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Title

Nitrogen deposition: The up and down side for production agriculture

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Introduction

Nitrogen compounds are major contributors to air pollution. Gaseous and particulate nitrogen-containing pollutants are generated by industrial, agricultural, and transportation activities. Oxidized forms may be present as primary pollutants such as NO, NO₂, or N₂O from combustion processes and soil microbes, or in the reduced forms of NH₃ and NH⁺, which are primarily from agricultural activities, but also some urban sources and catalytic conversion of automobile exhaust (Fraser and Cass, 1998). Once emitted, nitrogenous pollutants engage in many chemical reactions leading to secondary pollutants, both organic such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), and inorganic such as the synthesis of HNO₃ vapor. Transport and deposition of these pollutants have serious consequences for managed and unmanaged ecosystems (Lovett, 1994). Both NH₃ and HNO₃ pollutants, and their aerosol or particulate reaction products, deposit to landscapes, over time contributing to the native fertility. Nitrogen deposition, in general, has been implicated in a wide variety of ecosystem response (Vitousek et al. 1997) including eutrophication of streams (Fenn and Poth, 1999), lakes and estuaries (Hameedi et al., 2007), changes in plant community composition (Brooks, 2003, Clark and Tilman, 2008) and general decline in forest health (Katzensteiner et al., 1992).

Nitrogen compounds dissolve in rain, fog, or snow depositing as “wet deposition” or, using the older nomenclature, “acid rain”. But they also accumulate on the landscape in dry molecular and particulate forms without solubilization in water. Of the two, dry deposition is the more difficult to quantify and study. Dry deposition results from a complex set of physical and chemical behaviors that is specific to the individual chemical species (Seinfeld and Pandis, 1998). Large particles are deposited via gravitational forces, but deposition of smaller particles and molecules are driven by physico-chemical parameters specific to both the compound and the surface that it is interacting with.

Of the plant nutrient containing air pollutants NH₃ and HNO₃, HNO₃ vapor may have the broader ecosystem importance (which is not to say that NH₃ is innocuous). In part, this is because the precursor sources, fossil fuel combustion, is more ubiquitous as compared to large agricultural operations. And, in part, because of differences in chemical behavior between the two. Ammonia emitted from a feed lot, for example, typically redeposits within a kilometer or two of the sources (Walker et al, 2000). Nitric acid is synthesized in the atmosphere as the air mass moves along. So while the deposition velocity of HNO₃ is very high, it tends to be more widely dispersed.

The effects of dry deposition of HNO₃ on unmanaged ecosystems have been source of concern for the Forest Service, National Park Service and the Bureau of Land Management for many years. The effects of dry deposition of HNO₃ on managed and agricultural ecosystems are poorly understood. Air pollution studies in agricultural ecosystems have focused on the oxidation effects of ozone and acidification effects of acid rain, but little work has been conducted on the physico-chemical effects of dry deposition of HNO₃. This paper lays out the fundamental principles relevant to dry deposition of HNO₃ on plant nutrition in agricultural ecosystems.

Atmospheric chemistry of HNO₃

Nitric acid vapor is a secondary air pollutant common to urban areas throughout the world. It is synthesized from the same volatile organic carbon and nitrogen oxides precursors, in the presence of sunlight that form ozone (Seinfeld and Pandis, 1998). Therefore, HNO₃ and ozone are usually co-contaminants. Real time ambient measurements of HNO₃, independent of other

nitrogen oxides, is difficult and expensive on a commercial scale, but extrapolation from more common ozone measurements indicates a diurnal pattern of very low HNO_3 concentrations pre-dawn, an increase with sunrise that peaks roughly midday. Once formed HNO_3 generally does not participate in further gaseous phase reactions, but becomes quite reactive with aqueous and solid phase substrates. Nitric acid vapor readily dissolves in water droplets, it adheres to dust particles, participates in the formation of aerosols, particularly ammonium nitrate aerosols or particulates, and interacts directly with many exposed surfaces including plants and soils. The rate at which HNO_3 moves out of the air and into terrestrial and aquatic ecosystems is among the highest of the atmospheric gases; the residence time is usually less than a week (Seinfeld and Pandis, 1998), as compared to CO_2 which may remain in the atmosphere for a century or more.

