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## Retention or Loss of N in IFS Sites and Evaluation of Relative Importance of Processes

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## 6. Nitrogen Chemistry, Deposition, and Cycling in Forests

### Overview

D.W. Cole

At the conception of the Integrated Forest Study (IFS) program, a series of questions were raised specific to the effect of N input on ecosystem nutrient cycling processes including those mechanisms responsible for the retention, transformation, and loss of N through leaching from forest ecosystems. The fact that comparable data were collected at 17 sites (covering a wide array of forest types, elevations, climatic conditions, and atmospheric N input regimes) allowed us to integrate the results from this program and begin to answer some of the questions that could not be addressed from the results generated from any single individual site.

A large portion of this chapter will be centered around the concept of N saturation, its occurrence and causes, and how it is affected by atmospheric N deposition. The term has emerged in the last decade in the context of acid rain effects (e.g., Agren and Bosatta 1988; Dempster and Manning 1988; Aber et al. 1989), although this ecosystem condition can also be achieved without large anthropogenic N inputs, as is discussed later. In simple terms, N saturation can be defined as that forest soil condition whereby the N flux density (i.e., N input from N mineralization plus atmospheric N input) exceeds the system's retention capacity and  $\text{NO}_3^-$  starts leaching out of the system (e.g., Agren and Bosatta 1988). The choice of measurable  $\text{NO}_3^-$

leaching as an indicator of N saturation will be discussed in greater detail later in Chapter 6. The term “N saturation” as defined here is related to, but generally broader than the terms “excess N deposition” [i.e., the point at which the system’s N retention capacity is exceeded by atmospheric N inputs (Dempster and Manning 1988)], or “critical N load” [i.e., the maximum allowable N inputs so as to avoid excess  $\text{NO}_3^-$  leaching (Nilsson and Grennfelt 1988)] in that it also recognizes and accounts for natural N sources and sinks within the ecosystem.

The questions posed at the onset of the IFS program regarding N dynamics were as follows:

- Is N saturation and  $\text{NO}_3^-$  leaching a common process within our forest ecosystems or is it limited to unique conditions associated with disturbance or special ecosystem types?
- If N saturation and  $\text{NO}_3^-$  leaching are common processes, do they follow any consistent pattern? Can we understand, or at least predict, where saturation and leaching is most likely to occur by following the cycling processes within the ecosystems under question?
- How important are cloud water interception and dry deposition as mechanisms of N addition to forest ecosystems? Does their importance vary with forest composition, climatic conditions, and other features of the environment or is there consistency between sites? Can these measurements realistically be made?
- Can atmospheric N deposition alone cause N saturation and trigger  $\text{NO}_3^-$  leaching?
- Does the leaching of nitrate at N-saturated sites significantly change soil solution properties including pH, cation leaching, and Al concentration? Will these changes in turn cause changes to soil properties?
- Are these changes reversible? If so, which ones, how long will it take, and can the process be accelerated?
- Are these changes of sufficient significance to affect ecosystem productivity?

Although it was not feasible within the 3-year monitoring period of this program to adequately answer all these questions, the integrated nature of the study has nevertheless allowed a comprehensive analysis of these questions and has generated answers to many.

To determine if N saturation and nitrification are common in forest ecosystems, whether internal processes or external inputs are of greater significance in triggering nitrification, and to what extent nitrification and  $\text{NO}_3^-$  leaching significantly alter soil and soil solution properties, it was essential to examine these questions over a broad range of ecosystem conditions and within the context of the mineral cycle. Specifically, at 13 of the sites the various dry and wet N input fluxes were established (see pp. 152–166 Chapter 6). For those sites where only bulk precipitation N inputs were measured, total N inputs were estimated on the basis of ecosystem characteristics, and

the relationship between wet and dry N deposition observed at the intensive monitoring sites as discussed later in Chapter 6. In addition, the rates and processes of N retention, transformation, and leaching were documented. The impact of N input and cycling on other ecosystem properties were also followed. Using  $\text{NO}_3^-$  as an indicator of N saturation, the data sets collected over this broad range of forest types and air pollution regimes allowed us to analyze, through multiple regression analysis, the relative role of various dynamic and static ecosystem properties in explaining variations in  $\text{NO}_3^-$  leaching losses among the different sites within the IFS network. The results from these efforts are discussed in detail in the following sections.

## **Atmospheric Deposition and Canopy Interactions of Nitrogen**

G.M. Lovett

### **Processes of N Deposition**

The importance of the atmospheric deposition of N to terrestrial ecosystems was firmly established by the pioneering work (and heated controversy) of Liebig, Lawes, Gilbert, and Boussingault in the mid-nineteenth century (Aulie 1970; Paul 1976). Since that time, N has been undoubtedly the most studied element in forest nutrient cycling because of its key role in plant nutrition and the fact that it generally limits forest production in the temperate zone. Nitrogen is also an important element in the atmosphere, where  $\text{N}_2$  comprises about 78% by volume, and where reactive N species, although much less abundant, are crucial in atmospheric chemical reactions. These reactive species have natural and anthropogenic sources, the latter including both combustion and agriculture (Singh 1987; Warneck 1988). Therefore, the potential exists for human alteration of the N chemistry of the atmosphere to have a profound effect on the biosphere.

The reactive N species of primary concern from the standpoint of atmosphere–forest interactions include both oxidized forms ( $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , and  $\text{NO}_3^-$  ion) and reduced forms ( $\text{NH}_3$ ,  $\text{NH}_4^+$ , and organically bound N). Other N oxides (e.g.,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ , and  $\text{NO}_3$  radical) are present in the atmosphere and are thought to play important roles in atmospheric chemistry, but their concentrations are less well quantified (Singh 1987). The atmospheric chemistry of N oxides is complicated and incompletely understood, but it is known that combustion in motor vehicles, power plants, and industrial processes releases primarily  $\text{NO}$ , which is rather quickly oxidized to  $\text{NO}_2$  and then to  $\text{HNO}_3$  vapor in the gas phase (Singh 1987). Nitric acid vapor can be dry-deposited, dissolve in rain or cloud droplets, adsorb to atmospheric particles, or react with basic substances (e.g.,  $\text{NH}_3$ ) to form fine aerosols (e.g.,  $\text{NH}_4\text{NO}_3$ ). Natural processes in the soil can also release  $\text{NO}$  and  $\text{NO}_2$ , which will undergo the same reactions (Singh 1987).

Most of the  $\text{NH}_3$  in the lower atmosphere in North America and Europe appears to be a result of agricultural activities, mainly volatilization from animal wastes and fertilized soils (Soderlund and Svensson 1976; Warneck 1988). Volatilization of  $\text{NH}_3$  from unfertilized soils is small unless the soils are alkaline (Warneck 1988), a rare condition in moist temperate forests. Ammonia is the only alkaline trace gas of any significance in the atmosphere, and it reacts quickly with acidic compounds to form  $\text{NH}_4^+$ , either in dry particles or in droplets (Warneck 1988). Ammonia may also be dry-deposited to vegetation and soil surfaces.

The sources and forms of organic N in the atmosphere are poorly studied, and the concentrations are rarely measured, except in precipitation. Possible sources include particulate material entrained from soils and vegetation (e.g., pollen, soil dust, spores) and reaction products of N oxides with organic compounds (e.g., peroxyacetyl nitrate, PAN).

Thus, both natural and anthropogenic activities result in a wide variety of N compounds in the atmosphere in gaseous, particulate, and dissolved forms. Our primary purpose in this study was to determine the concentrations and deposition rates of the species that contribute the greatest amount of N deposition to forest ecosystems. Therefore, we focused on dry deposition of  $\text{HNO}_3$  vapor, particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , and dissolved  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in precipitation and cloud water. Concentrations of  $\text{NH}_3$  were not measured at most sites, but estimates were made during the growing season at the Oak Ridge loblolly pine (LP) site (Lindberg et al. 1990) and are discussed briefly. Organic N in precipitation was measured at some sites, and  $\text{NO}_2$  concentration and deposition were estimated for sites where data were available. Separate experimental studies investigated the factors controlling the deposition of  $\text{NO}_2$  and  $\text{HNO}_3$  at the leaf and branch level (see pp. 166–177). In addition, we measured N passing out of the canopy as stemflow and throughfall to elucidate the interactions of the various forms of N within the forest canopies.

## Methods and Sites

Data collection methods are described in detail in Chapter 2. Briefly, a three-stage filter-pack was used to measure atmospheric concentration of fine aerosols (on a Teflon filter),  $\text{HNO}_3$  vapor (on a nylon filter), and  $\text{SO}_2$  (on a  $\text{K}_2\text{CO}_3$ -impregnated filter) above each of the forest canopies. Concentrations of  $\text{NO}_2$  were measured continuously at or near some sites using chemiluminescence analyzers. Dry deposition of fine particles (approximately  $<2\text{-}\mu\text{m}$  diameter) and  $\text{HNO}_3$  were calculated using a deposition model slightly modified from Hicks et al. (1987), which uses measured canopy structure and meteorological parameters to estimate dry deposition velocities. Dry deposition fluxes were calculated as the product of mean atmospheric concentrations and mean deposition velocities for sampling periods of several days to 1 week. Coarse-particle dry deposition fluxes were measured on plastic petri dishes exposed

above the canopies and were extrapolated to full-canopy deposition rates using a scaling factor derived by using  $\text{Ca}^{2+}$  in throughfall as a "tracer" of coarse-particle deposition. Precipitation and throughfall were measured on an event basis using automated wetfall-only collections. Cloud water was collected for chemical analysis using harplike string collectors above the canopy at the mountain sites and an active collector at the Oak Ridge loblolly pine site. Deposition of cloud water was calculated from analysis of the water balance in the canopy (Lovett 1988).

The study sites are described in Chapter 2. Some sites in the IFS project were not included in this analysis because of the lack of the full complement of deposition data for particulate, gaseous, and dissolved forms of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Of the intensive deposition study sites considered here, 2 years of data collection (roughly 1986–1988) are available for all areas except the ST, LP, and CP sites (3 years) and the MS and FS sites (1 year). The data from the FS and MS sites should be interpreted with caution because the record is short. In the bar graphs in this section, the order of sites is as follows: first, the southeastern sites in order of elevation; then, the northeastern sites in order of elevation; then, the western sites; and finally, the site in Norway.

### Atmospheric Concentrations and Dry Deposition

The sum of the concentrations of  $\text{HNO}_3$  vapor and fine-particle  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ranged between 0.62 and  $2.2 \mu\text{g N m}^{-3}$  (Figure 6.1). The highest values are for the LP and DL sites, probably because these are the IFS sites closest to urban areas. Of these three constituents, fine-particle  $\text{NH}_4^+$  consistently dominated, with concentrations of 0.34 to  $1.6 \mu\text{g N m}^{-3}$  ( $0.43$ – $2.0 \mu\text{g NH}_4^+ \text{ m}^{-3}$ ). Concentrations of  $\text{HNO}_3$  vapor ranged from 0.18 to  $0.62 \mu\text{g N m}^{-3}$  ( $0.82$ – $2.8 \mu\text{g HNO}_3 \text{ m}^{-3}$ ), and fine-particle  $\text{NO}_3^-$  concentrations were generally less than  $0.14 \mu\text{g N m}^{-3}$  ( $0.62 \mu\text{g NO}_3^- \text{ m}^{-3}$ ). Note that sampling artifacts in the filter-pack technique may affect the relative proportions of particulate and gaseous  $\text{NO}_3^-$  (Appel and Tokiwa 1981), but this problem has been shown to be minor in a study near our WF site (Kelly et al. 1984); in any event, the measurement of total atmospheric  $\text{NO}_3^-$  is not affected. Concentrations of aerosol  $\text{NO}_3^-$  and  $\text{NH}_4^+$  seem to vary in concert between sites, such that the  $\text{NH}_4^+$  fraction of the total is always in the range 50% to 70%, and in most cases is between 60% and 70% (Figure 6.2).

Despite the dominance of  $\text{NH}_4^+$  in the air,  $\text{HNO}_3$  dominates the total dry deposition of N (Figure 6.3) such that the contribution of aerosol  $\text{NH}_4^+$  is always less than 50% and usually less than 30% of the total (Figure 6.2). This occurs because  $\text{HNO}_3$  is a very reactive gas that adsorbs readily to most surfaces after diffusing through the quasi-laminar boundary layer immediately adjacent to the surface (Huebert and Robert 1985). Particulate  $\text{NH}_4^+$ , however, is generally in the 0.1- to  $1.0\text{-}\mu\text{m}$  size range (Lindberg et al. 1986), a class of particles that cannot be transported easily across boundary layers

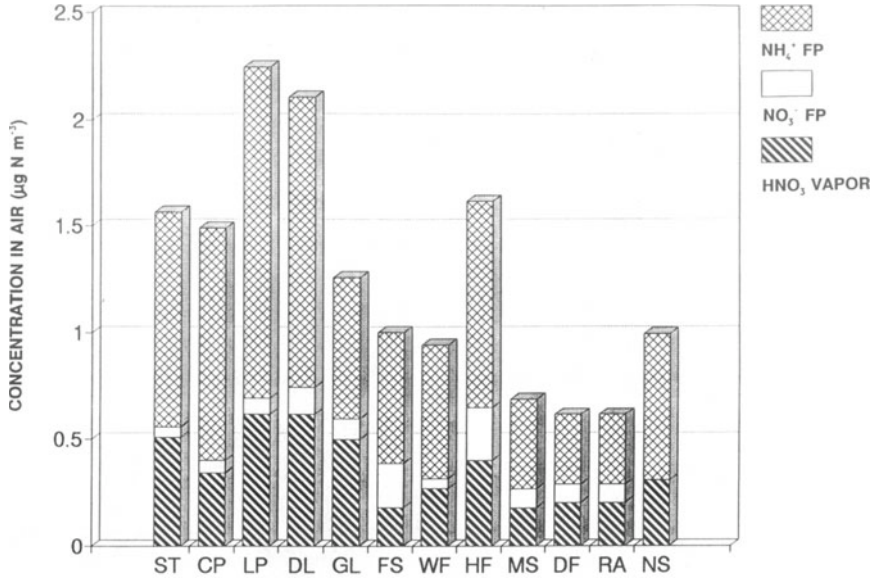


Figure 6.1. Concentrations ( $\mu\text{g N m}^{-3}$ ) of  $\text{HNO}_3$  vapor and fine-particle ( $< \sim 2 \mu\text{m}$ )  $\text{NH}_4^+$  and  $\text{NO}_3^-$  at the intensive study sites (see Chapter 2 for abbreviations).

by impaction, sedimentation, or diffusion. The model-calculated average deposition velocities for  $\text{HNO}_3$  vapor range from 1.3 to 6.0  $\text{cm s}^{-1}$  (with the highest values at the windy, high-elevation sites), while those for fine particles range from 0.02 to 0.4  $\text{cm s}^{-1}$  (see the Appendix).

