

Ecological ramifications of the direct foliar uptake of nitrogen

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Abstract The foliar incorporation of various reactive forms of nitrogen (N) has been identified and studied for nearly 30 years. However, the ecosystem-level ramifications of this uptake pathway have only recently been considered by the scientific community. In this review, I present our current understanding of the foliar uptake process and then discuss why this pathway of N addition to ecosystems should be considered separately from the bulk deposition of N to the soil surface. Direct foliar uptake is a direct addition of N to plant metabolism and could potentially more readily influence plant growth compared to soil-deposited N. Current ecosystem process models do not partition reactive N between foliar and soil entry pathways and the influence of N deposition on ecosystem C sequestration is likely inadequately represented in most models. I also outline several research priorities for the future understanding of the ecological consequences of foliar uptake of reactive N.

Keywords Nitrogen · Nitrogen dioxide · Nitric acid · Peroxyacetyl nitrate · Ammonia

Introduction

Throughout history, the lack of reactive nitrogen (N) has largely limited the food production needed to sustain

human population growth. A desire to increase food production by the use of fertilizer and the increase in the use of fossil fuels has led to an excess in reactive N delivered to the biosphere each year, resulting in a array of human health and ecological issues (e.g., Cowling et al. 2001; Galloway et al. 2003, 2008; Erisman et al. 2007).

One major ramification of increased global reactive N is a large increase in the reactive N gases delivered to the atmosphere each year and the eventual deposition of this reactive N back to the earth's surface. Galloway et al. (2004) suggest that total global atmospheric deposition of reactive N increased from 31.6 to 103 Tg N year⁻¹ from 1860 to the mid-1990s and is expected to further increase to 195 Tg N year⁻¹ by 2050.

The response of entire ecosystems to added reactive N is the subject of a large and varied body of literature (e.g., Holland and Lamarque 1997; Aber et al. 2003; Galloway et al. 2004) and well beyond the scope of this review. The current review was prepared with the following goals in mind: to summarize the existing literature describing the foliar incorporation of reactive N, to present several arguments for why foliar and soil pathways of N incorporation into biota should be considered separately, and to suggest future avenues of research to more fully elucidate the importance of canopy incorporation of N.

The sources of reactive N in the atmosphere

Oxidized forms of N (NO_y) and ammonia (NH₃) emissions to the atmosphere result from natural sources, food production, and the generation of energy (Galloway et al. 2004). Total NO_y emissions to the atmosphere are currently estimated to be ~46 Tg N year⁻¹ with the largest contribution coming from the combustion of fossil fuels

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($\sim 20 \text{ Tg N year}^{-1}$). Total NH_3 emissions to the atmosphere are $\sim 57 \text{ Tg N year}^{-1}$ with the largest contribution coming from volatilization from animal wastes ($\sim 23 \text{ Tg N year}^{-1}$) (van Aardenne et al. 2001). Both of these estimates are increasing with time and are predicted to be $>50\%$ larger by 2050 (Galloway et al. 2004).

The various forms of NO_y and NH_3 are reactive gases that readily deposit back to the surface at relatively short time scales (minutes to days) after emission. Global deposition estimates (Lelieveld and Dentener 2000) reflect this rapid deposition and suggest a large proportion of all emissions are deposited back to the surface on a less than annual time scale.

Plant cover plays an important and controlling role in the rate of deposition of most reactive compounds including N. In general, plant canopies greatly increase the rate of deposition. However, the ultimate rates at which reactive N compounds are transferred between the atmosphere and the surface are the result of several interconnected ecological, biochemical, chemical, and edaphic controls and the overarching meteorological conditions. The challenges associated with the measurement and modeling of these fluxes has been at the forefront of ecology, biometeorology and biogeochemistry for two decades and much uncertainty still exists (e.g., Baldocchi and Wilson 2001; Monson and Holland 2001). However, there is little doubt that some proportion of the downward flux of reactive compounds interacts with, and may be absorbed, by plant canopies.

Historical perspective of foliar uptake

The role of atmospheric deposition in plant nutrition has been acknowledged and described for nearly 200 years (e.g., Von Liebig 1827). However, the foliar uptake of N was not studied intensively until the mid-twentieth century. With the general recognition of N-based air pollution, plant scientists described the foliar interactions with several reactive N compounds (Dugger et al. 1963; Hill and Bennett 1970; Spierings 1971; Wellburn et al. 1972; Zeevaart 1976 among others). The pioneering work of these early authors led to two observations that have guided much of the research in the field: at some atmospheric concentration, reactive N compounds cause phytotoxicity; the endpoint chemical products formed in the apoplast during fumigation [most commonly nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+)] are compounds assimilated by the normal plant N assimilation pathways. Therefore, the potential for both detrimental and beneficial, through fertilization, effects of foliar uptake have been considered since the earliest measurements.