Continental deposition patterns

Nitrogen deposition is a global issue, but of greater concern in highly urbanized and industrial countries. While wet deposition is relatively easy to measure directly, dry deposition estimates are frequently accomplished by a combination of atmospheric monitoring and modeling. The National Atmospheric Deposition Program (NADP) has provided the national picture of wet deposition trends for 30 years (<http://nadp.sws.uiuc.edu>). The Program is designed to show regional trends by placing samplers away from major pollutant sources. Total N deposition is highest in the upper Midwest and Northeast section of the US (Figure 1, NADP, 2009). This reflects both pollution sources such as large agricultural operation in the Midwest and major industrial centers in the Ohio River valley area, and prevailing wind patterns that transport emissions into the less industrialized areas of the northeast.

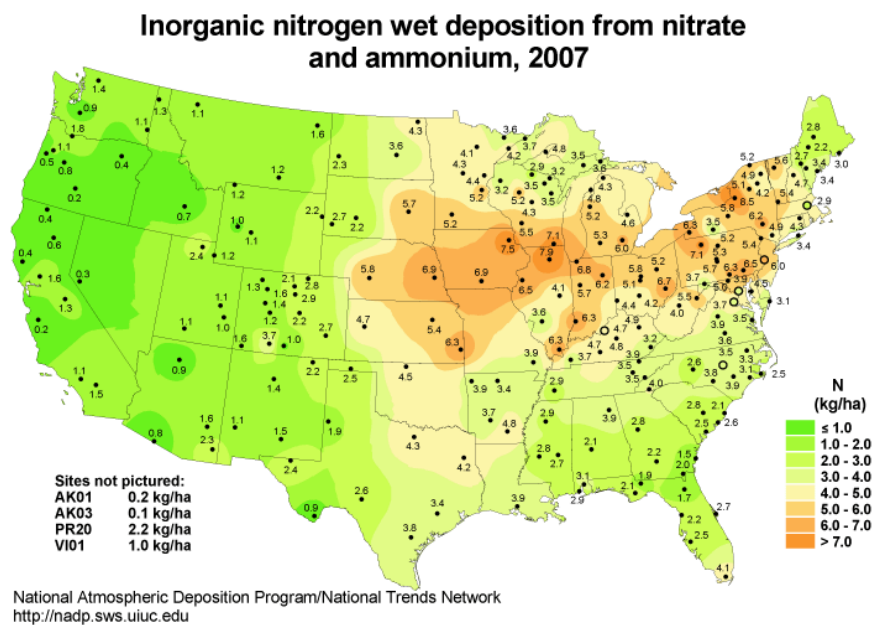


Figure 1. Annual wet deposition of inorganic nitrogen for 2007. (NADP 2009)

Deposition data from NADP is, obviously, skewed toward areas with frequent rainfall. In the arid southwestern part of the US, deposition loads are dominated by dry mechanisms. The CASTNET program operated by the US Environmental Protection Agency is the dry analog to

NADP (<http://www.epa.gov/castnet>), but coverage in the west is limited. A more comprehensive model with finer resolution is the Community Multiscale Air Quality (CMAQ) Simulator (Figure 2, <http://www.cmaq-model.org>). Data from CMAQ clearly delineates deposition “hot spots” around the highly urbanized Los Angeles basin, and through much of the agricultural Central Valley. At the 4km by 4km resolution scale total N deposition ranges in the 20 to 32 kg ha⁻¹yr⁻¹ in these areas (CMAQ, 2009).

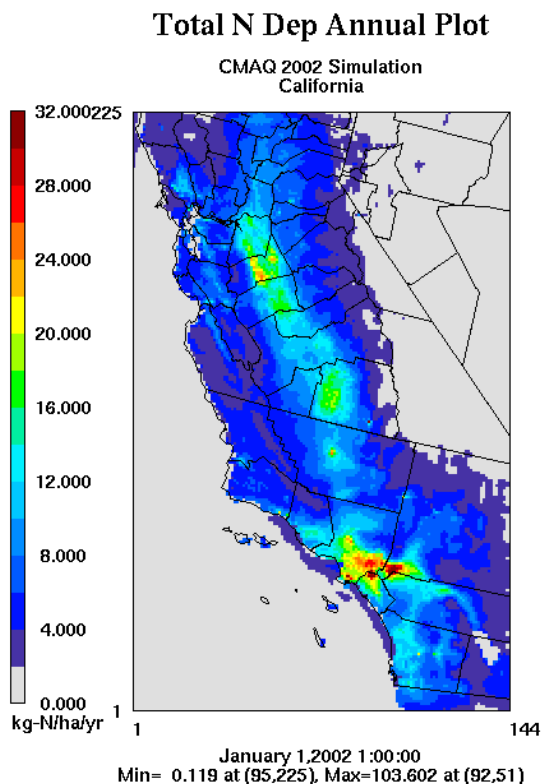


Figure 2. Total (wet + dry) nitrogen deposition in California simulated by the CMAQ (CMAQ, 2009).