Concentrations of coarse particles are not included in Figure 6.1 because these larger particles are not sampled efficiently by standard air filtration (Noll et al. 1985). We measured coarse-particle deposition directly on artificial-surface collectors that we previously tested and compared to individual leaves and full canopies (Lindberg and Lovett 1985; Lovett and Lindberg 1986). The coarse-particle deposition fluxes of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  can add substantially to the total dry deposition of N, contributing up to 60% to 80% at the FS, MS, DF, and RA sites, where  $\text{HNO}_3$  vapor concentrations are lowest (Figure 6.3).

In the discussion thus far, we have ignored the dry deposition of  $\text{NH}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$ . We did not measure  $\text{NH}_3$ , but some studies have shown it to be low in both concentration and deposition in the sort of rural, nonagricultural areas that characterize most sites in this study (Tjepkema et al. 1981). A short-term study at the LP site showed  $\text{NH}_3$  concentrations of about 0.2  $\mu\text{g N m}^{-3}$  during the growing season, and  $\text{NH}_3$  at this concentration was estimated to contribute about 5% of the total growing-season N deposition, assuming an average deposition velocity for  $\text{NH}_3$  of 1.0  $\text{cm s}^{-1}$  (Lindberg et al. 1990).

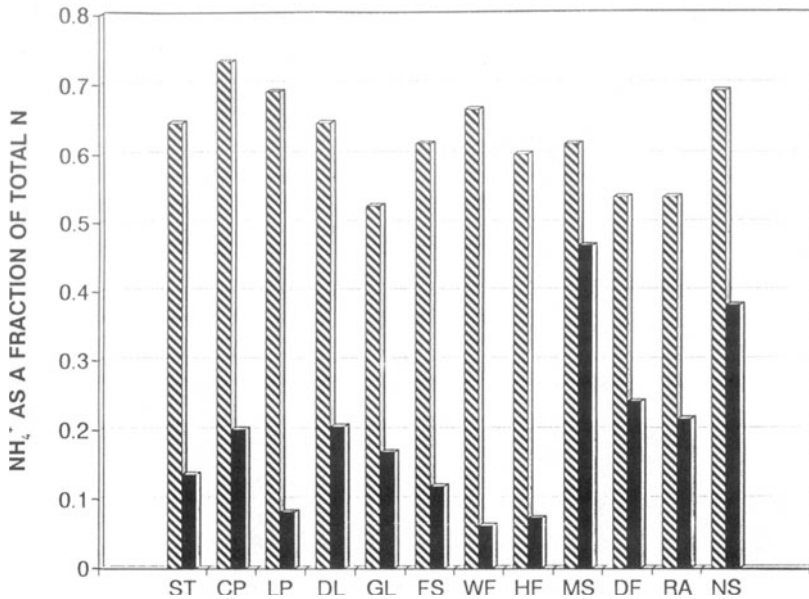


Figure 6.2. Ammonium as fraction of ammonium plus nitrate in atmospheric concentrations and in dry deposition at study sites.

Concentration of  $\text{NO}$  is generally low outside urban source regions (Warneck 1988), and its deposition velocity was also found to be quite low compared to  $\text{NO}_2$  or  $\text{HNO}_3$ . However,  $\text{NO}_2$  can reach quite high concentrations, and occasionally high deposition levels, especially in urban areas. Later in Chapter 6, Hanson et al. report measured  $\text{NO}_2$  concentrations of  $4.6 \mu\text{g N m}^{-3}$  at the LP site and  $1.2 \mu\text{g N m}^{-3}$  at the HF and WF sites, and they estimate concentrations of  $0.57$  to  $2.8 \mu\text{g N m}^{-3}$  at the other sites. These concentrations are equal to or higher than the concentrations of the N species shown in Figure 6.1, especially for the sites closest to urban areas (LP and DL), indicating that  $\text{NO}_2$  may be the dominant form of reactive N in the atmosphere. However, because of the low deposition velocity, Hanson et al. (pp. 166–177) estimated the dry deposition of  $\text{NO}_2$  to range from only  $10 \text{ mol ha}^{-1} \text{ yr}^{-1}$  at the WF site to  $82 \text{ mol ha}^{-1} \text{ yr}^{-1}$  at the DL site. This suggests that accounting for  $\text{NO}_2$  could increase the total dry deposition by only 2% to 20% over the values shown in Figure 6.3.

Annual, volume-weighted, mean concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in precipitation both vary in the range  $5\text{--}30 \mu\text{mol L}^{-1}$  among the sites, with  $\text{NO}_3^-$  concentrations generally slightly higher than  $\text{NH}_4^+$  concentrations. Surprisingly, there was no correlation between concentrations of these ions in precipitation and their corresponding concentrations in the air. At the three sites (ST, LP, and WF) that measured cloud or fog water chemistry,



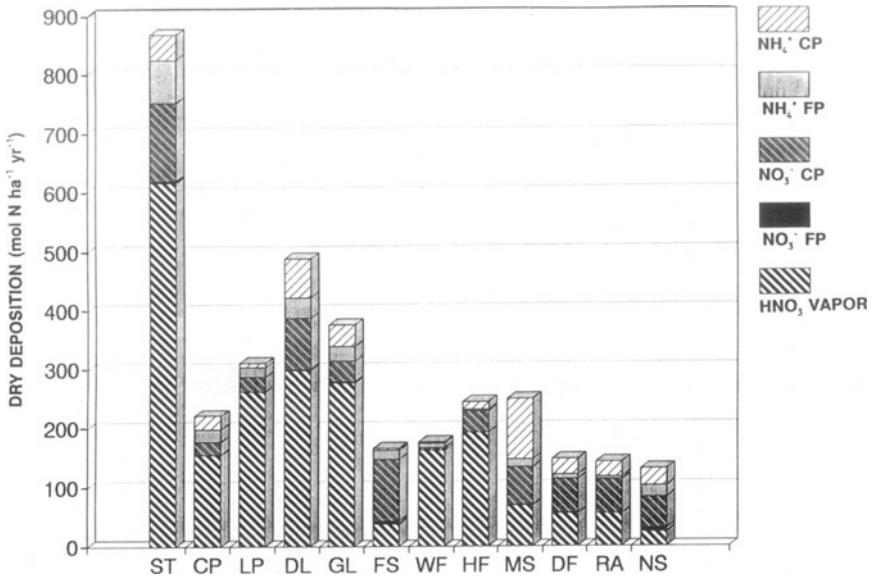


Figure 6.3. Dry deposition ( $\text{mol ha}^{-1} \text{yr}^{-1}$ ) of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  via  $\text{HNO}_3$  vapor, fine-particle (FP), and coarse-particle (CP)  $\text{NH}_4^+$  and  $\text{NO}_3^-$  to study sites.

concentrations in cloud water were substantially higher than corresponding concentrations in precipitation. For  $\text{NO}_3^-$ , the cloud to rain ratio for annual mean concentrations was 5.8 at the ST site, 3.8 at LP, and 6.9 at WF. For  $\text{NH}_4^+$ , the ratios were 8.5, 18, and 11 for the three sites, respectively. While this indicates that cloud and fog water was on average many times more concentrated than rain, and more so for  $\text{NH}_4^+$  than for  $\text{NO}_3^-$ , Weathers et al. (1988) cautioned that these ratios can vary greatly from event to event.

### Total Deposition

Total atmospheric deposition of N (the sum of wet, dry, and cloud water deposition) ranged from  $340 \text{ mol ha}^{-1} \text{yr}^{-1}$  ( $4.7 \text{ kg ha}^{-1} \text{yr}^{-1}$ ) at the RA site to  $1900 \text{ mol ha}^{-1} \text{yr}^{-1}$  ( $27 \text{ kg ha}^{-1} \text{yr}^{-1}$ ) at the ST site (Figure 6.4). (Note that  $50\text{--}100 \text{ kg N ha}^{-1} \text{yr}^{-1}$  is added to the red alder (RA) site by symbiotic N fixation, which could be considered a form of atmospheric deposition.) For the lowland sites in the eastern United States, N deposition varied from  $500$  to  $1000 \text{ mol ha}^{-1} \text{yr}^{-1}$ , with all except the DL site less than  $700 \text{ mol ha}^{-1} \text{yr}^{-1}$  (roughly  $10 \text{ kg ha}^{-1} \text{yr}^{-1}$ ). Although it appears in Figure 6.4 that total N deposition is generally higher in the southeast than in the northeast, this may be an artifact of having chosen sites closer to urban areas in the southeast. Hanson et al. (pp 166–177) estimated that inclusion of  $\text{NO}_2$  deposition would add less than 10% to the total deposition at the IFS sites in

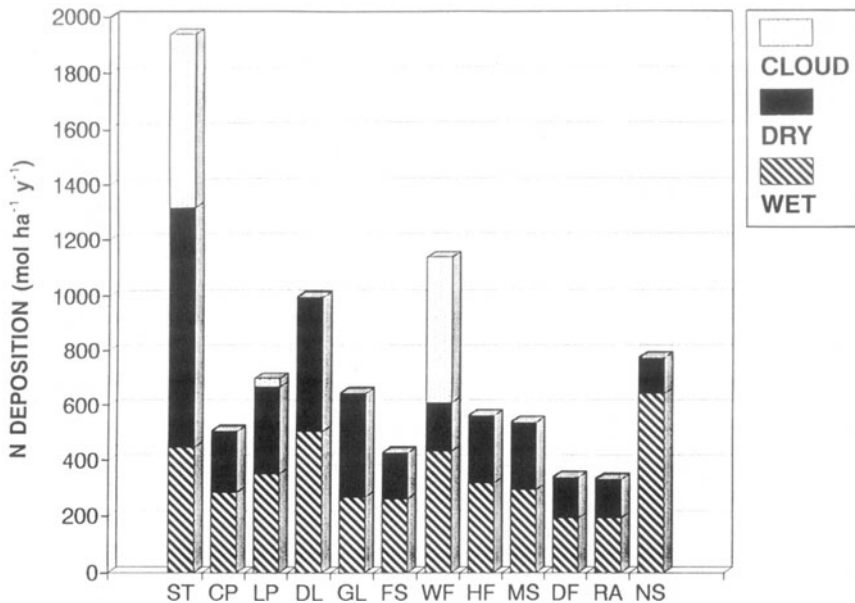


Figure 6.4. Wet deposition, dry deposition, and cloud water deposition of N ( $\text{mol ha}^{-1} \text{yr}^{-1}$ ) to study sites.

Figure 6.4. Deposition of  $\text{NO}_3^-$  (including  $\text{HNO}_3$  vapor) exceeded that of  $\text{NH}_4^+$  at all sites, usually by a factor of 2 or more.

Dry deposition varied more than wet deposition between sites and made a significant contribution to the total deposition at all sites. Cloud water deposition is a very important source of N for the high-elevation sites and made ST and WF the sites with the highest N deposition in this project. Nonetheless, the cloud water deposition at these sites might be lower than that of many mountain summit sites in the eastern United States (Lovett and Kinsman 1990), because the ST site was estimated to be in cloud only 10% of the time and the WF site 7% of the time. By contrast, cloud immersion frequencies are estimated to be 28%–35% for the summit of Mt. Mitchell, North Carolina, and 40%–45% for the summit of Whiteface Mt., New York (Mohnen 1988).

In an effort to simplify the process for estimating total N deposition, it is valuable to address the question of whether total deposition can be predicted from the more easily measured wet deposition. Figure 6.5 shows the considerable scatter in the relationship between the two variables; regression analysis indicated that wet deposition explains only 35% of the variance in total deposition when all the sites are considered. However, if we restrict the analysis to low-elevation sites in the United States (i.e., exclude ST, WF, and NS), then wet deposition explains 90% of the variance in total deposition (see Figure 6.5). The regression line in Figure 6.5, which is based

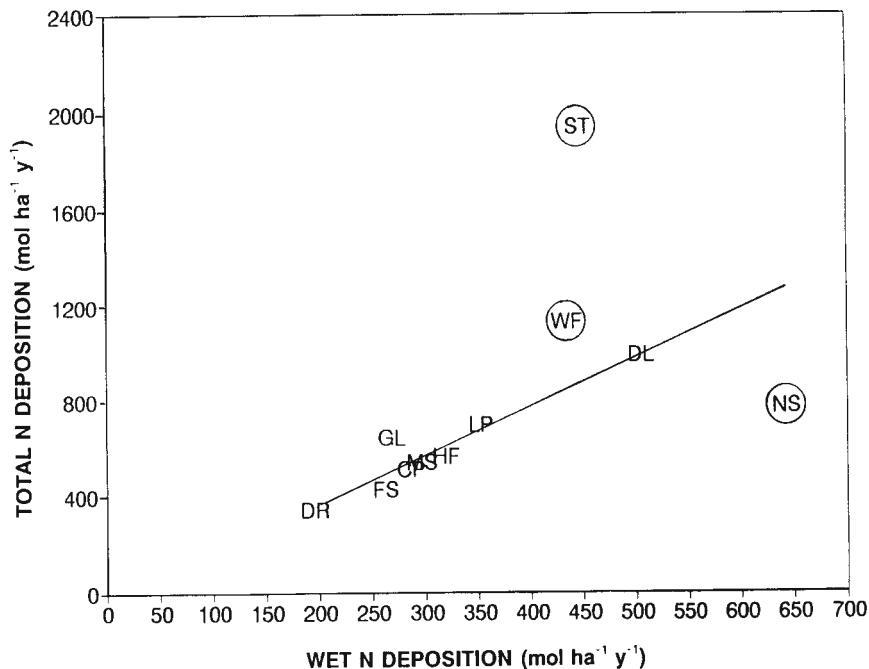


Figure 6.5. Wet deposition versus total deposition ( $\text{mol ha}^{-1} \text{yr}^{-1}$ ) of  $\text{NH}_4^+$  plus  $\text{NO}_3^-$  for study sites. Regression line ( $y = -49 + 2.1x$ ,  $r^2 = .90$ ) excludes circled points (see text). DF and RA points have nearly identical coordinates and are plotted together as DR.

on the data excluding the ST, WF, and NS sites, has a slope of  $2.1 (\pm 0.3 \text{ SE})$  and an intercept that is not significantly different from zero. Thus, it appears that in general total deposition can be assumed to be roughly twice as great as wet deposition for low-elevation forests in the United States. Considering the sites individually, dry deposition of N contributes a mean of 46% of total deposition, with a range from 39% (FS site) to 59% (GL site); both of these extremes are from sites with only 1 year of data. This indicates that wet and dry deposition are roughly equal for these low-elevation United States sites. For sites subject to high levels of cloud water deposition, total deposition will be further enhanced. Note that at the NS site, wet deposition greatly exceeds dry deposition; this probably results from the location of the NS site far from major  $\text{NO}_x$  emission sources. These deposition estimates are higher than many N inputs reported in the literature for forested ecosystems, mainly because we specifically included dry and cloud water deposition while many previous estimates were based on bulk deposition alone.

Significant uncertainties are associated with these total deposition estimates because of the combination of measurements and models that are used. We estimate that the overall uncertainty in total N deposition is about  $\pm 50\%$

at the high-elevation sites and  $\pm 30\%$  at the low-elevation sites, with the largest potential sources of error associated with the specification of deposition velocities for  $\text{HNO}_3$  vapor and the N fluxes with cloud water.