Most of the early experiments were laboratory fumigations of entire plants. Due to the technology available for

both gas production and measurements, these experiments were done at high concentrations, well above those observed in the field. Therefore, phytotoxic leaf damage was often observed. For example, Zeevaart (1976) described necrotic leaf damage of up to 87% in several herbaceous plant species after 2 days of fumigation. However, the fumigation level used in this experiment was 4–11 p.p.m. (a level 100 times higher than that currently observed in the atmosphere). Interestingly, during this same experiment, Zeevaart (1976) observed large increases in the NO_2^- content of leaves, leaving open the possibility of plant fertilization even at these unnaturally high levels of fumigation.

These early experiments provided insight into many of the phytotoxic effects of reactive N and described much of the mechanisms of uptake. However, it was not until the past 25 years that adequate methodologies for controlling and monitoring gas concentration at levels representative of the atmosphere were applied to physiological measurements.

Physiological ecology of foliar uptake

Uptake mechanisms

Figure 1 describes the general understanding of the leaf uptake pathways of oxidized and reduced forms of reactive N. Nitric oxide (NO), nitrogen dioxide (NO_2), and NH_3 dissolve in the leaf apoplast to primarily form nitrous acid (HONO , HNO_2) and nitric acid (HNO_3) that then dissociate to NO_2^- , NO_3^- , and protons and NH_4^+ , respectively (Zeevaart 1976; Wellburn 1990; Gessler and Rennenberg 1998). The NO/NO_2 reaction is irreversible and dependent upon the concentration of $\text{NO}_2^-/\text{NO}_3^-$ in the apoplastic solution (Remmler and Campbell 1986; Stulen et al. 1998). The dissolution of NH_3 into the leaf apoplast is driven by the gradient in concentration between the NH_3 concentration in the air of the substomatal space and the surrounding mesophyll tissue. This gradient is variable depending upon the ambient NH_3 concentration and in many areas far from point sources of NH_3 , a net emission of NH_3 is observed from leaves. This suggests NH_3 has a leaf-level compensation point (Krupa 2003). A compensation point has also been reported for NO_2 (Thoene et al. 1991; Sparks et al. 2001; Teklemariam and Sparks 2006) but it is usually small ($<50 \text{ pmol}$) and often does not appear congruent with whole canopy estimates (Lerdau et al. 2000). It has been suggested there is some level of storage (in the apoplast or in cellular vacuoles) of NO_3^- and NH_4^+ before eventual assimilation (Grundmann et al. 1993; Qiao and Murray 1997). However, these studies were conducted at very high concentrations and similar storage has not been reported in studies conducted at realistic atmospheric concentrations.

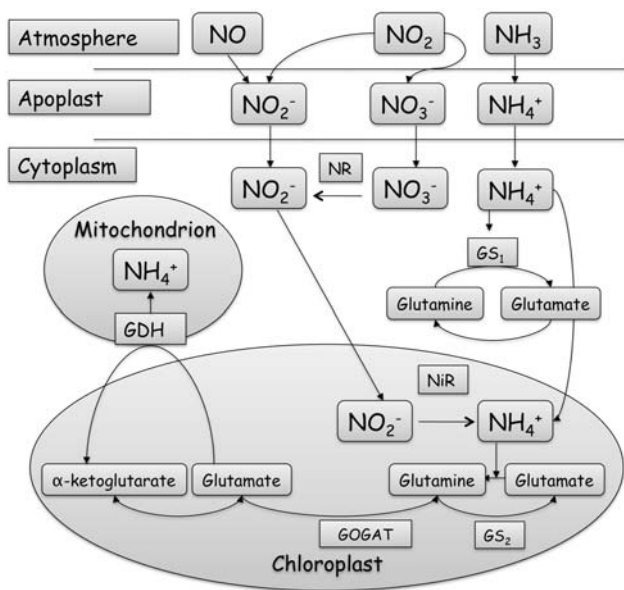


Fig. 1 Primary biochemical processes describing the foliar uptake and assimilation of atmospheric ammonia (NH_3), nitric oxide (NO), and nitrogen dioxide (NO_2). Adapted from Stulen et al. (1998). GS_1 Cytosolic isoform of glutamine synthetase, GS_2 chloroplastic isoform of GS, NR nitrate reductase, NiR nitrite reductase, $GOGAT$ glutamate synthase, NO_2^- nitrite, NO_3^- nitrate, NH_4^+ ammonium

Once in the apoplast, NH_4^+ is transported into the cell and assimilated by the glutamine synthetase (GS) and glutamate synthase (GOGAT) systems (Lea and Mifflin 1974; Tischner 1987; Wallsgrave 1987; Krupa 2003). The other major source of NH_3 in the cytosol is photorespiratory and, as such, the NH_3 derived from foliar uptake interacts directly with photorespiratory processes. Glutamate dehydrogenase has also been suggested as an alternative to the GS/GOGAT system (Srivastava and Singh 1987; Stulen et al. 1998), but appears to play a minor role in the assimilation of atmospheric NH_3 (Rhodes et al. 1989; Krupa 2003). GS is often found in plants as two isoforms, one cytosolic and the other chloroplastic (Fig. 1). The relative importance of GS_1 and GS_2 varies across plant species (Mifflin and Habash 2002) and both may be involved in the assimilation of NH_3 .