Detailed and very fine resolution of dry deposition loads has been shown by several campaign-style studies such as those described by Fenn et al. 2003, and in Padgett et al, 1999, Burns 2003, and Baron, 2006. These studies have shown local deposition values as high as 80 kg ha⁻¹yr⁻¹ and overall values at least an order of magnitude higher than natural background levels.

Results and Discussion

Dry deposition on HNO₃ accumulates on soil and leaf surfaces

Nitrogen deposition in the low to mid elevations of southern California ranges from 20 kg ha⁻¹yr⁻¹ to as high as 80 kg ha⁻¹yr⁻¹ depending on the vegetation patterns, prevailing winds and other meteorological conditions (Fenn et al., 2003). Deposition to soil surfaces under experimental fumigation conditions exhibits a linear dose-response (Figure 3). Deposition patterns also indicate a significant difference among soil particles sizes typical of ion exchange capacity. The data shown here were from HNO₃ exposures to air dried soils. When the soils were moistened, deposition rates greatly increased suggesting that moist soil would tend to accumulate substantially more NO₃⁻ due to solubilization in water (Padgett and Bytnerowicz, 2001).

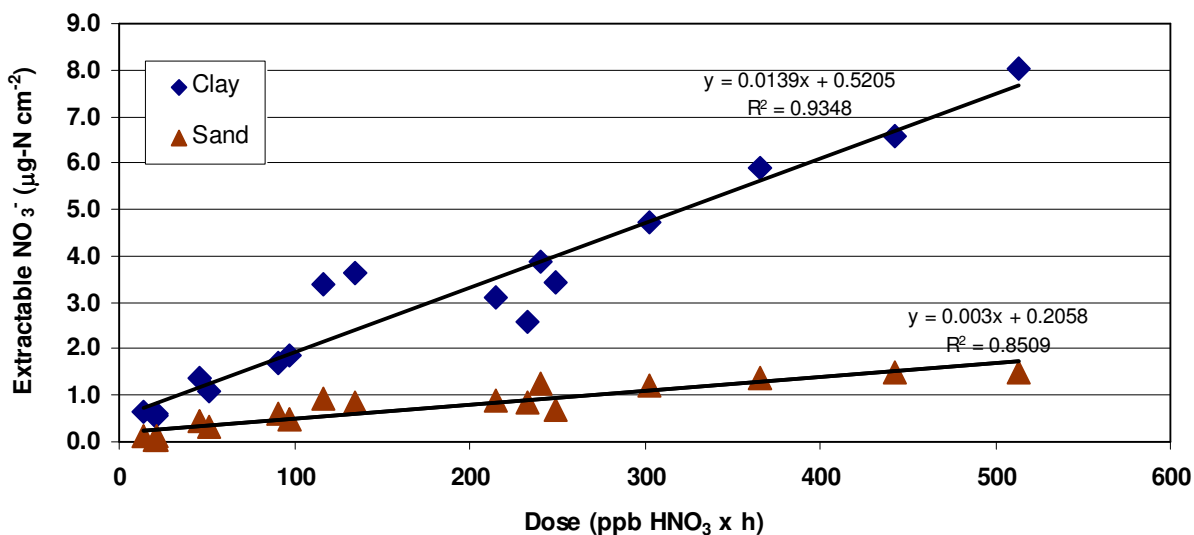


Figure 3. NO₃⁻ extracted from clay and sand fractions after exposure to atmospheric HNO₃ under controlled fumigation conditions. From Padgett and Bytnerowicz, 2001.

Plant surfaces also capture deposited HNO₃. But unlike soil surfaces leaf surfaces, at least under experimental conditions, saturate with respect to total deposition (Figure 4). The dose at which a leaf saturates is species-dependent. These data are for shrub species native to the semi-arid west. Similar differences in total deposition have been shown for other perennial species as well. The reasons for this are not well understood, but are most likely caused by leaf surface physical and chemical characteristics and canopy architecture.

