitrogen deposition across Europe. Environ Pollut 194: 50–59.

Harmens H, Norris DA, Cooper DM, Mills G, Steinnes E, Kubin E, Thöni L, Aboal JR, Alber R, Carballeira A, et al. (2011) Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. Environ Pollut 159: 2852–2860.

Heaton THE (1990) 15N/14N ratios of NOx from vehicle engines and coal-fired power stations. Tellus B 42: 304–307.

Heaton THE, Wynn P, Tye AM (2004) Low 15N/14N ratios for nitrate in snow in the High Arctic (79°N). Atmos Environ 38: 5611–5621.

Heldt HW, Piechulla B (2011) Plant Biochemistry, Ed 4. Academic Press, London, England, pp 273–305.

Hicks WK, Leith ID, Woodin SJ, Fowler D (2000) Can the foliar nitrogen concentration of upland vegetation be used for predicting atmospheric nitrogen deposition? Evidence from field surveys. Environ Pollut 107: 367–376.

Hietz P, Wanek W, Wania R, Nadkarni NM (2002) Nitrogen-15 natural abundance in a montane cloud forest canopy as an indicator of nitrogen cycling and epiphyte nutrition. Oecologia 131: 350–355.

Hoering T (1957) The isotopic composition of the ammonia and the nitrate ion in rain. Geochim Cosmochim Acta 12: 97–102.

Jones L, Provins A, Holland M, Mills G, Hayes F, Emmett B, Hall J, Sheppard L, Smith R, Sutton M, et al. (2014) A review and application of the evidence for nitrogen impacts on ecosystem services. Ecosyst Serv 7: 76–88.

Kendall C, Elliott EM, Wankel SD (2007) Tracing anthropogenic inputs of nitrogen to ecosystems. In Michener R, Lajtha K, eds. Stable Isotopes in Ecology and Environment Science, Ed 2. Wiley-Blackwell, Oxford, pp 375–449.

Kenkel JA, Sisk TD, Hultine KR, Sesnie SE, Bowker MA, Johnson NC (2016) Indicators of vehicular emission inputs into semi-arid roadside ecosystems. J Arid Environ 134: 150–159.

Li D, Wang X (2008) Nitrogen isotopic signature of soil-released nitric oxide (NO) after fertilizer application. Atmos Environ 42: 4747–4754.

Liu XY, Koba K, Liu CQ, Li XD, Yoh M (2012a) Pitfalls and new mechanisms in moss isotope biomonitoring of atmospheric nitrogen deposition. Environ Sci Technol 46: 12557–12566.

Liu XY, Koba K, Makabe A, Li XS, Yoh M, Liu CQ (2013a) Ammonium first: natural mosses prefer atmospheric ammonium but vary utilization of dissolved organic nitrogen depending on habitat and nitrogen deposition. New Phytol 199: 407–419.

Liu XY, Koba K, Takebayashi Y, Liu CQ, Fang YT, Yoh M (2012b) Preliminary insights into δ15N and δ18O of nitrate in natural mosses: a new application of the denitrifier method. Environ Pollut 162: 48–55.
Liu XY, Xiao HY, Liu CQ, Li YY, Xiao HW (2008a) Atmospheric transport of urban-derived NH₃(x): evidence from nitrogen concentration and δ¹⁵N in epilithic mosses at Guiyang, SW China. *Environ Pollut* 156: 715–722.

Liu XY, Xiao HY, Liu CQ, Li YY, Xiao HW (2008b) Stable carbon and nitrogen isotopes of the moss *Haplocladium microphyllum* in an urban and a background area (SW China): the role of environmental conditions and atmospheric nitrogen deposition. *Atmos Environ* 42: 5413–5423.

Liu XY, Xiao HY, Liu CQ, Li YY, Xiao HW (2008c) Tissue N content and ¹⁵N natural abundance in epilithic mosses for indicating atmospheric N deposition in the Guiyang area, SW China. *Appl Geochem* 23: 2708–2715.

Liu X, Zhang Y, Han W, Tang A, Shen J, Cui Z, Vitousek P, Erisman J, Goulding K, Christie P, et al. (2013b) Enhanced nitrogen deposition over China. *Nature* 494: 459–462.

Lu C, Tian H, Liu M, Ren W, Xu X, Chen G, Zhang C (2012) Effect of nitrogen deposition on China’s terrestrial carbon uptake in the context of multifactor environmental changes. *Ecol Appl* 22: 53–75.

Markert BA, Breure AM, Zechmeister HG (2003) Definitions, strategies and principles for bioindication/biomonitoring of the environment. In Markert BA, Breure AM, Zechmeister HG, eds. *Bioindicators & Biomonitors, Principles, Concepts and Applications. ELSEVIER, Oxford*, pp 3–40.

Moore H (1977) The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere. *Atmos Environ* 11: 1239–1243.

Morgan SM, Lee JA, Ashenden TW (1992) Effects of nitrogen oxides on nitrate assimilation in bryophytes. *New Phytol* 120: 89–97.