After dissolution to NO_2^- and NO_3^- from NO_2 in the apoplast, both forms are transported into the cell where NO_3^- is rapidly reduced to NO_2^- by the enzyme nitrate reductase (Stulen and ter Steege 1995). NO_2^- is then transported into the chloroplast and reduced to NH_4^+ by nitrite reductase and eventually incorporated into plant proteins (Lea et al. 1994; Fig. 1). The source of NO_3^- in the leaf can therefore be from both foliar uptake and root transport. However, many trees, especially conifers, preferentially absorb NH_3 at the root surface or reduce N in the roots and do not transport appreciable amounts of NO_3^- in the xylem to the leaves. Therefore, in these species,

atmospheric N may be the only or most significant source of NO_3^-/NO_2^- to the leaves.

NH_4^+ and NO_3^- accumulate on leaf surfaces from the dry deposition of both gases and particles (Davidson and Wu 1990; Bobbink et al. 1992). A large body of evidence comparing bulk deposition to canopy throughfall has suggested an uptake of leaf-surface N (e.g., Lovett et al. 1985; Garten and Hanson 1990; Bobbink et al. 1992 among others). However, the mechanisms of how these ions enter the leaf are still unclear. Often throughfall measurements reveal a net release of other ions (e.g., K^+ , Mg^{2+} , Ca^{2+}) suggesting a process of cation exchange in the canopy. Diffusion through stomata and cuticular transport have also been suggested as mechanisms (Bowden et al. 1989; Boyce et al. 1996).

The uptake mechanisms governing the leaf uptake of HNO_3 vapor have remained elusive due to the extreme reactivity of this compound. A large body of literature using primarily micrometeorological techniques has provided estimates of total HNO_3 flux to ecosystems (e.g., Meyers et al. 1989; Janson and Granat 1999; Sievering et al. 2001; Pryor et al. 2004). However, these methods do not necessarily help to elucidate the uptake mechanisms at the leaf level. Mechanistic work has suggested HNO_3 , in contrast to other reactive N gases, is primarily deposited to the cuticle rather than taken up via stomata (Dasch 1989; Marshall and Cadle 1989). Modeling based on the chemical characteristics of HNO_3 (Taylor et al. 1988; Hanson and Taylor 1990) and ^{15}N - HNO_3 tracer studies (e.g., Vose and Swank 1990) have further supported that HNO_3 is primarily deposited to leaf cuticles.

Leaf uptake of HONO has been reported (Schimang et al. 2006) and the pathway of assimilation would likely be similar to that of NO_2 . The leaf uptake of the organic form of nitrogen peroxyacetyl nitrate ($CH_3C(O)O_2NO_2$; PAN) has also been described (Okano et al. 1990; Sparks et al. 2003; Teklemariam and Sparks 2004). These authors suggest the assimilatory pathway after incorporation into the leaf apoplast would mirror that for NO_2 . However, the mechanism of how PAN disassociates into the apoplastic water remains unresolved.

Leaf-level controls

The primary control over the foliar uptake rate of most reactive N gases is the size of the stomatal aperture. The rate of the uptake of NO_2 into the leaf has been reported to be strongly related to stomatal conductance in a multitude of studies (Saxe 1986; Hanson and Lindberg 1991; Hargreaves et al. 1992; Weber and Rennenberg 1996; Sparks et al. 2001; Gut et al. 2002; Teklemariam and Sparks 2006; Eller and Sparks 2006 among others). This relationship appears to be linear for most plants and is the primary factor controlling the magnitude of flux into the leaf. Similarly, the leaf uptake of

gaseous NH_3 is strongly controlled by the stomatal aperture (Duyzer et al. 1994; Hanstein et al. 1999; Gessler et al. 2000, 2002). However, as described in “Uptake mechanisms”, the concentration of NH_4^+ in the apoplastic water strongly influences the flux rate (and direction) of NH_3 flux and the strong control of stomatal conductance is often minimized under physiological or environmental conditions leading to high apoplastic NH_4^+ concentrations (Gessler and Rennenberg 1998; Wyers and Erisman 1998; Herrmann et al. 2001). Although the complete uptake mechanisms have yet to be elucidated for HONO and organic forms or reactive N (primarily PAN), the leaf uptake of both of these gases is strongly related to stomatal aperture (Sparks et al. 2003; Schimang et al. 2006; Teklemariam and Sparks 2006). Because of high reactivity, the flux of HNO_3 is often unrelated to stomatal conductance (Meyers et al. 1989; Pryor and Klemm 2004). The flux of particulate forms of NH_4^+ and NO_3^- into leaves is likely related to the stomatal aperture. However, this relationship has yet to be demonstrated experimentally.