In the past, N input measurements for ecosystem studies were frequently made using continuously open funnels or buckets, called bulk deposition collectors. From our best estimates, total deposition significantly exceeds bulk deposition at most sites where both measurements were made (Table 6.1), especially at those sites where dry and cloud water deposition are important. This suggests that bulk deposition measurements seriously underestimate total N deposition for many forests.

### Canopy Exchange

If one considers only precipitation (PPT), throughfall (TF), and stemflow (SF) fluxes, it appears that the canopies at all of these sites release  $\text{NO}_3^-$  [i.e.,  $\text{PPT} < (\text{TF} + \text{SF})$ ], and most of them take up  $\text{NH}_4^+$  [ $\text{PPT} > (\text{TF} + \text{SF})$ ]. Consideration of dry deposition and cloud water deposition changes that conclusion, however. Our best estimate of the true role of the canopy is the net canopy exchange (NCE), which we define as total deposition (wet + dry + cloud water) minus  $(\text{TF} + \text{SF})$ . The NCE for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  is negative for all sites, indicating that the canopies clearly are sinks for inorganic N (Figure 6.6). The apparent  $\text{NO}_3^-$  release from the canopies (when only wet deposition is considered) can be completely accounted for by washoff of dry-deposited nitrate. Our data for organic N are less reliable because at some sites organic N was not measured at all and at some sites it was measured only in bulk deposition collectors, which were left in the field for a week or more after a precipitation event, possibly allowing microbial transformation of N in the collectors. However, the available data indicate a release of organic N (i.e.,  $\text{NCE} > 0$ ) from all canopies for which it was measured (Figure 6.6).

Table 6.1. Comparison of Total Deposition<sup>a</sup> (wet + dry + cloud/fog) and Bulk Deposition of Inorganic N at IFS Sites Where Both were Measured

Site	Total Deposition			Bulk Deposition		
	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{NO}_3^- + \text{NH}_4^+$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{NO}_3^- + \text{NH}_4^+$
ST	1200	700	1900	315	12	327
CP	330	180	510	220	150	370
DL	590	410	1000	270	330	600
GL	470	180	650	190	160	350
HF	420	150	570	260	180	440
DF	240	110	350	140	75	215
RA	240	100	340	140	75	215
NS	420	360	780	310	310	620

<sup>a</sup> Data are annual averages,  $\text{mol ha}^{-1} \text{yr}^{-1}$ .

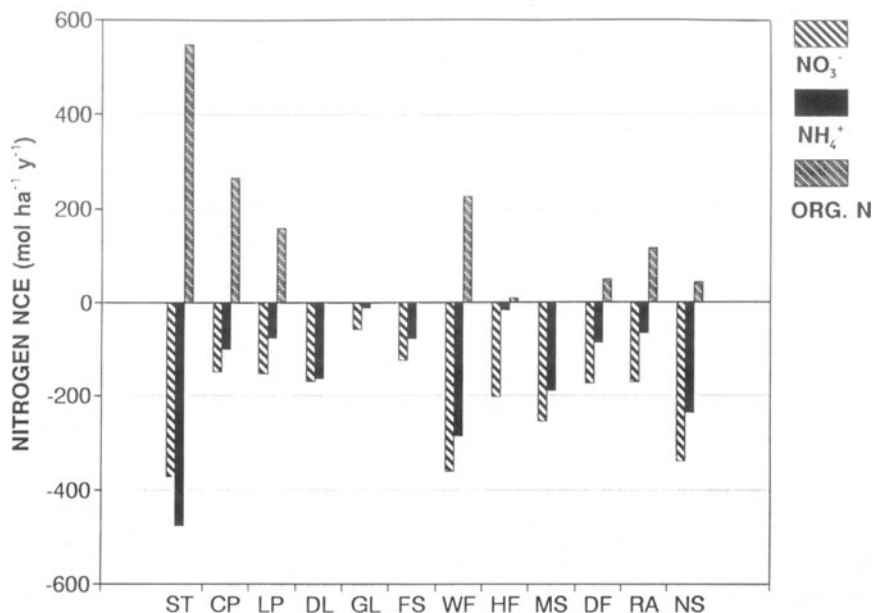


Figure 6.6. Net canopy exchange (NCE, defined as total atmospheric deposition minus throughfall and stemflow deposition) for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and for some sites, organic N. Negative values indicate sink in canopy; positive values indicate source.

We cannot determine the source of the organic N or the fate of the inorganic N from these data. Both denitrification and nitrification can cause N to be lost via gaseous release (as  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NO}$ ), but neither is likely to be important in these canopies. Denitrification requires anaerobic sites, which must certainly be rare in forest canopies, except in cases where large amounts of organic detritus accumulate on limbs or in crotches. If nitrification were responsible for the loss of  $\text{NH}_4^+$ , we would expect a significant release of  $\text{NO}_3^-$  from the canopies, which does not occur. Chen et al. (1983) considered nitrification to be responsible for the decrease in  $\text{NH}_4^+$  and the increase in  $\text{NO}_3^-$  in precipitation passing through a northern hardwoods canopy. Dry deposition of  $\text{NO}_3^-$  was inadequately characterized in that study, and the data presented here indicate that dry deposition could probably have accounted for the increase in  $\text{NO}_3^-$ .

On the other hand, biological uptake of N by canopy surfaces is well documented. Trees have been demonstrated experimentally to be capable of absorbing and incorporating gaseous  $\text{NO}_2$  and  $\text{HNO}_3$  (see, for example, the next part of Chapter 6 in this volume), as well as  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in solution (Reiners and Olson 1984; Bowden et al. 1989). Epiphytic lichens have also been shown to be active absorbers of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in solution (Lang et al. 1976, Reiners and Olson 1984). We note that the strongest sinks (most

negative NCE values) for inorganic N are seen in the spruce and spruce-fir forests (ST, WF, MS, NS), all of which also have a high biomass of epiphytic lichens.

Leaf-surface bacteria and fungi should also show active uptake of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , although this has not been well researched. Microorganisms are unlikely to be a quantitatively significant sink for deposited N, however, because their populations should quickly reach a steady state on canopy surfaces. Microbes could play an important role in the conversion of inorganic to organic N, if that occurs.

The organic N in TF + SF probably arises from the efflux of N-containing compounds (e.g., amino acids, proteins) from internal pools and surfaces of plants, lichens, and microbes, although microparticulate detritus could also contribute (Schaefer and Olson 1984). The NCEs of organic and inorganic N are not significantly correlated across sites, but it is nonetheless possible that some of the lost inorganic N might be transformed to organic N by biological action in the canopy.

Because of the in-canopy sink for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , the below-canopy flux (TF + SF) is depleted in inorganic N relative to the total deposition flux, and a plot of these two fluxes shows that all points fall below the 1:1 line (Figure 6.7). The slope of the best-fit regression line is 0.59, indicating

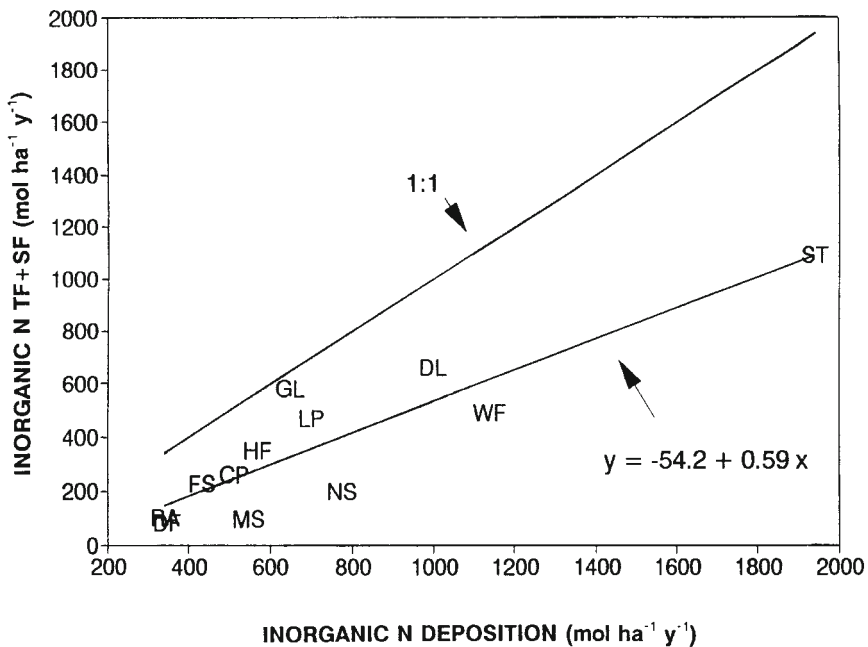


Figure 6.7. Total deposition versus throughfall plus stemflow (TF + SF) for inorganic N ( $\text{mol ha}^{-1} \text{ yr}^{-1}$ ), including 1:1 line (inputs = outputs for canopy) and regression line ( $r^2 = .80$ ).

that, on average, about 60% of the inorganic N deposited to these canopies passes through as TF + SF, while the other 40% is taken up by biological surfaces, converted to organic N in TF or SF, or rereleased to the atmosphere. The fact that the slope of this line is less than 1 implies that the sink strength for inorganic N in the canopy is correlated with the amount of deposition, such that increased deposition results in NCEs that are more strongly negative (Figure 6.8). Close examination of Figure 6.7 suggests that the spruce and spruce-fir canopies (MS, NS, WF, ST) fall on one line and that the rest of the sites fall on another, with the latter having a slope close to 1. This is reflected in Figure 6.8 as a strong relationship between N deposition and canopy uptake for the spruce and spruce-fir sites and a very weak relationship for the other sites. One interpretation is that the four “spruce” sites have some characteristic, perhaps the spruce trees themselves or their epiphytic lichens, that causes greater canopy uptake in response to greater N inputs. The other canopies appear to have a moderate level of N uptake (about  $200 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ), with little response to deposition amount.

For all the sites except CP, the “uptake” of inorganic N exceeds the release of organic N, so the NCE of total N (inorganic + organic) is negative. For the CP site, this number is only slightly positive. The regression line for total deposition versus TF + SF for total N has a slope of 0.84 (Figure 6.9), indicating that only 84% of the change in total N deposition from site

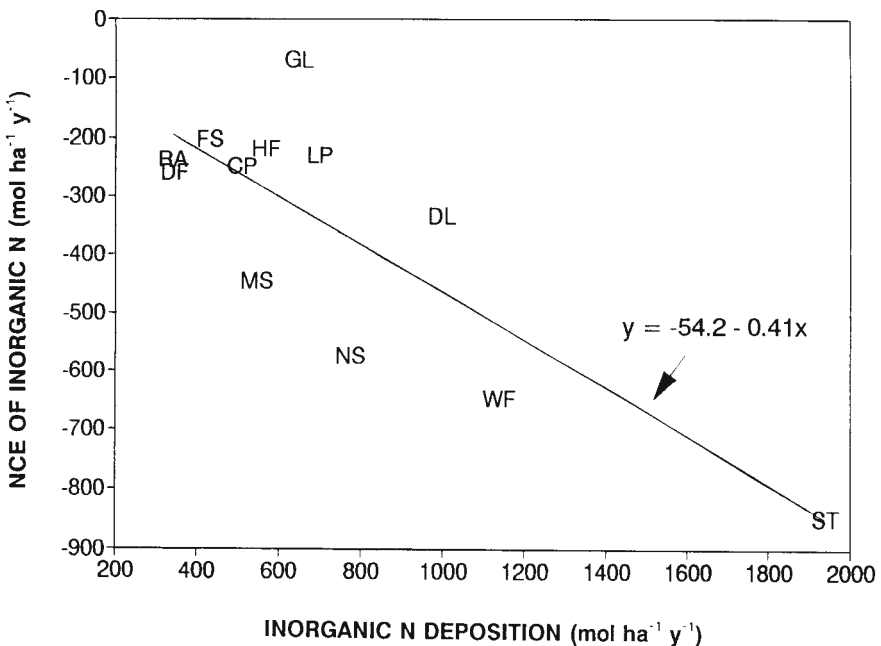


Figure 6.8. Total deposition versus net canopy exchange (NCE) of inorganic N, including regression line ( $r^2 = .66$ ).

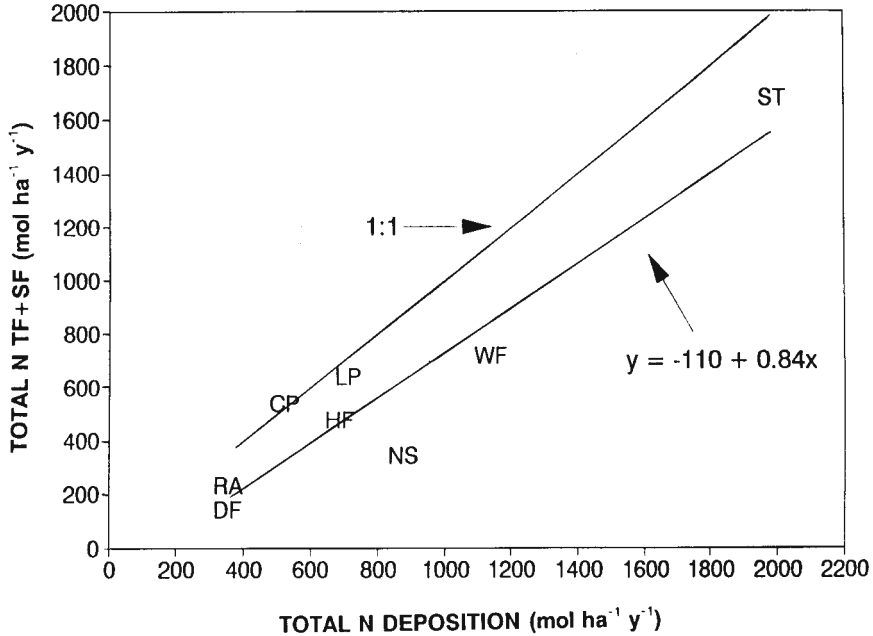


Figure 6.9. Total deposition versus TF + SF for total N (inorganic plus organic), including 1:1 line and regression line ( $r^2 = .89$ ).

to site is reflected in a corresponding change in the below-canopy flux of N. The remainder (16%) must be taken up by the canopy or rereleased to the atmosphere.

The NCE of total N in these canopies ranges from  $+21 \text{ mol ha}^{-1} \text{ yr}^{-1}$  (CP site) to  $-531 \text{ mol ha}^{-1} \text{ yr}^{-1}$  (NS site). Most of the eastern United States sites fall in the range of  $-200$  to  $-450 \text{ mol ha}^{-1} \text{ yr}^{-1}$  ( $-2.8$  to  $-6.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ), with the highest values in the spruce and spruce-fir canopies (MS, WF, ST) and in the DL pine site, which receives high  $\text{HNO}_3$  deposition. These NCE values have considerable uncertainty because they are calculated as difference between two numbers, both measured with uncertainty. However, because dry deposition of  $\text{NO}_2$ , HONO, and  $\text{NH}_3$  was ignored in these calculations, we feel the NCE values are probably conservative.