Nakaji T, Fukami M, Dokiya Y, Izuta T (2001) Effects of high nitric acid load on growth, photosynthesis and nutrient status of *Cryptomeria japonica* and *Pinus densiflora* seedlings. *Trees* 15: 453–461.

Ochoa-Hueso R, Allen EB, Branquinho C, Cruz C, Dias T, Fenn ME, Manrique E, Pérez-Corona ME, Sheppard MJ, Stock WD (2011) Nitrogen deposition effects on Mediterranean-type ecosystems: an ecological assessment. *Environ Pollut* 159: 2265–2279.

Ollinger SV, Smith ML, Martin ME, Hallett RA, Goodale CL, Aber JD (2002) Regional variation in foliar chemistry and n cycling among forests of diverse history and composition. *Ecology* 83: 339–355.

Padgett PE, Cook H, Bytnerowicz A, Heath RL (2009) Foliar loading and metabolic assimilation of dry deposited nitric acid air pollutants by trees. *J Environ Monit* 11: 75–84.

Pardo LH, Templer PH, Goodale CL, Duke S, Groffman PM, Adams MB, Boeckx P, Boggis J, Campbell J, Colman B, et al. (2006) Regional assessment of N saturation using foliar and root. *Biogeochemistry* 80: 143–171.

Payne RJ, Dise NB, Field CD, Dore AJ, Carpan SJ, Stevens CJ (2017) Nitrogen deposition and plant biodiversity: past, present, and future. *Front Ecol Environ* 15: 431–436.

Pearson J, Wells DM, Seller KJ, Bennett A, Soares A, Woodall J, Ingrouille MJ (2000) Traffic exposure increases natural ¹⁵N and heavy metal concentrations in mosses. *New Phytol* 147: 317–326.

Phoenix GK, Hicks WK, Cinderby S, Kuylenstierna CJ, Stock WD, Dentener FJ, Giller KE, Austin AT, Lefroy DB, Gimeno BS, et al. (2006) Atmospheric nitrogen deposition in world biodiversity hotspots: the need for a greater global perspective in assessing N deposition impacts. *Glob Change Biol* 12: 470–476.

Pinho P, Barros C, Augusto S, Pereira MJ, Máguez C, Branquinho C (2017) Using nitrogen concentration and isotopic composition in lichens to spatially assess the relative contribution of atmospheric nitrogen sources in complex landscapes. *Environ Pollut* 230: 632–638.

Pitcairn C, Fowler D, Leith I, Sheppard L, Tang S, Sutton M, Famlardi U (2006) Diagnostic indicators of elevated nitrogen deposition. *Environ Pollut* 144: 941–950.

Pitcairn CER, Leith ID, Sheppard LJ, Sutton MA, Fowler D, Munro RC, Tang S, Wilson D (1998) The relationship between nitrogen deposition, species composition and foliar nitrogen concentrations in woodland flora in the vicinity of livestock farms. *Environ Pollut* 102: 41–48.

Power SA, Collins CM (2010) Use of Calluna vulgaris to detect signals of nitrogen deposition across an urban–rural gradient. *Atmos Environ* 44: 1772–1780.

Reyes-Garcia C, Griffiths H (2009) Ecophysiological studies of perennial bromeliaceae family in a dry forest: strategies for survival. *In de la Barrera E, Smith WK, eds. Perspectives in Biophysical Plant Ecophysiology, A Tribute to Park S. Nobel. Universidad Nacional Autónoma de México, Ciudad de México*, pp 121–151.

Rosman KJR, Taylor PDP (1997) Isotopic compositions of the elements. *Pure Appl Chem* 70: 1593–1607.

Sala OE, Chapin FS III, Armesto JJ, Berlow E, Bloomfield J, Dirzo R, Huber-Sanwald E, Huenneke LF, Jackson RB, Kinzing A, et al. (2000) Global biodiversity scenarios for the year 2100. *Science* 287: 1770–1774.

Schmidtlein S, Feilhauer H, Bruelheide H (2012) Mapping plant strategy types using remote sensing. *J Veg Sci* 23: 395–405.

Sheng W, Yu G, Fang H, Liu Y, Wang Q, Chen Z, Zhang L (2014) Regional patterns of ¹⁵N natural abundance in forest ecosystems along a large transect in eastern China. *Sci Rep* 4: 4249.

Shi XM, Song L, Liu WY, Lu HZ, Qi JH, Li S, Chen X, Wu JF, Liu S, Wu CS (2017) Epiphytic bryophytes as bio-indicators of atmospheric nitrogen deposition in a subtropical montane cloud forest: response patterns, mechanism, and critical load. *Environ Pollut* 229: 932–941.

Simkin SM, Allen EB, Bowman WD, Clark CM, Belnap J, Brooksf ML, Cade BS, Collins SL, Geiser LH, Gilliam FS, et al. (2016) Conditional vulnerability of plant diversity to atmospheric nitrogen deposition across the United States. *Proc Natl Acad Sci USA* 15: 4086–4091.