After stomatal resistance to diffusion, the strongest control over leaf uptake of reactive N gases is the dissolution of the gases into the apoplastic water and transport into mesophyll cells. Several authors have suggested resistance at the level of the mesophyll to plant uptake (Thoene et al. 1991, 1996; Hereid and Monson 2001; Sparks et al. 2001; Gut et al. 2002; Teklemariam and Sparks 2006; Eller and Sparks 2006). The primary hypotheses presented have proposed antioxidant compounds in the apoplast facilitating rapid uptake (Ramage et al. 1993; Teklemariam and Sparks 2006; Eller and Sparks 2006; Haberer et al. 2006) and regulation of the transport and consumption of the apoplastic endpoint products (NO_2^- , NO_3^- , and NH_4^+) by downstream enzymatic activity (Zeevaert 1976; Murray and Wellburn 1985; Rowland et al. 1987; Bender et al. 1991; Thoene et al. 1991; Hur and Wellburn 1994; Hufton et al. 1996; Wellburn 2002; Eller and Sparks 2006). Eller and Sparks (2006) suggested the uptake of NO_2 to leaves could be predicted with fidelity using a correlative model considering stomatal conductance, apoplastic ascorbate, and leaf nitrate reductase activity. However, this model described only a single plant species and it is unclear if such a model would be applicable across multiple plant species or functional types.

Leaf- and canopy-level fluxes of NH_3 are usually modeled using a compensation model originally developed by Sutton et al. (1998). This is a canopy resistance model that uses a stomatal compensation point for NH_3 and soil emission. The stomatal compensation point is calculated (see Nemitz et al. 2000) as a function of temperature and the leaf emission potential (the ratio of NH_4^+ to H^+ in the apoplast). This method has been used successfully in several experimental and modeling studies (Flechard and Fowler 1998; Schjoerring et al. 1998; Milford et al. 2001; Sparks et al. 2008).

The transport of leaf-surface NO_3^- and NH_4^+ ions primarily occurs through cuticular diffusion (Peuke et al. 1998). The indirect evidence for this stems from the observation that NH_4^+ leaf uptake is higher than NO_3^- leaf uptake in most tracer experiments (e.g., Garten and Hanson 1990; Peuke et al. 1998). Our current understanding of plant cuticles suggests cations are transported much more readily through cuticles than anions (Tyree et al. 1990). Plant cuticles tend to be positively charged at pH values >3 (Schonherr and Bukovac 1973) and negatively charged ions are excluded from cuticular diffusion.

A mechanism for stomatal transport has been presented. Burkhardt and Eiden (1994) suggested continuous water layers connect the leaf surface to the mesophyll through the stomata during wetting allowing the diffusion of ions. However, this hypothesis has not been fully tested to date.

Relative magnitude compared to other sources of N

Determining the relative magnitude of foliar incorporation of N compared to soil-derived N has been challenging. Sievering et al. (2007) have suggested that nearly 50% of the N demand of a forest in Colorado, USA, is met by canopy incorporation of reactive N. However, this is one of the highest estimates seen in the literature and canopy uptake of reactive N is variably reported as 0–50% of plant N demand (e.g., see review of Harrison et al. 2000). The variability of such estimates is probably driven by two factors: the inherent challenges in estimating canopy uptake from throughfall measurements, and an incomplete closure of the N budget at any given site. Although variable, the estimates of canopy uptake do suggest it is a consequential pathway for N entry into ecosystems.

At the whole-plant level, Vallano and Sparks (2007) used combined fumigation/hydroponic systems and isotopic tracers to estimate that up to 16% of total plant growth N can be derived from atmospheric NO_2 . This agreed relatively well with earlier modeled estimates by Muller et al. (1996) and Ammann et al. (1999). This study considered only one chemical species of reactive N and it is likely the sum of all potential foliar inputs of N would be higher and could potentially match those reported in some field throughfall estimates.

Phytotoxicity versus airborne nutrition

Laboratory estimates of phytotoxicity compared to field observations

All plant foliage is sensitive to reactive N at high enough concentrations (Wellburn 1990; Okano et al. 1990; Krupa 2003). However, at concentrations reflective of the current

atmosphere (even in polluted areas) visible signs of phytotoxicity due to direct exposure are rarely observed or at least are not discernable from the influence of bulk deposition.

Field experiments have shown variable effects of leaf exposure to reactive N on overall plant growth with both increased and decreased growth rates observed (e.g., Adaros et al. 1991; Saxe 1994; Hufton et al. 1996). However, detrimental physiological responses including decreased photosynthesis (Saxe 1986), effects on plasma membranes (Russell et al. 1999) and plant water-use efficiency (Siegwolf et al. 2001) have been reported coincident with leaf fumigation with reactive N.