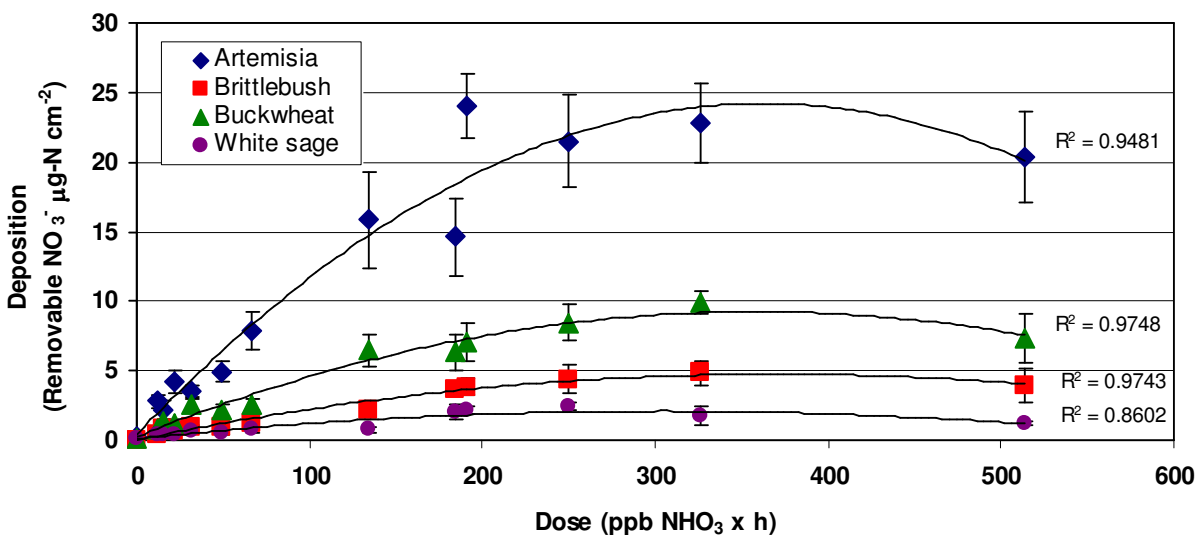


Figure 4. NO₃⁻ washed from leaf surfaces after exposure to atmospheric HNO₃ under controlled fumigation conditions.

Uptake and assimilation of dry HNO₃ deposition

Nitric acid seems to be unique among the air pollutants in that not only is it absorbed by plants through the stomata during normal gas exchange, but it penetrates the cuticular boundary (Marshall and Cadle, 1989, Cadle et al., 1991). Once in the apoplastic space it is transported across the plasmalemma and assimilated as any NO₃⁻ molecule would be (Vose and Swank, 1990, Padgett et al., 2008). An investigation of adsorption and assimilation of dry HNO₃ deposition in trees native to the western mixed conifer forests using controlled fumigation equipment showed that deposition as measured by washing foliage varied by species (Figure 5A). Using ¹⁵N labeled HNO₃, it was clear that after the leaves were rinsed, a significant portion of the deposited NO₃⁻ remained on, or in, the foliage (Figure 5B). Isolation and analysis of the soluble protein fraction demonstrated that atmospheric HNO₃ was assimilated into the cellular nitrogen pool (Figure 6).