Although most of the NCE for total N probably results from plant uptake, this amount of uptake is generally small compared to the N needs of the forests. Figure 6.10 contrasts the canopy uptake ( $= -1 \times \text{NCE}$ , assuming all NCE is biological uptake) with the annual stand requirement (defined as the sum of the N contained in current growth of foliage, branches, boles, and, for some sites, roots) and foliar increment (N in current foliage only). In most cases, canopy N uptake is only a small fraction of both the requirement and the foliar increment. The obvious exception is the NS site, for



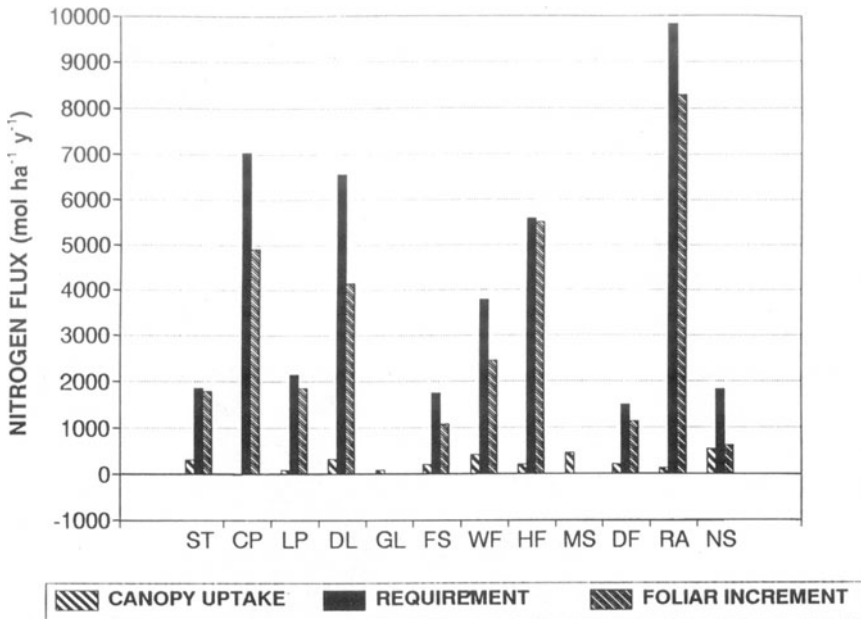


Figure 6.10. Canopy uptake of organic plus inorganic N compared to forest requirement and foliar increment.

which canopy uptake is nearly equal to the foliar increment. Although the canopies are probably absorbing more N from the atmosphere than they were before the advent of air pollution, in general most of their overall N requirement is still being met by root uptake and retranslocation (resorption). Canopy uptake of N is most important nutritionally at the high-elevation sites, which have high uptake and low N requirements.

### Summary

Particulate  $\text{NH}_4^+$  constitutes 50% to 70% of the total atmospheric N concentrations measured in this study (including  $\text{HNO}_3$  vapor and fine-particle  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ). Nitric acid vapor is the dominant species contributing to dry deposition, however, and coarse-particle  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can also be quite important. Although  $\text{NO}_2$  is probably the reactive N species of highest concentration in the atmosphere at many of the sites, it is estimated to contribute less than 20% of the total dry deposition (and <10% of the total deposition) of N and was not directly measured at most sites. The highest total deposition levels were found at the southeastern sites. Total deposition of N averaged about twice the wet deposition for the low-elevation sites in the United States, indicating that dry deposition was roughly equal to wet deposition. Cloud water deposition added substantially more N at the high-

elevation sites ST and WF, which received 1900 and 1100 mol ha<sup>-1</sup> yr<sup>-1</sup>, respectively, of total N deposition.

The net canopy exchange of both NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> was negative (implying canopy uptake), but the NCE of organic N was always positive. Inorganic N in throughfall and stemflow (TF + SF) was about 60% of the inorganic N deposited to the canopy, suggesting that the canopy retained or transformed the other 40%. Total N (organic + inorganic) in TF + SF was about 84% of total N deposition. Canopy uptake of N ranged up to 531 mol ha<sup>-1</sup> yr<sup>-1</sup> but was generally small compared to the N requirements of the forests.

## **Experimental Laboratory Measurements of Reactive N Gas Deposition to Forest Landscape Surfaces: Biological and Environmental Controls**

P.J. Hanson, G.E. Taylor, Jr., and J. Vose

### **Introduction**

As discussed earlier, natural or anthropogenically produced oxides of N occur in the atmosphere in various forms including nitric oxide (NO), N dioxide (NO<sub>2</sub>), and nitric acid vapor (HNO<sub>3</sub>). Ambient concentrations of these oxides reflect a balance between natural or anthropogenic emissions, atmospheric chemical cycling with ozone, and deposition to landscape surfaces (Russel et al. 1985; Finlayson-Pitts and Pitts 1986). Nitrogen dioxide is typically the most concentrated form of atmospheric N oxides ranging from 1 to 2 nl L<sup>-1</sup> in rural (pristine) areas, 5 to 10 nl L<sup>-1</sup> in suburban areas, and as much as 50 nl L<sup>-1</sup> in highly polluted urban/industrial regions (EPA 1982; Bytnerowicz et al. 1987). However, HNO<sub>3</sub>, with concentrations commonly in the range from 0.5 to 1 nl L<sup>-1</sup>, is the principal chemical sink for removal of NO<sub>x</sub> from the atmosphere (Cadle et al. 1982; Galbally and Roy 1983).

Oxides of N can be harmful to plants, depending on a variety of biological and environmental factors. However, the threshold concentrations of NO<sub>2</sub> known to directly impede plant physiological responses are seldom attained under ambient conditions (Hill and Bennett 1970; Furukawa and Totsuka 1979; Kress et al. 1982; Saxe 1986a). Atmospheric sources of N, including NO<sub>2</sub> and HNO<sub>3</sub>, have also been hypothesized to contribute to forest decline in several ways: disrupting the normal development of winter hardiness (Nihlgård 1985; Waring 1987), creating nutrient imbalances (Schulze 1989), and increasing shoot:root ratios (McLaughlin 1983). Conversely, as a source of N for plant growth, atmospheric oxides of N have been shown to contribute N for amino acid production within leaves (Rogers et al. 1979a; Kaji et al. 1980), to enhance the nutrition of plants growing under conditions of low fertility (Yoneyama and Sasakawa 1979), and to increase the activity of N-assimilating enzyme systems (Norby et al. 1989).

Deposition of  $\text{NO}_2$  and  $\text{HNO}_3$  to forest landscape surfaces may represent a potentially significant addition of N to the biogeochemical cycle of forest ecosystems, as discussed earlier in Chapter 6. Unfortunately, quantitative data describing rates and locations of  $\text{NO}_2$  and  $\text{HNO}_3$  deposition to woody plant tissues are not widely available. Deposition measurements are needed as input data for models of atmospheric chemistry, biogeochemical cycling, and studies of pollutant effects on plants (Hosker and Lindberg 1982). Foliar sites of N deposition (internal versus external) must be determined to predict the fate of dry-deposited gases. In addition, because bark or forest floor surfaces account for between 20% and 40% of the total landscape area available for deposition (100% for broadleaf forests in winter; Halldin 1985), deposition to these surfaces must also be quantified. Laboratory studies were conducted to provide direct deposition data for use in evaluating assumptions of the IFS stand-level deposition model. The objectives of the laboratory studies were to characterize deposition of  $\text{NO}_2$  and  $\text{HNO}_3$  to a variety of landscape surfaces, to evaluate the significance of the leaf surface and the leaf interior as sites for  $\text{NO}_2$  or  $\text{HNO}_3$  deposition, and to contrast the deposition characteristics of  $\text{NO}_2$  and  $\text{HNO}_3$ . Because the N budgets summarized previously in Chapter 6 do not include estimates of  $\text{NO}_2$  deposition, we assessed the amount of additional N deposition that may have resulted from  $\text{NO}_2$  inputs. Laboratory measurements of foliar conductances to  $\text{NO}_2$  were used together with available information on ambient  $\text{NO}_2$  concentrations to estimate the probable contribution of  $\text{NO}_2$  to N deposition in the IFS research sites.

### Direct Measurements and Controlling Factors: Laboratory Mass Balance Techniques

Bare-root seedlings of the following species were obtained from commercial nurseries and grown under glasshouse conditions before measurements: red maple (*Acer rubrum* L.), white ash (*Fraxinus americana* L.), tulip poplar (*Liriodendron tulipifera* L.), white oak (*Quercus alba* L.), sycamore (*Platanus occidentalis* L.), red spruce (*Picea rubens* L.), white pine (*Pinus strobus* L.), and loblolly pine (*Pinus taeda* L.). Bark samples were obtained from branches or boles of four mature tree species, including shagbark hickory [*Carya ovata* (Mill.) K. Koch], tulip poplar (*Liriodendron tulipifera*), loblolly pine, and southern red oak (*Quercus falcata* Michx. var. *falcata*). Forest floor samples from loblolly pine or mixed hardwood forest stands near Oak Ridge, Tennessee, were collected as undisturbed cylindrical cores approximately 19 cm in diameter. Hanson et al. (1989) provided complete details of the growing conditions and measurement procedures for these representative forest surfaces.

Mass balance measurements of  $\text{HNO}_3$  and  $\text{NO}_2$  deposition to elements representative of a forest landscape (e.g., foliage, bark, soil) were conducted in an open gas-exchange system. The system simultaneously monitored the

exchange of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and either  $\text{NO}_2$  or  $\text{HNO}_3$  under controlled conditions of temperature, light, vapor pressure, and soil water availability. Techniques for  $\text{HNO}_3$  deposition measurements were similar, but employed a technique based on thermal decomposition (Burkhardt et al. 1988) for measurements of  $\text{HNO}_3$  concentration. Deposition rates ( $\text{nmol m}^{-2} \text{s}^{-1}$ ) were calculated as the product of flow rate and the inlet-outlet concentration differential normalized for surface area and corrected for losses to chamber walls. Measurements of  $\text{HNO}_3$  and  $\text{NO}_2$  deposition to foliage shoots were conducted under light and dark conditions to establish patterns of diurnal variability associated with stomatal conductance. Shoot conductance ( $K_s$ ) to a reactive N gas, a leaf-level measurement analogous to the deposition velocity ( $V_d$ ), was determined by dividing the rate of deposition by the ambient concentration of the gas being measured.

### *Field $^{15}\text{N}$ Exposures*

To quantify internal deposition of  $\text{HNO}_3$ , foliage in the upper canopy of mature eastern white pine trees at the Coweeta Hydrologic Lab was exposed to  $\text{H}^{15}\text{NO}_3$  in branch cuvettes (9.0-L volume) constructed from Teflon film.  $\text{H}^{15}\text{NO}_3$  was generated from calibrated permeation tubes (KIN-TEK Laboratories, Texas City, Texas) and mixed with  $\text{HNO}_3$ -free air created by pulling ambient air through a nylon filter (Nylasorb, Gelman) at a flow rate of  $9.0 \text{ L min}^{-1}$ . Three treatments were imposed to represent a range of exposure conditions: (1) 10 ppb for 30 h; (2) 50 ppb for 12 h; and (3) 100 ppb for 30 h. After exposures, foliage was immediately rinsed with 1000 ml deionized water to remove surface-deposited  $\text{H}^{15}\text{NO}_3$  (Marshall and Cadle 1989), separated by age-class (current year and 1 year), dried at  $60^\circ\text{C}$  for 48 h; and ground to  $100 \mu\text{m}$  using a ball mill. Tissue subsamples ( $n = 2$ ) were analyzed for total N and atom  $^{15}\text{N}\%$  using mass spectrometry (Europa Scientific Instruments, ISO-TEC Labs, Miamisburg, Ohio). Excess  $^{15}\text{N}$  was determined by subtracting total  $^{15}\text{N}$  of exposed foliage from total  $^{15}\text{N}$  of unexposed foliage. Additional details of the  $\text{H}^{15}\text{NO}_3$  exposure methodology have been provided by Vose et al. (1989).

### *Deposition of $\text{NO}_2$ to Plant Foliage*

Under daylight conditions and a mean concentration of  $33 \text{ nl L}^{-1}$ ,  $\text{NO}_2$  deposition to foliage of forest tree species varied by more than an order of magnitude, ranging from 0.35 (loblolly pine) to  $5.75 \text{ nmol m}^{-2} \text{ s}^{-1}$  (sycamore), and the flux to most broadleaf species was greater than deposition to conifers (Table 6.2 and Figure 6.11). For this comparison all surfaces of leaves containing stomata were used as the reference area for calculations (i.e., one side for the broadleaf species and all sides for the conifers). The broadleaf species exhibiting the highest rates of  $\text{NO}_2$  deposition had greater shoot conductance to water vapor (Figure 6.11). Interspecific variation in shoot conductance to water vapor reflects variation in stomatal frequencies

Table 6.2. Conductance of Various Terrestrial Surfaces to  $\text{NO}_2$  Deposition

Surface	Conductance to $\text{NO}_2^a$ ( $\text{cm s}^{-1}$ )
Distilled water	$0.021 \pm 0.02$
Bark	
Dry	$0.047 \pm 0.001$
Wet	$0.093 \pm 0.023$
Plant shoots <sup>b</sup>	
Deciduous	$0.093 \pm 0.042$
Coniferous	$0.049 \pm 0.015$
Forest floor	
Deciduous	$0.47 \pm 0.26$
Coniferous	$0.48 \pm 0.12$

<sup>a</sup> Data for bark and plant shoots are expressed on total area basis and on planar area for intact forest floor samples.

<sup>b</sup> Data for plant shoots correspond to conditions of maximal stomatal conductance.

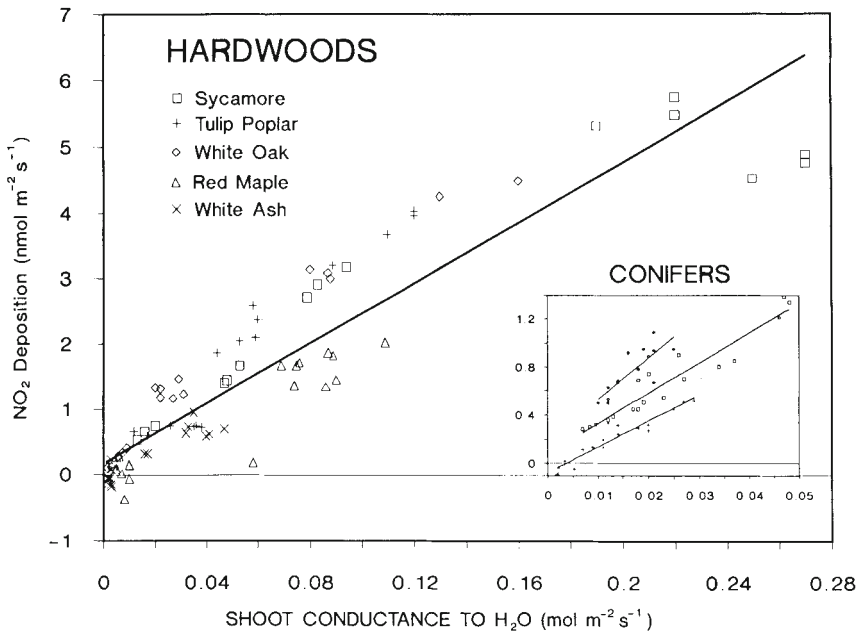


Figure 6.11. Linear relationship between  $\text{NO}_2$  deposition and shoot conductance to water vapor. Symbols represent individual measurements for five broadleaf (main graph) and three conifer species (inset). Data for broadleaf species are expressed on projected leaf area basis; those for conifers are on total area basis. Mean  $\text{NO}_2$  concentration was  $34 \text{ nl L}^{-1}$ . (Hanson et al. 1989. Reprinted with permission from Atmospheric Environment, vol. 23,  $\text{NO}_2$  Deposition to Elements Representative of a Forest Landscape, Copyright 1989 Pergamon Press PLC.)

and stomatal apertures. Stomatal frequencies of *Quercus* species (540 stomata  $\text{mm}^{-2}$ ) are greater than that of *Acer* and *Fraxinus* species (372 and 210 stomata  $\text{mm}^{-2}$ ; Kramer and Kozlowski 1979). The average rate of  $\text{NO}_2$  deposition to these species in the light followed the same trend: *Quercus alba* ( $2.05 \pm 1.44 \text{ nmol m}^{-2} \text{ s}^{-1}$ ) > *Acer rubrum* ( $0.78 \pm 0.11$ ) > *Fraxinus americana* ( $0.57 \pm 0.21$ ). Similarly, lower  $\text{NO}_2$  deposition to conifers with respect to broadleaf species is consistent with their lower conductance to water vapor (Körner et al. 1979). Okano et al. (1988) reported a positive correlation between  $\text{NO}_2$  uptake and stomatal conductance for eight different crop species that followed a trend associated with stomatal densities of the foliage, and Grennfelt et al. (1983) found a similar correlation for *Pinus sylvestris*.