Evidence for nutritive effects of foliar uptake in the field

There is significant debate about whether total N deposition to ecosystems significantly influences plant growth. Recent reviews suggest an enhanced growth effect of added N in both temperate and boreal forests of Europe and North America (Högberg 2007; Magnani et al. 2007). However, modeling efforts (Currie et al. 2004) based on long-term N addition experiments and short-term ^{15}N cycling studies (Nadelhoffer et al. 1999) suggest small to non-existent influences on plant growth. These efforts do not consider soil- and foliar-derived N separately. It would be intriguing to see if experiments which add reactive N to the soil surface would show increases in plant biomass if that N were applied to the canopy. However, large-scale experiments adding reactive N directly to the canopy are rare. The largest experiment to date was conducted at Howland Forest, Maine, USA where NH_4NO_3 was added to the forest canopy as a liquid mist. The impacts of this addition to growth have yet to be published (although see Gaige et al. 2007). Experiments like this one will shed some light on the influence of ion additions of N to the canopy. However, the simulation of the addition of all N to the canopy, including gases and particles, remains a challenge for the future.

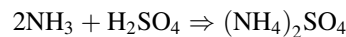
Why should foliar uptake of reactive N be considered separately from soil-deposited N?

The level of atmospheric reactive N available for foliar uptake and total rates of N deposition are obviously related; higher atmospheric concentrations drive both processes. Therefore, the obvious question is: are there reasons the foliar uptake and soil deposition pathways should be considered separately?

Transport distances of reactive N compounds

Table 1 describes the atmospheric lifetimes of the dominant chemical species involved in both foliar uptake and bulk N deposition. The lifetime of a molecule in the table does not necessarily indicate time until chemical destruction, but considers the rate of deposition to the surface. The factors assumed in the lifetime estimate are listed in the footnotes to Table 1.

Table 1 shows that there are significant differences among various forms of reactive N in lifetime and, hence, distances traveled from sources of emission. Further, the atmospheric chemistry of reactive N (Crutzen 1979) plays a significant role in transport distance. The primary emission compounds (NO , NO_2 , and NH_3) undergo chemistry that significantly lengthens the distanced traveled before deposition or foliar uptake. NO and NO_2 may react with oxidized hydrocarbons to form PAN. PAN is relatively stable in the atmosphere, deposits to the surface less readily than NO_2 , and allows reactive forms of oxidized N to be transported long distances. NH_3 (a compound that deposits to the surface very rapidly and has an atmospheric lifetime of less than 1 day) is the only strongly basic compound in the atmosphere and readily reacts with acids in the atmosphere by reactions such as:



Therefore, some portion of emitted NH_3 is converted to NH_4^+ in the atmosphere, significantly extending its

Table 1 Chemical formula and atmospheric lifetime of the major N-containing chemical species taken up directly by plant foliage

Chemical species	Chemical formula	Atmospheric lifetime
Ammonia/ammonium	$\text{NH}_3/\text{NH}_4^+$	1–10 days ^a
Nitric oxide	NO	57–600 s ^b
Nitrogen dioxide	NO_2	143 s (daytime) 7 h (nighttime) ^c
Nitrate radical	NO_3	5–6 s (daytime) ^d >1,000 s (nighttime)
Nitric acid	HNO_3	0.5 days ⁻¹ m ^e
Peroxyacetyl nitrate (PAN)	$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	2–600 h ^f

^a Estimates include lifetime of NH_3 and particulate NH_4^+ from Erismann et al. (2007) and Schlesinger and Hartley (1992)

^b Calculated for reactions with O_3 and HO_2 ; reaction coefficients from Finlayson-Pitts and Pitts (2000)

^c Reaction coefficients from Finlayson-Pitts and Pitts (2000)

^d Daytime zenith angle = 0° ; nighttime τ calculated for reactions with NO_2 and volatile organic compounds in an unpolluted atmosphere, from Brasseur et al. (1999)

^e Includes heterogeneous incorporation into clouds and aerosols, from Brasseur et al. (1999)

^f Assuming no new PAN synthesis, from Singh et al. (1990)

atmospheric lifetime as a particle, aerosol, or as an ion in water (Schlesinger and Hartley 1992). The effect of differential atmospheric lifetimes coupled with a non-random distribution of point sources suggests that sites arrayed across the landscape not only receive different amounts of total reactive N but also different proportions of chemical species in that deposition. In general, NO_2 and NH_3 will dominate deposition near point sources of emission, organic compounds like PAN will become more dominant further downwind after the air mass begins to oxidize, and highly oxidized forms like HNO_3 will dominate fully oxidized air masses. This is, of course, a simplified view and does not consider several factors including the disassociation of PAN back to NO_2 and the variability of air mass movement across the landscape. However, it is likely that different environments receive dramatically different amounts and compositions of reactive N.