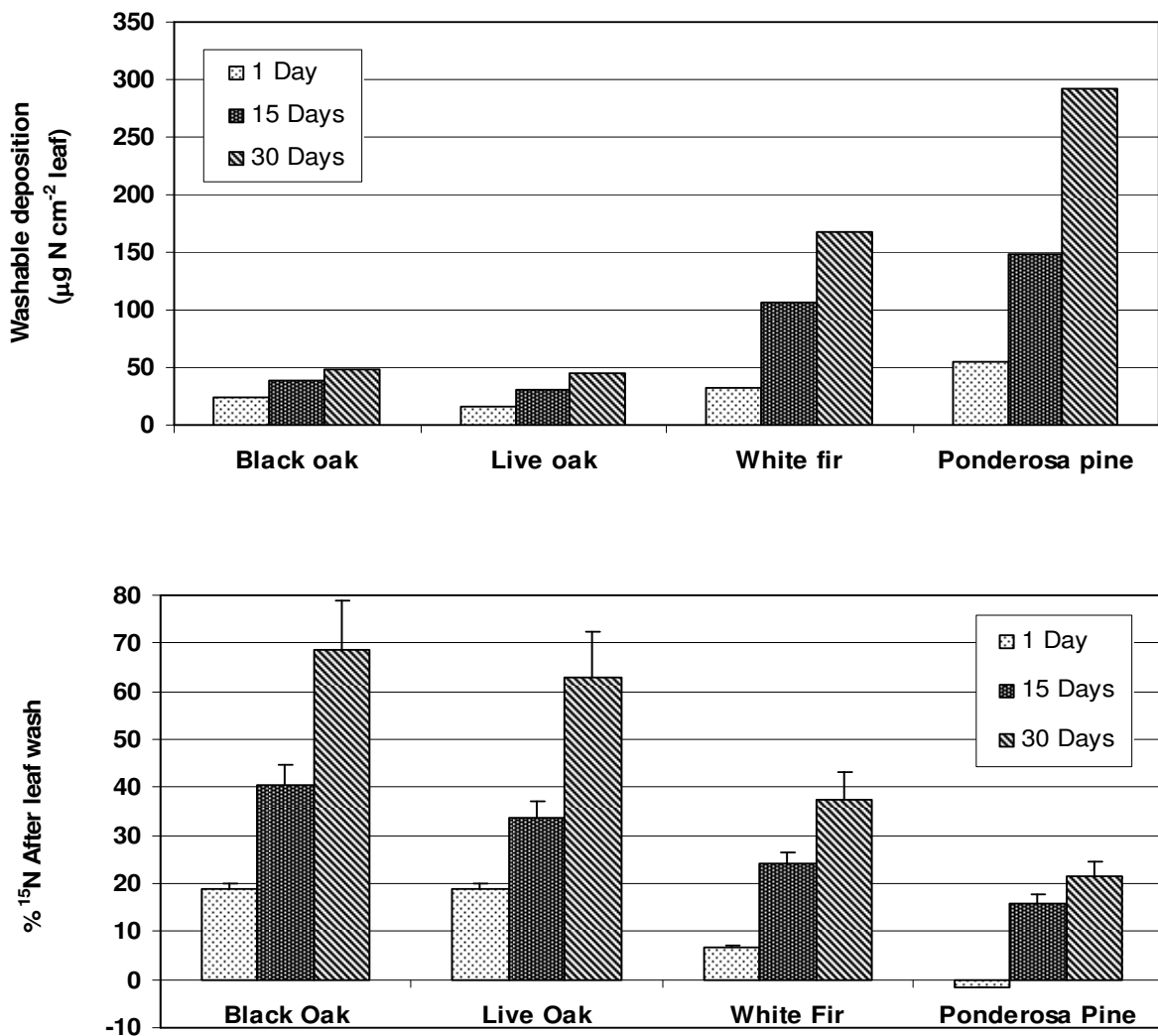


Figure 5. (Top) NO₃ washed from leaves after 1, 15 and 30 days exposure to moderate levels of atmospheric HNO₃. (Bottom) ¹⁵N remaining on the same sample eaves after washing. From Padgett et al. 2008.

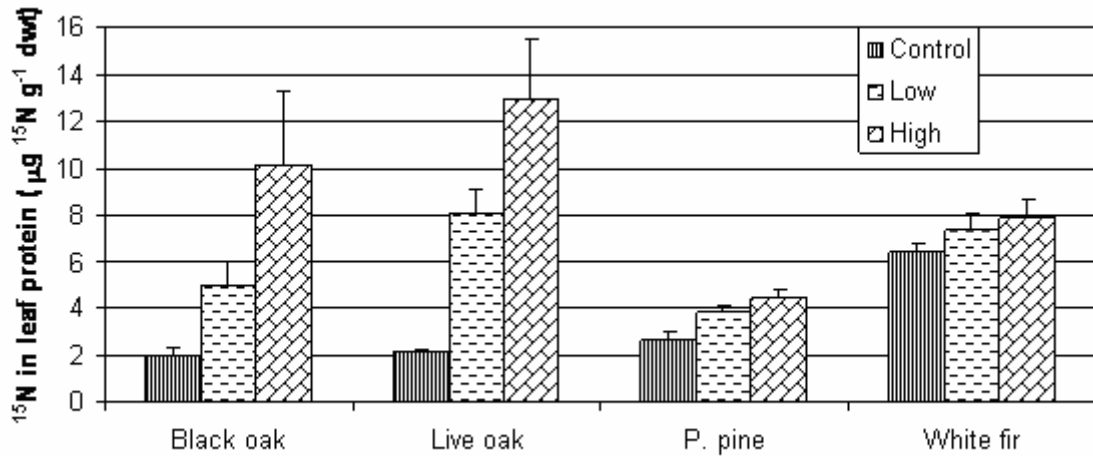


Figure 6. ¹⁵N incorporated into soluble proteins extracted from leaves after 30 days of exposure to zero, low and high levels of atmospheric H¹⁵NO₃. (From Padgett et al. 2008)