Measurements of  $\text{NO}_2$  deposition in the dark provided information to evaluate surface versus internal deposition of  $\text{NO}_2$ . The contrasting light:dark measurements of  $\text{NO}_2$  deposition indicated that the principal foliar site of  $\text{NO}_2$  deposition was the leaf interior, constituting typically more than 90% of total deposition to individual leaves (Hanson et al. 1989). These data confirm previous hypotheses of stomatal control over  $\text{NO}_2$  and other trace gas deposition (Rogers et al. 1979b; Weseley et al. 1982; Saxe 1986b; Taylor et al. 1988). Accordingly,  $\text{NO}_2$  deposition is strongly influenced by stomatal conductance, which is governed, in turn, by the plant's physiological state as well as a host of environmental factors (e.g., light, vapor pressure, water availability).

Because the atmosphere–leaf exchange of  $\text{NO}_2$  is strongly controlled by stomatal physiology, conventional modeling approaches of gas exchange operating at the level of individual leaves or within whole canopies (and based on analogy to water vapor) should be appropriate for characterizing  $\text{NO}_2$  deposition to vegetation surfaces. Although interspecific variation in  $\text{NO}_2$  deposition was high (see Figure 6.11), a linear regression of the combined data set for deposition to broadleaf shoots versus shoot conductance to water vapor accounted for 85% of the variation, indicating that a single relationship might be useful for predicting deposition to broadleaf forests. A linear regression of the combined data on  $\text{NO}_2$  deposition to conifer shoots against shoot conductance to water vapor explained 66% of the variation.

### *Deposition of $\text{HNO}_3$ to Plant Foliage*

For similar ambient concentrations and low shoot conductances to water vapor, surface deposition of  $\text{HNO}_3$  vapor to plant shoots exceeded that for  $\text{NO}_2$  (Figure 6.12). The  $\text{HNO}_3$  deposition measurements were necessarily limited to conditions of low humidity leading to plants with low shoot conductance to water vapor. Therefore, comparisons of deposition between  $\text{HNO}_3$  and  $\text{NO}_2$  were restricted to the  $\text{NO}_2$  measurements corresponding to leaves having closed stomata (low water vapor conductances). This limitation means that the data for foliar surfaces in Figure 6.12 should be viewed as a com-

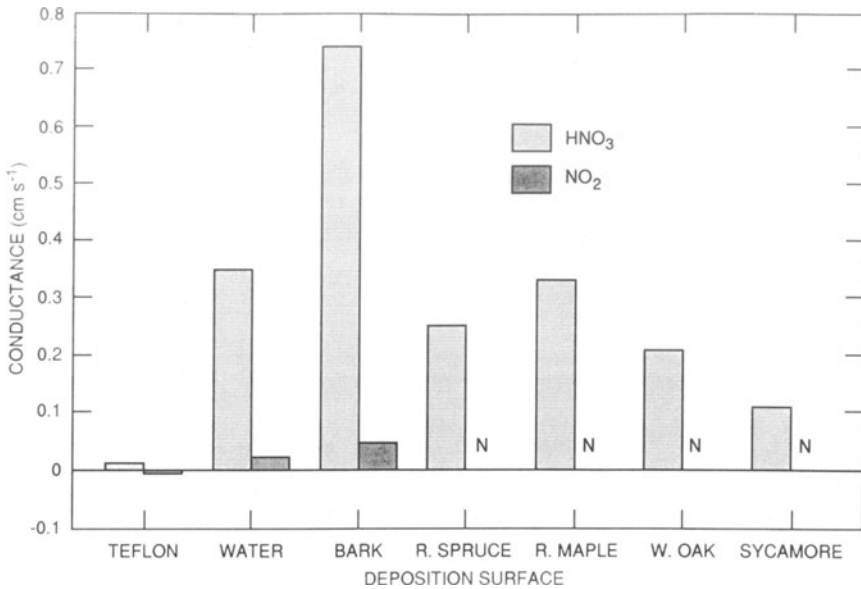


Figure 6.12. Comparison of conductance of NO<sub>2</sub> and HNO<sub>3</sub> to water, bark, and plant cuticular surfaces. Because dry conditions needed to measure HNO<sub>3</sub> exchange shoots resulted in reduced stomatal conductance, data are compared only with NO<sub>2</sub> data from Figure 6.1 that correspond to very low conductances. N, negligible.

parison of the deposition of HNO<sub>3</sub> and NO<sub>2</sub> to external cuticular leaf surfaces. Independent of these constraints on the laboratory data, the HNO<sub>3</sub> and NO<sub>2</sub> data are consistent with field observations that employed micrometeorological techniques (Wesely et al. 1982; Meyers et al. 1989).

Even though large variability and reduced stomatal opening limited rigorous quantification of internal versus external sites of HNO<sub>3</sub> deposition, our data indicated that part of HNO<sub>3</sub> deposition to the leaf interior through leaf stomata is likely to occur coincident with surface deposition (data not shown). More recent experiments employing <sup>15</sup>N-labeled HNO<sub>3</sub> have confirmed this dual pathway for HNO<sub>3</sub> deposition (P.J. Hanson, personal communication).

Field exposures of eastern white pine branches to <sup>15</sup>N-labeled HNO<sub>3</sub> yielded internal foliar deposition rates ranging from 5 to 53 nmol g<sup>-1</sup> s<sup>-1</sup> (Figure 6.13). These deposition rates correspond to a conductance of HNO<sub>3</sub> to white pine foliage of 0.0045 cm s<sup>-1</sup>, which is far lower than the values obtained using the mass balance approach that measures total deposition. The discrepancy results from efficient removal of surface-deposited HNO<sub>3</sub> during the postexposure rinse of the needles (see methods described previously). Marshall and Cadle (1989) found that 97% and 59% of foliar-deposited HNO<sub>3</sub> was recovered in aqueous leaf washings after 2 and 16 hours, respectively.

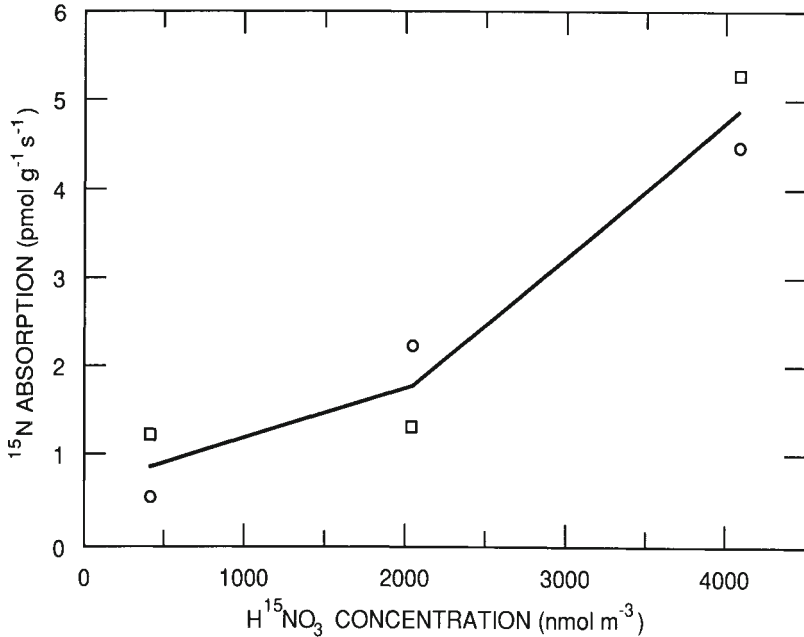


Figure 6.13. <sup>15</sup>N absorption rate as function of HNO<sub>3</sub> concentration for white pine foliage of two age-classes. Squares and circles are 1- and 2- year foliage, respectively. Data are normalized to needle dry weight.

Garten and Hanson (1990) have also shown that 70% to 90% of the nitrate ions in solution deposited to foliar surfaces remain available for subsequent removal by aqueous solutions after a 48-hour period. Because HNO<sub>3</sub> is likely to dissociate into H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> on contact with foliar surfaces, a similar tendency for removal in an aqueous rinse is plausible, and the <sup>15</sup>N-HNO<sub>3</sub> data in Figure 6.13 are probably representative of significant deposition to internal foliar surfaces. Longer residence times for NO<sub>3</sub><sup>-</sup> on foliar surfaces between rain events (>48 h) might allow for more internal deposition through the cuticle than was suggested by the work of Garten and Hanson (1990).

#### *Deposition to Nonfoliar Landscape Elements*

Deposition of NO<sub>2</sub> varied among forest elements measured. Foliar, bark, and forest floor surfaces typically showed greater conductance to NO<sub>2</sub> than distilled water alone, and forest floor surfaces showed a disproportionately high conductance when compared to bark or foliage (see Table 6.2). The average conductance to NO<sub>2</sub> of the materials measured ranged from -0.0045 to 0.48 cm s<sup>-1</sup>. The deposition of NO<sub>2</sub> to distilled water was relatively low by comparison to bark and foliage, but the measured conductance of NO<sub>2</sub> from the atmosphere to water (0.021 cm s<sup>-1</sup>) was similar to the 0.010 cm s<sup>-1</sup> value reported by van Aalst (1982). Conductance to NO<sub>2</sub> of dry bark



was similar to that for conifer shoots (0.047 and 0.049  $\text{cm s}^{-1}$ , respectively), and conductance to  $\text{NO}_2$  of wet bark was similar to values for broadleaf shoots (0.093 and 0.093  $\text{cm s}^{-1}$ , respectively). Conductance to  $\text{NO}_2$  was not influenced by species of bark (data not shown);  $\text{HNO}_3$  conductance to bark surfaces was 15 times greater than  $\text{NO}_2$  conductance to the same surface (see Figure 6.12).

Conductance to  $\text{NO}_2$  of the forest floor, based on a ground area basis, was six- to sevenfold greater than conductance to foliar surfaces or dry bark (see Table 6.2). This high conductance to  $\text{NO}_2$  is, at least in part, a result of unaccounted-for convolutions in the samples (i.e., high surface area). The true area of the forest floor samples might easily have been two- or threefold times greater than the actual ground area and would have resulted in deposition values closer to those of leaves and bark surfaces. Judeikis and Wren (1978) observed similar or higher conductance of  $\text{NO}_2$  to both a sandy loam and an adobe clay soil (average velocity of 0.68  $\text{cm s}^{-1}$ ), which compares favorably with our conductance values of 0.47 and 0.48  $\text{cm s}^{-1}$  for the broadleaf and conifer forest floor samples, respectively. Measured conductance to  $\text{NO}_2$  for autoclaved or oven-dried soils (data not shown) were similar to values for unsterilized soil, indicating that soil microorganisms were not responsible for the high conductances. Abeles et al. (1971) and Ghiorse and Alexander (1976) also observed no effect of microorganisms on  $\text{NO}_2$  deposition.

### Calculated $\text{NO}_2$ and $\text{HNO}_3$ Deposition to Forest Stands

To demonstrate the use of leaf-level data for making estimates of stand-level  $\text{NO}_2$  deposition, laboratory observations were extrapolated to 10 of the conifer and hardwood forest canopies in the Integrated Forest Study (see Chapter 2, this volume) and to the forest canopy of the Walker Branch Watershed (WB). The Walker Branch Watershed represents a oak-hickory forest located in a suburban area near Knoxville, Tennessee (Johnson 1989) that has higher levels of gaseous pollutants (Table 6.3). Surface conductances for N oxides ( $K_i$ ) measured in the laboratory were used to approximate the analogous measure for forest canopies (i.e., the deposition velocity,  $V_d$ ) using the following equation:

$$V_d = K_i * \text{LAI} \quad [6.1]$$

where LAI is the leaf area index (Jarvis 1971; O'Dell et al. 1977; Hicks et al. 1987). Rates of total growing season N deposition contributed by  $\text{NO}_2$  for each forest site were then approximated from the product of the stand  $V_d$ , the mean daytime concentration of  $\text{NO}_2$  for those stands, and the effective hours of daytime deposition (Table 6.3). A more detailed discussion of this calculation has been provided by Hanson et al. (1989). Calculated growing season rates of  $\text{HNO}_3$  deposition were also determined, based on the

Table 6.3. Estimated Growing Season N Deposition from Nitrogen Dioxide (NO<sub>2</sub>-N) and Nitric Acid Vapor (HNO<sub>3</sub>-N) to 10 IFS Sites, a Suburban Site (WB) and a Hypothetical Urban Deciduous and Coniferous Forest Stand (UD and UC) (modified from Hanson et al. 1989 with permission from Atmospheric Environment, volume 23, Copyright 1989 Pergamon Press PLC.)