Soderlund RSB (1976) The global nitrogen cycle. *Ecol Bull* 22: 23–73.

Sølga A, Burkhardt J, Zechmeister HG, Frahm JP (2005) Nitrogen content, ¹⁵N natural abundance and biomass of the two pleurocarpous
mosses *Pleurozium schreberi* (Brid.) Mitt. and *Scleropodium purum* (Hedw.) Limpr. in relation to atmospheric nitrogen deposition. *Environ Pollut* 134: 465–473.

Stewart G, Aidar MP, Joly CA, Schmidt S (2002) Impact of point source pollution on nitrogen isotope signatures (δ15N) of vegetation in SE Brazil. *Oecologia* 131: 468–472.

Sulzman EW (2007) Stable isotope chemistry and measurement: a primer. In Michener R, Lajtha K, eds. *Stable Isotopes in Ecology and Environmental Science*, Ed 2. Blackwell Publishing Ltd, Oxford, pp 1–21.

Sutton MA, Pitcairn CER, Whitfield CP (2004) Bioindicator and Biomonitoring Methods for Assessing the Effects of Atmospheric Nitrogen on Statutory Nature Conservation Sites, JNCC Report No: 356. Countryside Council for Wales, English Nature, Joint Nature Conservation Committee and Centre for Ecology and Hydrology. http://jncc.defra.gov.uk/pdf/jncc356.pdf (last accessed, 5 November 2016).

Taiz L, Zeiger E (2002) *Plant Physiology*, Ed 3. Sinauer Associates, Sunderland, p 690.

Vallano DM, Sparks JP (2008) Quantifying foliar uptake of gaseous nitrogen dioxide using enriched foliar δ15N values. *New Phytol* 17: 946–955.

Wanek W, Pörtl K (2008) Short-term 15N uptake kinetics and nitrogen nutrition of bryophytes in a lowland rainforest, Costa Rica. *Funct Plant Biol* 35: 51–62.

Wang W, Pataki DE (2009) Spatial patterns of plant isotope tracers in the Los Angeles urban region. *Landsc Ecol* 25: 35–52.

Wang W, Pataki DE (2011) Drivers of spatial variability in urban plant and soil isotopic composition in the Los Angeles basin. *Plant Soil* 350: 323–338.

Wania R, Hietz P, Wanek W (2002) Natural 15N abundance of epiphytes depends on the position within the forest canopy: source signals and isotope fractionation. *Plant, Cell Environ* 25: 581–589.

White JF Jr, Johnson H, Torres MS, Irizarry I (2012) Nutritional endosymbiotic systems in plants: bacteria function like "Quasi-Organelles" to convert atmospheric nitrogen into plant nutrients. *J Plant Pathol Microb* 3: e104.

Widory D (2007) Nitrogen isotopes: Tracers of origin and processes affecting PM10 in the atmosphere of Paris. *Atmos Environ* 41: 2382–2390. DOI:10.1016/j.atmosenv.2006.11.009.

Wiedermann MM, Gunnarsson U, Ericson L, Nordin A (2009) Ecophysiological adjustment of two Sphagnum species in response to anthropogenic nitrogen deposition. *New Phytol* 181: 208–217.

Xiao HY, Liu CQ (2002) Sources of nitrogen and sulfur in wet deposition at Guiyang, Southwest China. *Atmos Environ* 36: 5121–5130.

Xiao HY, Tang CG, Xiao HW, Liu XY, Liu CQ (2010) Mosses indicating atmospheric nitrogen deposition and sources in the Yangtze River Drainage Basin, China. *J Geophys Res* 115: D14301.

Xiao HW, Xiao HY, Long AM, Wang YL (2012) Who controls the monthly variations of NH4+ nitrogen isotope composition in precipitation? *Atmos Environ* 54: 201–206.

Zambrano A, Medina C, Rojas C, López D, Chang L, Sosa G (2009) Distribution and sources of bioaccumulative air pollutants at Mezquital Valley, Mexico, as reflected by the atmospheric plant Tillandsia recurvata L. *Atmos Chem Phys* 9: 6479–6494.

Zechmeister HG, Richter A, Smidt S, Hohenwallner D, Roder I, Maringer S, Wanek W (2008) Total nitrogen content and δ15N signatures in moss tissue: indicative value for nitrogen deposition patterns and source allocation on a nationwide scale. *Environ Sci Technol* 42: 8667–8667.

Zhang R, Zhou Z, Luo W, Wang Y, Feng Z (2013) Effects of nitrogen deposition on growth and phosphate efficiency of *Schima superba* of different provenances grown in phosphorus-barren soil. *Plant Soil* 370: 435–445.

Zotz G, Wiebe B, Hietz P, Nadine K (2010) Growth of epiphytic bromeliads in a changing world: The effects of CO2, water and nutrient supply. *Acta Oecol* 36: 659–665.