The ability of HNO₃ to cross the cuticular boundary has been established by several research groups, but the mechanism for uptake remains unidentified. One possible mechanism has emerged from studies of leaf surfaces using scanning electron microscopy. After exposure to atmospheric concentrations consistent with high, but realistic pollutant loads, the protective epicuticular layer exhibited significant damage (Figure 7). At least a dozen perennial plant species have been investigated for foliage damage from dry HNO₃ deposition and all of them exhibit a similar suite of reproducible damage features. The working hypothesis is that HNO₃, being a strong oxidizer, attacks the vulnerable double bonds of the lipid and waxes that make up the cuticle, essentially dissolving them and exposing the more hydrophilic cutin layer below allowing NO₃⁻ to penetrate into the apoplastic space.

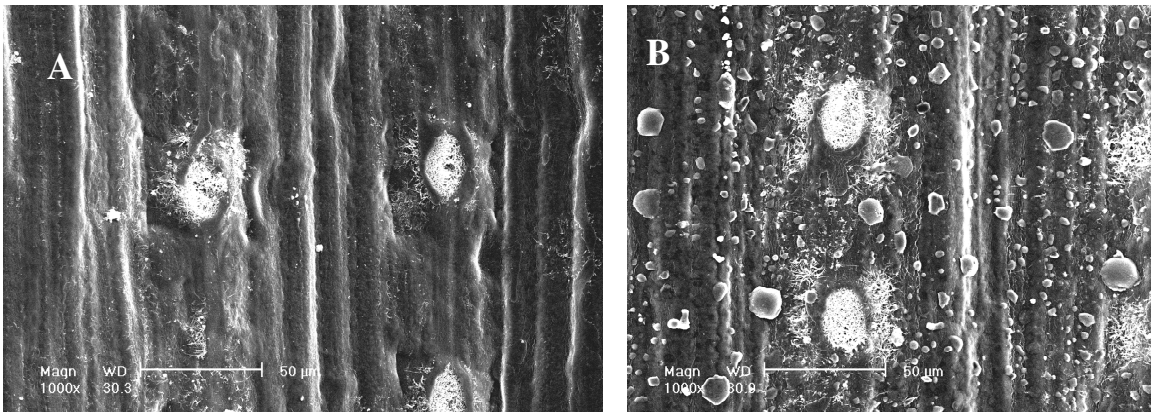


Figure 7. The effect of dry deposition on HNO₃ on the epicuticular surface of ponderosa pine needles. Left panel (A) needle after 30 days in controlled fumigation chamber. Right panel (B) needle after 30 days at high levels of HNO₃ (from Padgett et al., 2009a)

Implications for Agriculture

Since the emphasis for nitrogen deposition has been focused on native plant species and natural ecosystems, very little work has been done on plant species relevant to production agriculture. However, the principles of fertility and damage do have application in agriculture, in particular, nitrogen management in annual crops and foliar damage in fruit and nut crops.

Percolation into groundwater and surface run off from agricultural lands continues to be a source of conflict for producers and natural resource managers. Mass balance approaches for estimating N inputs and utilization rarely account for the atmospheric component. In regions such as the central valley in California where the atmospheric component is substantial – 12 to 20 kg ha⁻¹yr⁻¹ and water resources are competitive, failure to account for N deposition can result in substantial increases in N contamination of limited water resources. What is not assimilated and taken off with the crop remains behind. For tree and vine crops N deposition may an addition N resource, but the damage to leaves likely offsets any enhanced fertility. In forest trees damage to the protective cuticle boundary is hypothesized to accelerate water loss decreasing drought resistance, enhance ozone damage, and possibly reduce resistance to diseases and pests (Strenbom et al., 2002).

Deposition of plant nutrient atmospheric N has important ramifications for production agriculture. There are, however, opportunities for mitigation. The first step is better monitoring of input loads and increased understanding of the effects.

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