Site <sup>a</sup>	Concentration <sup>b</sup> [EDH] <sup>c</sup>		Estimated NO <sub>2</sub> -N Deposition <sup>d</sup> (mol ha <sup>-1</sup> yr <sup>-1</sup> )	Estimated HNO <sub>3</sub> -N Deposition <sup>d</sup> (mol ha <sup>-1</sup> yr <sup>-1</sup> )	NO <sub>2</sub> -N deposition: N as % of total N deposition <sup>e</sup> (%)
	LAI (m <sup>2</sup> m <sup>-2</sup> )	NO <sub>2</sub> (μg m <sup>-3</sup> )			
Pine					
FS	5.1	1.9 [3402]	20	44	5
LP	3.6	15.1 [2394]	62	69	9
DL	6.5	9.2 [2859]	82	152	8
CP	16.9	3.8 [2394]	48	213	9
Spruce					
WF	4.6	3.8 [1800]	10	25	<1
MS	5.5	2.8 [2179]	11	26	2
NS	10.5	1.9 [2124]	13	71	2
ST	9.0	3.8 [1995]	21	120	1
Douglas fir					
DF	10.6	1.9 [2940]	23	82	7
Northern hardwoods (maple)					
HF	4.7	3.8 [2179]	54	79	9
Oak-hickory					
WB	5.5	15.1 [2394]	200	109	21
Urban					
UD	5	55.2 [2394]	1258	125	NA <sup>f</sup>
UC	5	55.2 [2394]	331	68	NA

<sup>a</sup> Research site abbreviations are as follows [EPR1 sites]: CP, white pine, North Carolina; DF, Douglas fir, Washington; DL, Loblolly pine, North Carolina; FS, slash pine, Florida; HF, N. hardwoods, New York; LP, loblolly pine, Tennessee; MS, red spruce, Maine; NS, Norway spruce, Norway; RA, red alder, Washington; ST, red spruce, North Carolina; WF, red spruce, New York; [Non-EPR1 sites]: WB, oak/hickory, Tennessee; UB and UC, hypothetical urban deciduous and coniferous forests.

<sup>b</sup> Ambient NO<sub>2</sub> concentrations for stand LP and WB are from Kelly and Meagher (1986) and from personal communications with investigators of the nine IFS sites (WF, HF); the others are extrapolated from Galbally and Roy (1983) and EPA (1982) for pristine (41 nmol m<sup>-3</sup>) and rural polluted sites (200 nmol m<sup>-3</sup>). HNO<sub>3</sub> concentrations are from site data on pp. 154–157.

<sup>c</sup> EDH, Estimated hours of deposition.

<sup>d</sup> Estimates are based on laboratory measurements of conductance of NO<sub>2</sub> and HNO<sub>3</sub> to seedling shoots and assume constant concentration of NO<sub>2</sub> or HNO<sub>3</sub> throughout forest canopy and negligible leaf boundary layer (i.e., well-mixed conditions).

<sup>e</sup> Percent was based on total N deposition values (pp. 157–160) that do not include estimates of NO<sub>2</sub> deposition.

<sup>f</sup> NA, Not available.

assumption that deposition of  $\text{HNO}_3$  during the night was to external canopy surfaces and during the day to external surfaces and to internal leaf sites via open stomata. The “growing season”  $\text{HNO}_3$  deposition rates included in Table 6.3 and used in Figure 6.14 are provided for direct comparison to the rates estimated for  $\text{NO}_2$ . The growing season estimates for  $\text{HNO}_3$  deposition are not equivalent to the more rigorous estimates obtained from the IFS model, which uses additional meteorological and stand structure characteristics to predict gaseous deposition for an entire year (see pp. 152–166; Lindberg et al. 1989).

Estimates of growing season  $\text{NO}_2$ -N deposition to the different forest canopy types varied 20 fold from a minimum of 10 for the New York red spruce-fir site (WF) to a maximum of 200  $\text{mol NO}_2\text{-N ha}^{-1} \text{ yr}^{-1}$  for the oak-hickory site in Oak Ridge (WB). The mean  $\pm$  SE among all forest sites was  $49 \pm 17 \text{ mol NO}_2\text{-N ha}^{-1} \text{ yr}^{-1}$ . The estimates for the sites with the lowest ambient concentrations of  $\text{NO}_2$  (FS, NS, DF) averaged 19  $\text{mol NO}_2\text{-N ha}^{-1} \text{ yr}^{-1}$ , whereas the two most polluted sites exhibited  $\text{NO}_2$  deposition rates as

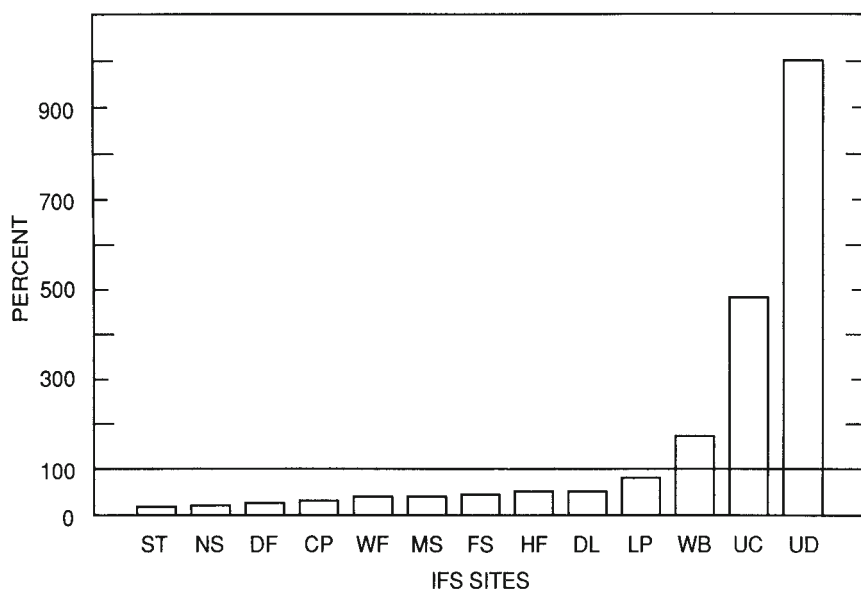


Figure 6.14. Calculated growing season deposition of  $\text{NO}_2$ -N as percentage of calculated  $\text{HNO}_3$ -N. Horizontal line at 100% indicates equivalent molar amounts of  $\text{HNO}_3$  and  $\text{NO}_2$  deposition. Forest site abbreviations are as follows: [EPRI sites] CP, white pine, North Carolina; DF, Douglas fir, Washington; DL, loblolly pine, North Carolina; FS, slash pine, Florida; HF, northern hardwoods, New York; LP, loblolly pine, Tennessee; MS, red spruce, Maine; NS, Norway spruce, Norway; RA, red alder, Washington; ST, red spruce, North Carolina; WF, red spruce, New York; [Non-EPRI sites] WB, oak hickory, Tennessee; UB and UC, hypothetical urban deciduous and coniferous forests.

much as 10 fold higher, of 62 (LP) and 200 mol  $\text{NO}_2\text{-N ha}^{-1} \text{ yr}^{-1}$  (WB). Higher deposition to the WB and LP site can be accounted for principally by higher  $\text{NO}_2$  concentrations and  $K_f$ . The high predicted deposition of  $\text{NO}_2$  to the CP site is a result of its large LAI. Extrapolated measurements of  $^{15}\text{N-HNO}_3$  deposition from Figure 6.13 to the stand level indicate that of the total  $\text{HNO}_3$  deposited perhaps only 10% to 20% is absorbed immediately by the forest canopy. If sufficiently short intervals were to occur between precipitation events, this observation would indicate that most dry-deposited  $\text{HNO}_3$  is removed to the forest floor in throughfall. These data corroborate the earlier conclusions in this chapter that  $\text{NO}_3^-$  losses from the IFS canopies in throughfall were predicted to result from the accumulation of dry-deposited  $\text{NO}_3^-$  from  $\text{HNO}_3$  between rain events.

The dry deposition of  $\text{NO}_2$  is not included in the N budgets presented in the preceding portion of Chapter 6. However, growing season  $\text{NO}_2$  deposition was less than 10% of annual total N deposition for the IFS sites. Only the non-IFS WB site with mean  $\text{NO}_2$  concentrations of  $15.1 \mu\text{g m}^{-3}$  and high foliar conductances to  $\text{NO}_2$  was predicted to have a substantially higher percentage (21%) of N deposition resulting from  $\text{NO}_2$  (see Table 6.3). Forest canopies for which estimated  $\text{NO}_2$  deposition contributed more than 5% of total N deposition included pristine (DF), intermediate (CP and HF), and polluted sites (DL, LP, and WB).

If we contrast the predicted rates of  $\text{NO}_2$  and  $\text{HNO}_3$  deposition obtained from the extrapolated laboratory measurements (see Figure 6.14), we find that  $\text{NO}_2$  deposition will only exceed  $\text{HNO}_3$  deposition to forest canopies under conditions of high ambient  $\text{NO}_2$  concentrations [i.e., the WB, urban deciduous (UD), and urban coniferous (UC) forest sites]. In or near urban environments,  $\text{NO}_2$  concentrations often reach concentrations as high as  $60 \text{ nl L}^{-1}$  and are routinely greater than  $30 \text{ nl L}^{-1}$  throughout the day (Lefohn and Tingey 1984; Bytnerowicz et al. 1987; Laxen and Noordally 1987). To estimate  $\text{NO}_2$  deposition to deciduous or coniferous "urban forests" for comparison to the IFS and WB sites, we used calculations similar to those described for the 11 IFS forest canopies (see Table 6.3). Estimated  $\text{NO}_2\text{-N}$  deposition to urban forest canopies ranged from  $330$  to  $1260 \text{ mol ha}^{-1} \text{ yr}^{-1}$  for coniferous and deciduous trees, respectively. These hypothetical urban  $\text{NO}_2\text{-N}$  deposition estimates are an order of magnitude higher than the rates of deposition calculated for "natural" forest canopies, suggesting that dry deposition of  $\text{NO}_2$  must be considered in or near urban areas.

The estimates of  $\text{NO}_2$  deposition to forest canopies presented in Table 6.3 are first approximations that assume maximum canopy conductance, throughout the growing season. They do not account for the impact of drought conditions on stomatal conductance, which leads to an overestimate of dry deposition. However, they also do not include estimates of deposition to bark and forest floor surfaces, resulting in an underestimate that would partially offset such an overestimate. Independent of the shortcomings of these

first-approximation estimates, we believe that the extrapolations from the laboratory measurements indicate that current concentrations of  $\text{NO}_2$  in conjunction with other forms of atmospheric N (wet and dry) provide physiologically significant inputs of N to forest systems. The estimated inputs of  $\text{NO}_2$ -N and  $\text{HNO}_3$ -N listed in Table 6.3, ranging from 10 to 213 mol N ha<sup>-1</sup> yr<sup>-1</sup>, are similar to inputs expected for temperate forest systems from nonsymbiotic N-fixing bacteria (0–214 mol N ha<sup>-1</sup> yr<sup>-1</sup>; Waring and Schlesinger 1985).

### Summary

Laboratory measurements have shown that comprehensive estimates of atmospheric inputs N to forest stands should consider inputs of  $\text{NO}_2$  and  $\text{HNO}_3$  along pathways leading to foliage, bark, and forest floor surfaces. For most of the IFS sites, contributions of N from dry-deposited  $\text{NO}_2$  would remain small because of low atmospheric  $\text{NO}_2$  concentrations. However, where the concentration of  $\text{NO}_2$  is significant (near polluted urban areas), the following points need to be considered:  $\text{NO}_2$  deposition to foliage of forest tree species varied by more than an order of magnitude, and deposition of  $\text{NO}_2$  to most broadleaf species was greater than deposition to conifers. Measurements of  $\text{NO}_2$  deposition under light and dark conditions indicated the principal foliar site of  $\text{NO}_2$  deposition to be the leaf interior and supported previous observations of stomatal control over  $\text{NO}_2$  deposition. Vegetation surfaces typically showed greater conductance to  $\text{NO}_2$  uptake than distilled water alone, and forest floor surfaces showed a disproportionately high conductance to  $\text{NO}_2$  when compared to bark or foliage surfaces.

For a similar atmospheric molar concentration, the rate of deposition of  $\text{HNO}_3$  will always exceed that for  $\text{NO}_2$ , but the relative contribution from each reactive N gas to dry deposition is largely controlled by existing ambient air concentrations. Unlike  $\text{NO}_2$ ,  $\text{HNO}_3$  vapor exhibits significant deposition to leaf cuticular surfaces, but a finite amount of internal deposition also occurs. Models for  $\text{HNO}_3$  uptake might be enhanced by recognizing two pathways of uptake: a cuticular path for surface deposition and a stomatal pathway leading to internal surfaces. A portion of surface-deposited  $\text{HNO}_3$  is likely to remain available for subsequent removal from foliar surfaces during rain events, in contrast to internal uptake of  $\text{HNO}_3$  and  $\text{NO}_2$ , which are likely assimilated into organic N forms.

Rates of growing season  $\text{NO}_2$  and  $\text{HNO}_3$  dry deposition to nonurban forests are similar to inputs expected from nonsymbiotic N-fixing bacteria in temperate forest ecosystems (0–214 mol N ha<sup>-1</sup> yr<sup>-1</sup>). Dry deposition of  $\text{NO}_2$  to the IFS sites was generally less than 10% of the total N deposited from other forms (wet, particle,  $\text{HNO}_3$ ), but  $\text{NO}_2$  should not be ignored as a source of dry N deposition when calculating total N loading to forest stands near urban areas.

## Nitrogen Distribution and Cycling

H. Van Miegroet, D.W. Cole, and N.W. Foster

### Ecosystem N Distribution

The forest ecosystems within the IFS network cover a wide array of climatic conditions (from cold boreal to subtropical), forest type (deciduous versus conifer), stand age, and disturbance history (from young plantations established on recently disturbed sites to overmature climax forests (see Chapter 2). These factors have contributed to the great variation in N distribution and cycling patterns among the 17 IFS locations. The total ecosystem N content varies from less than 120 kmol ha<sup>-1</sup> in the Florida Slash Pine (FS) to 1200 kmol ha<sup>-1</sup> in the high-elevation spruce forests at Whiteface Mountain (WF), while several sites contain about or more than 750 kmol N ha<sup>-1</sup> [i.e., high-elevation spruce and beech forests of the Great Smoky Mountains (ST, SB), hardwood at Turkey Lakes, Ontario (TL), and low-elevation red alder stands in Washington (RA)] (Figure 6.15). The low-elevation southern conifer sites [e.g., loblolly pine at Duke Forest (DL) and Oak Ridge (LP), white pine at Coweeta (CP), and slash pine in Florida (FS)], and the spruce

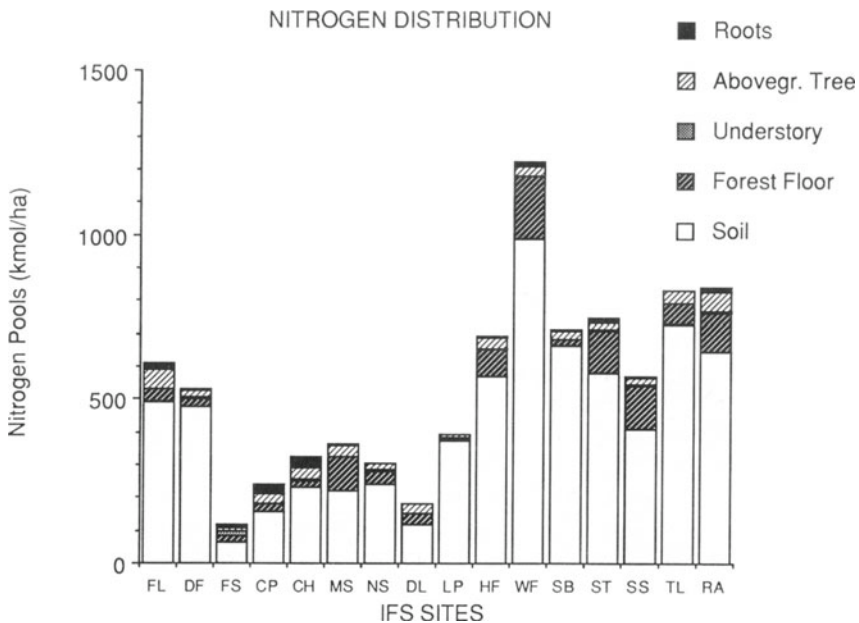


Figure 6.15. Total N content and N distribution in soil (0–60 cm), forest floor, understory vegetation, aboveground tree biomass, and roots (where available) at IFS sites ranked by NO<sub>3</sub><sup>-</sup> output.

sites in Maine (MS) and Norway (NS) generally fall at the lower end of the total N content scale.