Foliar uptake is likely to be most important in environments dominated by reactive N compounds likely to enter plant stomata at a rate higher than deposit to other surfaces in the environment. This appears to be the case for NO_2 (Sparks et al. 2001; Wellburn 2002), PAN (Sparks et al. 2003), and other forms of organic nitrate (Lockwood et al. 2008), but not the case for NH_3 and HNO_3 (Bytnerowicz et al. 1998; Nielsen et al. 2002). Therefore, the partitioning of total deposition between foliar uptake and deposition to other surfaces could be very different across environments.

The foliar incorporation pathway leads to a direct addition of NO_3^- and NH_4^+ to metabolism

The pathway of direct foliar uptake of reactive N is clearly fundamentally different from uptake of N deposited to other surfaces in the environment. Long- and short-term studies of N application to the soil surface (Nadelhoffer et al. 1999; Currie et al. 2004; Pregitzer et al. 2008) have shown that at least some of the deposited N is incorporated into soil organic matter and has some likelihood of returning directly back to the atmosphere as a gas (through nitrification, denitrification, or volatilization) or being leached from the system and never being incorporated into plants. In contrast, foliar uptake is a direct addition to plant metabolism and competes with no other process in supporting plant growth.

Whether foliar uptake of N supports net growth likely depends on the balance between plant N limitation and the phytotoxic effects of exposure. Phytotoxic effects are well documented for both NH_3 (Krupa 2003) and oxides of N (Wellburn 1990). However, the concentrations where injury or decreased performance occur are usually well above the concentrations seen in all but the most polluted

environments. It should be pointed out that the isolated effects of foliar uptake have been primarily assessed over short timescales and it is very likely long-term chronic influences on growth do occur.

Detrimental ecosystem-level effects of soil-added reactive N

Chronic soil deposition of reactive N has a suite of potential detrimental effects including increases in NO_3^- leaching and loss of base cations (Hultberg et al. 1994; Hedin et al. 1995), soil acidification (van Breeman et al. 1995), and forest decline (Aber 1992; Stoddard 1994; McNulty et al. 1996). Therefore, the growth response of plants to N deposition may be particularly sensitive to the partitioning between the foliar and soil pathways (i.e., the larger the proportion moving directly through foliage the larger the growth response).

Ecosystem-level considerations

Interaction with rising carbon dioxide concentrations

Consideration of foliar N uptake is compelling against the backdrop of global increases in atmospheric carbon dioxide (CO_2). The debate over the general relationship between simultaneous increases in CO_2 and reactive N is ongoing (Nadelhoffer et al. 1999; Högberg 2007) and the potential differential role of soil versus foliar incorporation of added N is not considered in most simulations (White et al. 2000; Pepper et al. 2005). Increases in available N at the site of carboxylation (i.e., the leaf) could potentially drive additional C gain in otherwise N-limited sites. However, very little experimental evidence exists for such a scenario.

Hufton et al. (1996) examined the combined influence of increased CO_2 and $\text{NO} + \text{NO}_2$ fumigation in hydroponically grown lettuce and found a 20% increase in growth in plants experiencing the combined fumigation compared to elevated CO_2 alone. The fumigation level of reactive N in this study was 10 times higher than that experienced by plants in the field (450 p.p.b.), but does suggest foliar uptake of N can influence growth under elevated CO_2 .

The influence of added N directly from the atmosphere to the apoplast is likely very complex. Bloom et al. (2001) observed NO_3^- accumulation in leaves under elevated CO_2 in wheat and suggested multiple mechanisms whereby NO_3^- assimilation is inhibited under elevated CO_2 . This suggests that the effect of additional NO_3^- from foliar uptake may either be unimportant under elevated CO_2 (if inhibition of NO_3^- is severe) or that the higher apoplastic concentrations of NO_3^- generated by foliar uptake may offset the slower rate of assimilation.

Herbivory

Increased atmospheric CO₂ levels have often been linked to herbivory through changes in leaf N content leading to increased levels of herbivory (e.g., Coviella and Trumble 1999; Hunter 2001). There is some debate as to whether this phenomenon occurs predictably in the field (Hamilton et al. 2004), but, if true, foliar uptake of N is likely to strongly influence this relationship.

A common observation of plants under fumigation by reactive N is an increase in at least some aspects of leaf N (Rowland 1986; Rowland et al. 1987; Segsneider et al. 1995; Hanstein et al. 1999; Takahashi et al. 2005) and there is some level of correspondence between natural variation in foliar uptake and leaf N contents (Calanni et al. 1999; Tomaszewski and Sievering 2007; Sievering et al. 2007). Therefore, foliar uptake has the potential to alter the stoichiometry of C and N in plant tissues in opposition to that driven by elevated CO₂. This would likely have an influence on herbivory and should be experimentally tested in the future.