In all ecosystems, most of the N is sequestered in the soil compartment, which accounts for 55% to 95% or an average of 80% of the total ecosystem N capital. The lowest percentages are found in the relatively young and nutrient-poor sandy soils derived from marine deposits in the FS site, and in the low-elevation Maine spruce site (MS) where a substantially greater portion of the total N pool resides in the forest floor. Soil N values to a rooting zone of approximately 60 cm depth range from less than 64 kmol ha<sup>-1</sup> (900 kg ha<sup>-1</sup>) in the FS site to almost 990 kmol ha<sup>-1</sup> (14,000 kg ha<sup>-1</sup>) at the WF site. Forest floor N contents and their contribution to total N vary more widely among the IFS sites: the lowest forest floor N content of 8 kmol ha<sup>-1</sup> (or 110 kg ha<sup>-1</sup>) is observed in the loblolly pine site at Oak Ridge, Tennessee (LP), compared to a high of 190 kmol ha<sup>-1</sup> (roughly 2,600 kg ha<sup>-1</sup>) at WF. The highest forest floor N contents are generally associated with significantly larger organic matter accumulation in the northern and high-elevation sites (ST, SS, WF, MS), probably a result of the colder climate in those areas and its negative effect on the decomposition process (Witkamp 1966; Meentemeyer 1978; Meentemeyer and Berg 1986).

By contrast, the high forest floor N content in the red alder forest (RA) reflects large annual inputs of N-rich litter material by this N-fixing tree species rather than prolonged N accumulation or slow organic matter decomposition (Cole et al. 1978). Understory and tree biomass generally contribute less than 10% of the total ecosystem N content, except in the North Carolina sites (CP, CH, DL) where low soil and forest floor N contents raise the contribution of the aboveground vegetation to approximately 20%. Living biomass N values do not differ greatly among ecosystems compared to total N capitals and range from 14 to 66 kmol ha<sup>-1</sup> (or 200–900 kg ha<sup>-1</sup>). Our observations are consistent with results from the International Biological Program (IBP), which similarly indicated a relatively minor role of the living biomass and the major contribution of the soil rooting zone in the overall ecosystem N distribution (Duvigneaud and Denaeyer-De Smet 1970; Cole and Rapp 1981).

### Factors Controlling N Retention and Release

The primary goal of this chapter was to evaluate the occurrence and causes of N saturation and excess NO<sub>3</sub><sup>-</sup> leaching from forest ecosystems, particularly the role of atmospheric N deposition. A simple ranking of the IFS sites by average NO<sub>3</sub><sup>-</sup> leaching output during a 2- to 3-year period (Figure 6.16) demonstrates that some of the sites are clearly leaching large amounts of NO<sub>3</sub><sup>-</sup> [e.g., the TL, RA, and Smoky Mountain sites (SS, ST, SB)], whereas there are others that show little or no N leaching loss. Although the Smoky Mountain sites receive the highest N input via dry and wet deposition within the IFS network, and low NO<sub>3</sub><sup>-</sup> leaching rates are generally observed in

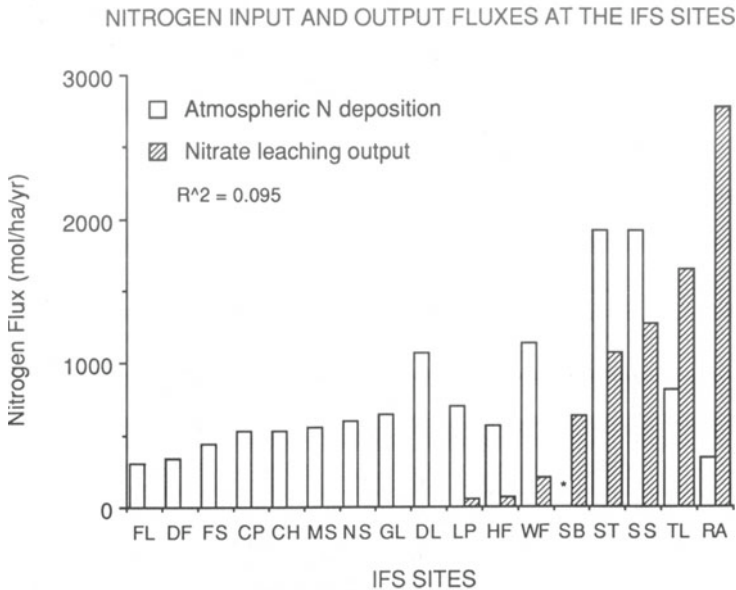


Figure 6.16. Total annual atmospheric N deposition input and  $\text{NO}_3^-$  leaching output in IFS forest ecosystems (\* indicates no deposition data available).

sites that receive low N inputs, there is only a weak positive correlation between annual N input and N output rates ( $r^2 \sim .10$ ) across all sites. In other words, atmospheric N deposition as a single factor is insufficient to explain differences in occurrence and rate of  $\text{NO}_3^-$  leaching among all sites within the IFS network. However, if only those sites are considered that are currently showing considerable  $\text{NO}_3^-$  leaching, then a somewhat stronger correlation between atmospheric N deposition and  $\text{NO}_3^-$  leaching outputs emerges [ $r^2 = .26$  excluding N-fixing RA;  $r^2 = .71$ , including RA with total atmospheric N input to RA = atmospheric N deposition + approximately  $6100 \text{ mol ha}^{-1} \text{ yr}^{-1}$  via N fixation (Cole et al. 1978)]. This suggests that once a system reaches N saturation, increasing N inputs will result in concomitant increases in  $\text{NO}_3^-$  leaching.

### *General Concepts Involved*

Nitrification is a microbial N transformation process mediated by nitrifying organisms whose activity is strongly controlled by N availability (Vitousek et al. 1979; Riha et al. 1986). The  $\text{NO}_3^-$  formed during this process is highly mobile (Kinjo and Pratt 1971; Johnson and Cole 1980) and will quickly leach through the soil profile and out of the rooting zone unless it is immobilized biologically. Thus, the nitrification potential of a site or the degree of  $\text{NO}_3^-$  retention following nitrification depends on the relative N source



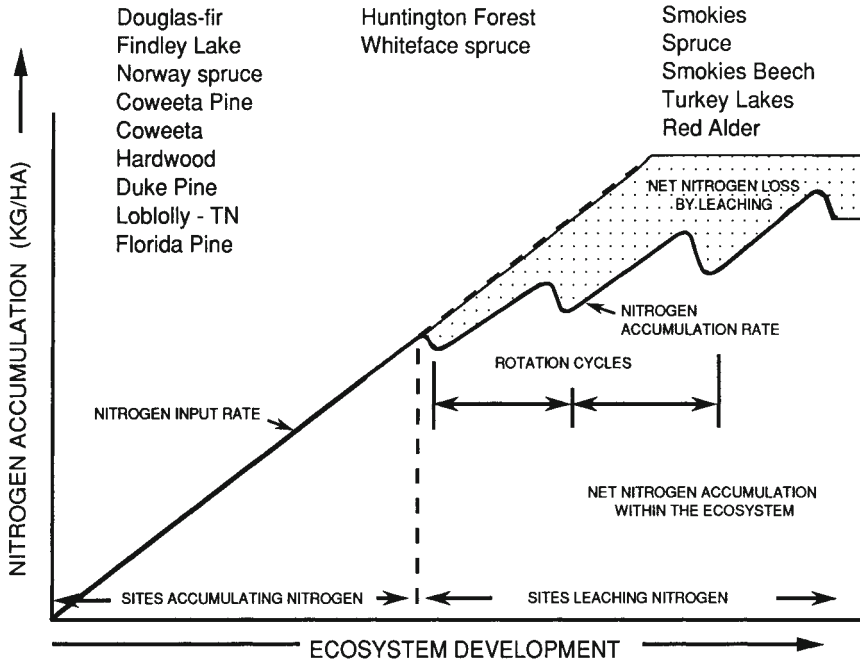
compared to sink strengths within the system. These, in turn, are determined both by natural ecosystem characteristics (e.g., age and type of vegetation, soil age, and organic matter accumulation) and anthropogenic influences on this system (e.g., management practices, pollution). Nitrogen may be added to the belowground compartment from external sources such as N fertilization, N fixation, and direct atmospheric N deposition, or may be released internally via mineralization of soil and forest floor organic matter.

Nitrogen sinks include N uptake by the vegetation, microbial N immobilization, and adsorption to the soil exchange complex (in the case of  $\text{NH}_4^+$ ). Nitrogen may also be lost in gaseous form, that is, through denitrification or  $\text{NH}_3$  volatilization, but these output fluxes are expected to play a minor role in the overall N budget of these systems. Volatilization of  $\text{NH}_3$  occurs under alkaline conditions and should therefore be insignificant in typically acid forest soils (Warneck 1988). Denitrification requires the presence of  $\text{NO}_3^-$ , and the values reported in the literature are generally small, even for systems with seemingly favorable conditions for denitrification [e.g., high-elevation spruce forests in the Southern Appalachians (Wells et al. 1988)].

In that nitrifiers are weak competitors for N against plants and heterotrophic decomposers, nitrification is generally restricted in systems that are N deficient, that is, where potential N sinks exceed or equal N inputs. When the N supply increases or N sinks decline, sufficient N may become available for nitrification after plant and heterotrophic N demands are met, and  $\text{NO}_3^-$  may leach out of the system. Thus, the production and leaching of  $\text{NO}_3^-$  suggest N availability in excess of biological retention capacity (i.e., plant and microbial immobilization), making  $\text{NO}_3^-$  leaching a practical indicator of N saturation.

The N retention capacity and, conversely, the leakiness of the system with respect to  $\text{NO}_3^-$  or degree of N saturation could also be placed in the context of the long-term ecological history of an area, forest ecosystem maturity or successional stage, and forest stand development and age as represented in Figure 6.17. Ecosystems on more recently developed soils (e.g., following deglaciation, volcanic ash deposition) such as DF and FL in Washington or whose organic C and N pool has been frequently or recently reduced by disturbance (e.g., fire or agricultural cropping) such as the southern conifer plantations (e.g., DL) are still at the stage of active organic matter (C) and N accumulation. Nitrogen retention in such systems should be near or at maximum, irrespective of age or vigor of the forest. In some cases late-rotation N deficiencies develop on sites with low N (e.g., Turner 1981). No  $\text{NO}_3^-$  leaching occurs, even with small increases in N inputs. The leaching process in such systems is mostly dominated by organic acid anions and bicarbonate resulting from the root respiration and decomposition of soil organic matter or by  $\text{SO}_4^{2-}$  originating from atmospheric deposition (Johnson and Cole 1980).

At the other extreme of the spectrum one could consider ecosystems that have accumulated large amounts of N and C, either over a long period with-



ROLE OF NITROGEN INPUT ON NITROGEN ACCUMULATION AND LEACHING LOSSES AT THE IFS SITES

Figure 6.17. Schematic representation of IFS sites with respect to N accumulation and N saturation according to forest ecosystem history and maturity.

out significant reduction by site disturbance (e.g., WF and the Smokies sites), or relatively rapidly with the presence of N fixers (e.g. RA site in Washington). Nitrogen storage capacity of the system has reached its upper limit with respect to its current C content (see section below and Figure 6.18), the level of which, in turn, is regulated by climatic conditions (Post et al. 1982, 1985). Nitrogen inputs in such systems are no longer retained, and  $\text{NO}_3^-$  leaching occurs. Stand age and vigor play a critical role in regulating the extent of the  $\text{NO}_3^-$  leaching output (see Figure 6.17): young or highly productive stands are able to curtail  $\text{NO}_3^-$  losses somewhat through plant N uptake (Vitousek and Reiners 1975). In mature to overmature stands, N uptake rates are generally low, and any disturbance of the stand structure with mortality may actually accelerate N mineralization and nitrification rates. Increases in N inputs to such systems will lead to concomitant increases in  $\text{NO}_3^-$  leaching (Foster et al. 1989a).

Forests may also be situated in an intermediate position in terms of N accumulation and retention. The combination of total N content, mineralization potential, stand age and vigor, and N input rates, that is, small changes

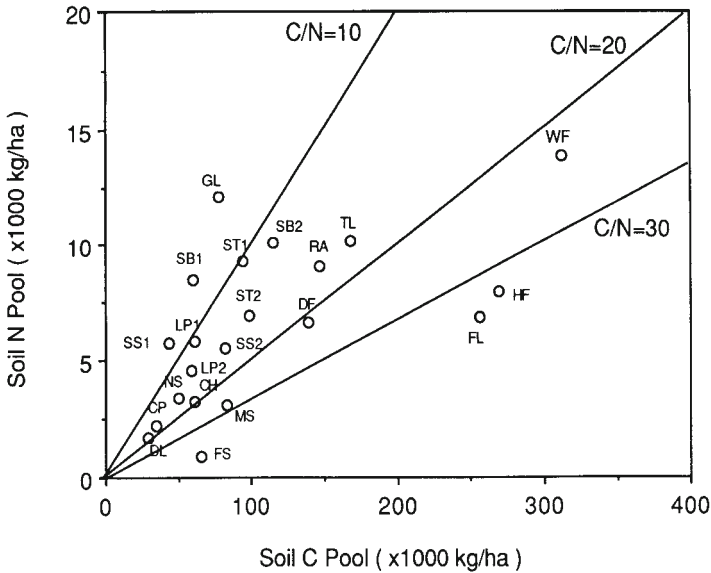


Figure 6.18. Total soil N and C accumulation in IFS sites.

in N source and N sink strengths, will play a critical role in such system in determining the extent of  $\text{NO}_3^-$  production and leaching.

### *Nitrogen Release*

A crude way to identify sites that are N saturated is by comparing atmospheric N inputs to annual N leaching losses (e.g., Dempster and Manning 1988; Nilsson and Grennfelt 1988). Based on the average annual N input-output budget, only the hardwood site in Ontario (TL) shows a net release from the system and could thus be designated as N saturated on the basis of this approach (see Figure 6.16). Indeed, in the red alder forest, symbiotic N fixation represents an additional N input of the order of 3,500 to 11,000  $\text{mol ha}^{-1} \text{yr}^{-1}$  (Zavtkovski and Newton 1968; Cole et al. 1978; Binkley 1981) suggesting some N is still being accumulated in the system. However, input-output budgets must be interpreted with some caution because of the uncertainties associated with the quantification of the dry deposition component (pp. 153–166) and of the total water flux from the rooting zone (Chapter 3). Using a simple input-output approach does not account for the role of internal processes and the release through mineralization of N accumulated previously in the ecosystem. Thus, based on these considerations and the foregoing discussions, we will use the occurrence of measurable  $\text{NO}_3^-$  leaching as an indication that N sources (internal and external) exceed the N sinks in the system; that is,  $\text{NO}_3^-$  leaching will serve as the operational definition of N saturation.