N-limited ecosystems

Many of the potential influences of foliar uptake of N compounds as highlighted in this review are focused on N-limited environments where the added N may have some influence on plant growth. N (and other nutrient) limitations to plant growth are common in many landscapes (Field 2001), but the likely impact of N deposition in general and the foliar uptake of N in particular must be interpreted in the context of the limitations to growth. For example, the influence of N deposition and the foliar uptake of N will be strongly modulated by water availability in arid and semi-arid regions. Most field research to date has largely focused on either N-limited ecosystems or ecosystems receiving large amounts of reactive N deposition due to human activities. Much less is known about the influence of overall N deposition and foliar uptake in non-N-limited/low deposition ecosystems.

Measurements at different levels of integration

Scaling from leaf-level measurements

As with all leaf-level physiological measurements, scaling up from estimates derived from single leaves is very challenging. Part of the problem is simply the extrapolation of small errors in precision. Small percentage errors in leaf-level measurements are compounded when extrapolated to whole plants and canopies. Further, leaf and branch measurements of foliar uptake often utilize a cuvette or

enclosure that, despite sophisticated levels of control, differs in many regards to the natural environment.

Despite these difficulties, the largest knowledge base regarding foliar uptake of reactive N comes from small-scale measurements and should be utilized in larger-scale process models and experiments. Currently, laboratory and field measurements have generated leaf-area specific flux rates for NO (e.g., Hereid and Monson 2001; Teklemariam and Sparks 2006), NO₂ (e.g., Thoene et al. 1996; Weber and Rennenberg 1996; Gessler et al. 2000, 2002; Sparks et al. 2001; Eller and Sparks 2006), NH₃ (e.g., Fangmeier et al. 1994; Hanstein et al. 1999; Ashraf et al. 2003; Castro et al. 2006), PAN (e.g., Sparks et al. 2003; Teklemariam and Sparks 2004), and HONO (e.g., Schimang et al. 2006). Direct estimates of leaf uptake of HNO₃ and ionic and particulate forms of NO₃⁻ and NH₄⁺ are less well resolved (e.g., Hanson and Taylor 1990; Burkhardt and Eiden 1994; Bytnerowicz et al. 1998; Peuke et al. 1998) and only first approximation estimates can currently be made. Many of the uptake estimates listed above can be expressed over a range of plant species, ambient gas concentrations and stomatal conductances. Until larger integration estimates are made (see below), leaf-level uptake estimates should be used to partition N additions to ecosystems between foliar and soil pathways in process models.

Throughfall measurements

In the early 1990s, Lovett and Lindberg (1993) examined precipitation and canopy throughfall chemistry at sites across Europe and North America and estimated that ~40% of all N deposited is retained by the canopy. Since that time, studies have interpreted the difference between total deposition (wet and dry) to the canopy and throughfall to be a measurement of canopy retention and potential assimilation of reactive N into plant biomass (e.g., Balestrini and Tagliaferri 2001; Gaige et al. 2007). Recently, Sievering et al. (2007) have put forth the idea of canopy N uptake (CNU) and related estimates of CNU to net ecosystem exchange of C (NEE). This general concept may be an integrated way to approach the relationship between foliar incorporation of N and plant growth. However, several shortcomings currently limit the usefulness of this approach. First, it remains difficult to link canopy retention to assimilation. For example, preliminary measurements from a large canopy-level application of ¹⁵N label to a forest in Maine indicated less than 5% of the label was recovered in live foliage and wood after 2 years of N addition to the canopy (Dail et al., in review). Second, most throughfall-based analyses do not account for gaseous losses of N from the canopy. We know that significant phytolysis of reactive N yielding gaseous losses occurs from snow and ice (Dibb et al. 1998; Munger et al. 1999;

Beine et al. 2002) and recent evidence suggests similar phytolytic losses occur from plant canopies (Raivonen et al. 2006). Such gaseous losses would cause canopy uptake estimates to decrease. Third, it has not been demonstrated the N added through CNU can influence physiology at the timescale Sievering et al. (2007) use for comparison to NEE. These authors use NEE and CNU estimates from time periods corresponding to the time between precipitation events (the timescale necessary for a canopy throughfall measurement). Often these time periods are short (a few to several days) and it is unclear if N assimilated into the canopy can influence physiology at this timescale.

Micrometeorological measurements

Perhaps some of the most powerful methods for assessing the integrated deposition of N are micrometeorological methods such as eddy covariance and relaxed eddy accumulation. These and other meteorological methods have been used to quantify fluxes of various components of reactive N to plant canopies (Pryor et al. 2001; Riedo et al. 2002; Pryor and Klemm (2004); Butterbach-Bahl et al. 2004; Farmer et al. 2006; Turnipseed et al. 2006). However, it is challenging to separate the foliar incorporation component from the overall flux estimate generated using these methods. Downward fluxes to canopies are the summation of deposition to surfaces, foliar (stomatal) deposition, and chemical destruction. The estimate is also strongly influenced by meteorological conditions (Baldocchi and Wilson 2001). Therefore, although meteorological methods can provide robust estimates of the fluxes of reactive N, additional information is needed to partition this flux among different pathways of deposition and chemical destruction.

Appropriate experiments for informing future modeling efforts

Modeling estimates of the global enhancement of forest growth due to atmospheric reactive N deposition vary dramatically between 0.1 and 2 Pg C year⁻¹ (Schindler and Bayley 1993; Townsend et al. 1996; Holland et al. 1997). Most of these efforts simply assume growth enhancement is proportional to N deposition and do not necessarily differentiate foliar incorporation from soil-deposited N.

The information most useful to process modeling is a reasonable partitioning of deposited N among pathways leading to plant assimilation (soil vs. foliar) and estimates of how this deposited N increases plant growth across a variety of ecosystems.

Producing these estimates will require a combination of ecosystem and fine-scale physiology measurements. Ideally, meteorological measurements of flux and leaf-level uptake measurements could be co-located at focal sites and coordinated with laboratory measurements of dominant plant species. A research science plan suggestive of such a strategy has been presented by a workshop aimed at increasing understanding of atmosphere-biosphere N interactions (Holland et al. 2005).

Important future research directions

Determine the relationship between instantaneous plant performance and foliar uptake of reactive N

Physiological responses to foliar incorporation of reactive N have been studied (see “[Physiological ecology of foliar uptake](#)” and “[Phytotoxicity versus airborne nutrition](#)” above). However, several important questions have rarely been addressed. Does the availability of reactive N to leaves influence short- and long-term photosynthetic capacity? What is the cost associated with overcoming the phytotoxic effects of the incorporation of reactive N by leaves and does it increase rates of respiration? How does the net effect of physiological alteration influence plant growth?

Advances in technology for determining dry N deposition

The monitoring of wet deposition is done routinely at many sites. However, the monitoring of dry deposition is much rarer. The best regional estimates of dry N deposition within North America come from the Environmental Protection Agency sponsored Clean Air Status and Trends Network (CASTNet) sites. However, CASTNet sites only measure a subset of dry-deposited N (particulate NO₃⁻ and NH₄⁺ and gas-phase HNO₃) and do not quantify several important species of gaseous N (e.g., NH₃, and major components of total NO_y including NO₂, dinitrogen pentoxide, HONO, PANs, and alkyl nitrates). In addition, CASTNet sites are relatively rare. Similar monitoring networks exist in Europe with many of the same problems. New technologies for the monitoring of dry deposition of reactive N are needed for any scaling exercise of both total N deposition and foliar uptake.

Examination of the affects of foliar N uptake under increased CO₂ concentrations

As discussed in “[Interaction with rising carbon dioxide concentrations](#)”, some evidence exists that direct foliar

incorporation of reactive N may increase the growth of plants under elevated CO₂. However, this relationship has not been tested rigorously and has only been examined in very few plant species. If a synergistic relationship exists between canopy uptake of reactive N and plant growth, the influence on C sequestration is potentially large and should be quantified in multiple plant functional types.

Develop methods for partitioning between foliar and root N uptake

Partitioning of deposited N among pathways of incorporation (foliar vs. soil) will be key to our future understanding of the influence of N deposition on ecosystem productivity. It is unlikely any single method can be used to determine this partitioning. However, a combination of methods that quantify total N deposition, rates of foliar uptake of various compounds, and the influence of incorporation on plant growth could be used to determine partitioning in key ecosystems.

Incorporation of the foliar uptake of reactive N into regional and global production models

As discussed in “[Appropriate experiments for informing future modeling efforts](#)”, current process models either do not consider foliar uptake of reactive N separate from total N deposition or make this separation without firm experimental evidence. Given the potential differences between soil- and canopy-deposited N, a future research priority should be to reasonably partition these pathways in process models.

Conclusions

In the past 30 years, large strides forward have been made in our understanding of the leaf uptake of reactive N. More work is needed to elucidate the leaf uptake mechanisms of ionic, particulate, and organic forms, but we do understand the basic mechanisms of uptake for the dominant inorganic forms (NO, NO₂, NH₃) of reactive N. However, similar strides have not been made in determining the ecological importance of foliar uptake. It is still unclear when or if foliar uptake enhances plant growth and what the direct connections are between uptake and physiological processes like photosynthesis.

Foliar uptake of reactive N is likely very different from the acquisition of N by plants after soil deposition and should be considered differently in ecosystem process modeling. In order to facilitate this, research priority should be placed on combined ecosystem and physiology

studies aimed at accurately partitioning the entry of reactive N into ecosystems between foliar and soil pathways.

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