Averaging solution concentrations over a given time period, however, tends to obscure occasional  $\text{NO}_3^-$  leaching pulses that may take place either seasonally or at any given year and which indicate that the N retention capacity of the system is at least temporarily exceeded by N inputs. This was the case in the Smokies spruce forests (Johnson et al. 1991), or in the northern hardwoods (Foster et al. 1989b; Shepard et al. 1990). Therefore, some low level of  $\text{NO}_3^-$  leaching should be deemed "normal" [e.g.,  $150 \text{ mol ha}^{-1} \text{ yr}^{-1}$  or roughly  $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  as used in the definition of critical N loads (Nilsson and Grennfelt 1988)] to account for the temporary  $\text{NO}_3^-$  release during the spring snowmelt period before the onset of the growing season.

The first step in determining the factors that cause N saturation in forest systems is identifying common characteristics among sites that currently show extensive  $\text{NO}_3^-$  leaching as well as those ecosystem properties that distinctly separate  $\text{NO}_3^-$  leaching from nonleaching sites. To that effect, simple linear regression and stepwise multiple regression analyses were performed using various N pools and N fluxes as independent variables and  $\text{NO}_3^-$  leaching as the dependent variable. Table 6.4 summarizes the results from the stepwise multiple regression analysis for those parameters that were found to have the greatest effect on  $\text{NO}_3^-$  leaching losses. Included in this table are only those sites or replicate plots for which information for all the independent variables was available. The following variables were found most important: N content of the mineral soils (0–60 cm depth) + forest floor; and as N fluxes: atmospheric N input, total tree N uptake (calculated from biomass increment and litterfall data as described in Chapter 2), and relative soil N mineralization rate [annual N mineralization in 0–10 cm of mineral

Table 6.4. Variation in  $\text{NO}_3^-$  Leaching Explained by Different Regulating Factors (16 IFS sites)

Independent Variable	Percent $\text{NO}_3^-$ Variation Explained
Mineralization <sup>a</sup>	44
Total N <sup>b</sup>	18
N Uptake <sup>c</sup>	15
Input <sup>d</sup>	11
Input, mineralization	64
Input, N uptake	41
Input, total N	25
Input, N uptake, mineralization	67
Input, N uptake, total N	45
Estimated leaching potential <sup>e</sup>	51

<sup>a</sup> Mineralization, N mineralization in 0–10 cm of mineral soil determined through in situ incubation using buried bag technique (Eno 1960).

<sup>b</sup> Total N, total N capital in forest floor and mineral soil (0–60 cm depth).

<sup>c</sup> Uptake, total uptake by overstory.

<sup>d</sup> Input, total input via atmospheric deposition + N fixation (in case of red alder).

<sup>e</sup> For explanation see text.

soil as determined by buried bag technique (Eno 1960) and expressed as percentage of the maximum rate (ST) observed among the IFS sites].

First, all  $\text{NO}_3^-$  leaching sites have large amounts of N accumulated in the mineral soil and forest floor, in contrast to the sites at the lower end of the N leaching spectrum (see Figure 6.15). Differences in total N content explain approximately 18% of the variation in  $\text{NO}_3^-$  leaching among the IFS sites (Table 6.4). In the case of the red alder (RA), this N accumulation has occurred over a fairly short time period (50 years), resulting from large N inputs via symbiotic N fixation (Cole et al. 1978; Van Miegroet et al. 1990). For the other N-saturated sites, the N accumulation likely took place over a longer time period. Total soil N content is positively correlated with the amount of organic C accumulated in the soil (see Figure 6.18), a relationship that has also been demonstrated in chronosequence studies on newly developed soils (e.g., Crocker and Major 1955), with forest succession on former agricultural soils (e.g., Hamburg 1984), and for other ecosystems worldwide (Post et al. 1985).

The correlation can be explained by N immobilization in C-rich organic material substrate until an equilibrium is attained between N demands of and C supply to the heterotrophs. When heterotrophic activity is restricted by C supply rather than by N availability, N is no longer retained and a net N release may occur. In some boreal soils where decomposition is restricted by extreme climatic conditions, both C and N availability may be low, causing strong competition for N among the different organism groups and in turn resulting in low  $\text{NO}_3^-$  leaching rates. The transition point between net N immobilization and net N mineralization is determined by the C:N ratio of the substrate: in general terms, net immobilization occurs at a substrate C:N > 30, whereas net N release only occurs at a substrate C:N < 20 (Alexander 1977), although Berg and Staaf (1981) have shown that this critical C:N value may vary with climate and organic matter composition.

Soil N and C contents and corresponding C:N ratios are shown in Figure 6.18. Soils that are located below the C:N = 20 line on the graph (i.e., soils with relatively low N contents compared to total C) are expected to retain N, whereas sites that are above the C:N = 20 line and particularly those above the C:N = 10 line (i.e., soils that have a relatively high N content compared to C content) are likely candidates for net N release through mineralization. These projections correspond very well with the results from the in situ mineralization assays. Although the buried bag technique used (Eno 1960) has its limitations in providing an absolute measure of mineralization under actual field conditions, it is nevertheless useful for comparisons between sites and as an indicator of relative mineralization potential.

The IFS sites again cover a wide array of soil mineralization and nitrification rates (Figure 6.19). The highest relative soil N mineralization rates are measured in those soils with high total soil N content (>350  $\text{kmol ha}^{-1}$  or 5000  $\text{kg ha}^{-1}$ ) between 0 and 60 cm soil depth and an overall C:N < 20 (e.g., ST, SS, SB, RA, TL). Those are precisely the sites that also showed

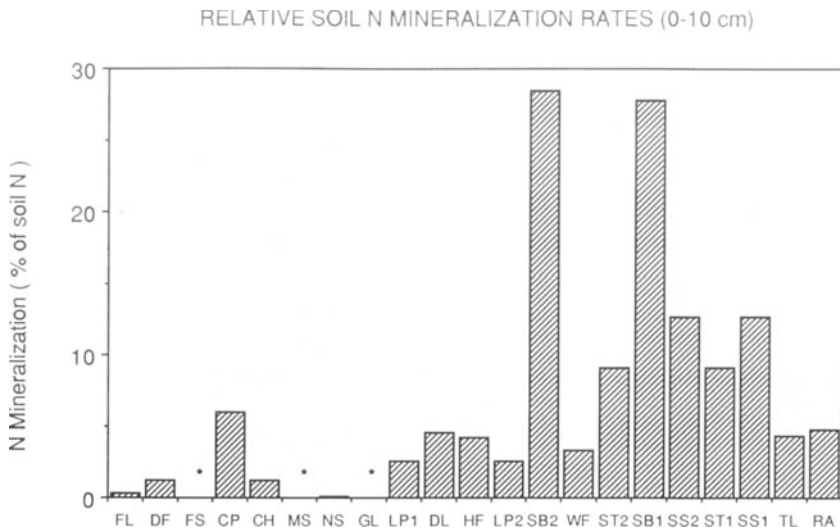


Figure 6.19. Relative soil N mineralization potential (N mineralized as percent of total soil N between 0 and 10 cm) of IFS sites ranked by  $\text{NO}_3^-$  output (\* indicates no mineralization data available).

high  $\text{NO}_3^-$  leaching rates (i.e.,  $>750 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ). On the other hand, the C:N ratio, which is greater than 20 in the soils under spruce (WF) or hardwood cover (HF) in New York and under subalpine fir forest in the Washington Cascades (FL), suggested low N release (mineralization) and high N immobilization potential despite the elevated soil N contents, mostly as a result of the even larger organic C pools (see Figure 6.18). Annual N mineralization at the WF and HF sites was less than half that calculated for the Southern Appalachian ST site. Low temperatures at the high-elevation FL and WF sites should further reduce mineralization rates, and little net N mineralization was measured at FL. As a single factor, differences in soil N mineralization potential (0–10 cm soil depth) are most important in explaining variations in  $\text{NO}_3^-$  leaching between the IFS sites (see Table 6.4). Nitrogen mineralization and atmospheric N deposition appear to be the most important sources regulating  $\text{NO}_3^-$  leaching, accounting together for about 64% of the variability in N losses among all IFS sites (see Table 6.4). These results further emphasize that both internal and external N sources play a role in N saturation.

#### *Nitrogen Retention*

In contrast to S (see Chapter 5), N is basically retained within in the system through biological rather than physicochemical processes. Microbial N immobilization in soil and forest floor is influenced by past N accumulation

and total N content, both in absolute terms and relative to the total organic C pool in soil and forest floor. The forest systems in the lower left corner of Figure 6.18 have lower organic matter and N contents, either because soils are still relatively young or because organic C and N pools have been reduced through prior disturbance(s) or land use. Nitrogen availability in such systems is limited, and because of this low total N content, the forests in that group should have a high capacity to retain and accumulate incoming N. This should in turn reduce the potential for  $\text{NO}_3^-$  leaching. Field observations confirm that these sites indeed show little or no net N mineralization, but rather periodically exhibit net N immobilization, and that solution  $\text{NO}_3^-$  concentrations are insignificant.

The high-elevation fir forest in Washington (FL) and the high-elevation spruce (WF) and hardwood forests (HF) in New York are also expected to have substantial N immobilization capacity, not so much because of a low total N content (total soil and forest floor N capital in those systems are 530, 1200, and 650  $\text{kmol ha}^{-1}$ , respectively) but because of a high soil C:N ratio. The HF and WF sites currently occupy an intermediate position on the relative N mineralization scale (see Figure 6.19), while inorganic N contents in the FL soil samples either decline (= net immobilization) or show only very small increases during incubation.

In systems where there is measurable net N mineralization, nitrification rates will be further affected by the degree of competition for  $\text{NH}_4$  between microbes and vegetation, while  $\text{NO}_3^-$  leaching can also be reduced by vegetation uptake. Calculated tree N uptake rates differ widely among the IFS sites (Figure 6.20), from a high of 3500  $\text{mol ha}^{-1} \text{yr}^{-1}$  (roughly 75  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) by alder (RA) to a low of 570  $\text{mol ha}^{-1} \text{yr}^{-1}$  (roughly 8  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) by subalpine fir (FL) in Washington, a reflection of the differences in forest type, stand age and vigor, and general growth conditions (such as climate and nutrient availability). Uptake rates are generally higher in deciduous than in coniferous forests, because annual replacement of the entire foliage requires more N (Cole and Rapp 1981): the uptake rates are of the order of 2500–3500  $\text{mol ha}^{-1} \text{yr}^{-1}$  (or 40–50  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) in the hardwood forests (TL, HF, CH), generally exceed 2000  $\text{mol ha}^{-1} \text{yr}^{-1}$  (30  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) for the different pine species in the southeastern United States (FS, DL, CP), and seldom exceed 1500  $\text{mol ha}^{-1} \text{yr}^{-1}$  (or 20  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) in the Douglas-fir stand (DF), at GL, and in the spruce-fir forests (FL, NS, MS, SS, ST). The WF and the LP sites with their calculated N uptake of 2900  $\text{mol ha}^{-1} \text{yr}^{-1}$  and 1300  $\text{mol ha}^{-1} \text{yr}^{-1}$ , respectively, represent exceptions in this respect. The low N uptake in the Oak Ridge plantation is probably a reflection of the low fertility status of that site.

Over the entire IFS data range one cannot demonstrate a significant correlation between N uptake and  $\text{NO}_3^-$  leaching (see Table 6.4 and Figure 6.20): high  $\text{NO}_3^-$  leaching rates occur in association with high (RA), intermediate (TL), or low N uptake rates (SS, ST), whereas low N uptake rates do not necessarily result in high  $\text{NO}_3^-$  leaching losses (e.g., NS, LP, DF,





The two northern hardwood forests (TL, HF) show a distinct seasonality in  $\text{NO}_3^-$  solution concentrations: peak  $\text{NO}_3^-$  levels are observed with snowmelt in early spring (Foster et al. 1989b; Shepard et al. 1990) and before significant root activity occurs. At TL they increase as a result of a flush of mineralization and nitrification toward the end of the dormant season. With the onset of the growing season  $\text{NO}_3^-$  solution levels decline in both forest types, probably as a result of increased root uptake, and at TL the mean growing season  $\text{NO}_3^-$  concentrations are lower than dormant season  $\text{NO}_3^-$  levels. At HF,  $\text{NO}_3^-$  solution concentrations remain fairly low throughout the rest of the year, and total  $\text{NO}_3^-$  leaching rates are less than  $100 \text{ mol ha}^{-1} \text{ yr}^{-1}$  (or  $5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) compared to  $1600 \text{ mol ha}^{-1} \text{ yr}^{-1}$  at the TL site. Both hardwood sites are subject to similar N input regimes and are generally comparable in terms of total N content and distribution. One of the features that distinguishes the sites is the slightly higher N uptake at HF;  $3500 \text{ mol ha}^{-1} \text{ yr}^{-1}$  ( $49 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) versus  $2500 \text{ mol ha}^{-1} \text{ yr}^{-1}$  ( $35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ). This difference, in association with a greater potential for N immobilization at the HF site as indicated by the C:N ratio of the soil (see Figure 6.18), may be responsible for the lower total  $\text{NO}_3^-$  leaching rates that are observed there.

Finally, an attempt was made to integrate the role of the relative N source and sink strengths into one parameter, designated as "leaching potential" (see Table 6.4). It was calculated as the sum of atmospheric N input (including N fixation in case of RA) and relative N mineralization rate minus N removal via tree uptake. Estimated  $\text{NO}_3^-$  leaching potential and measured  $\text{NO}_3^-$  leaching values were highly correlated ( $r = .72+$ ), but the leaching potential overestimated the measured values by a factor of 5:

$$[\text{NO}_3^- \text{ (measured)}] = 3.4 + 0.19 \text{NO}_3^- \text{ (potential)}$$

Although our approach proved too crude to accurately predict  $\text{NO}_3^-$  leaching rates, this parameter was able to clearly distinguish  $\text{NO}_3^-$  leaching from nonleaching sites (Figure 6.21), and explained more than half ( $r^2 = .51$ ) of the variability in  $\text{NO}_3^-$  leaching observed.

### Effect of Nitrification and $\text{NO}_3^-$ Leaching

Nitrification of N derived from atmospheric deposition or internal mineralization of organic N has a strongly acidifying effect on the soil and soil solution because of the net  $\text{H}^+$  release during this oxidation process, but more importantly because of the significant increase in total anion concentration (and ionic strength) of the percolating solution and the mobile nature of  $\text{NO}_3^-$  (Kinjo and Pratt 1971; Wiklander 1976). To keep the solution electrically neutral, such increase in total anion concentration must be accompanied by a concomitant increase in cations (Nye and Greenland 1960). Whereas the anion production (in this case nitrification) determines the total

## POTENTIAL VS. MEASURED N LEACHING LOSSES AT THE IFS SITES

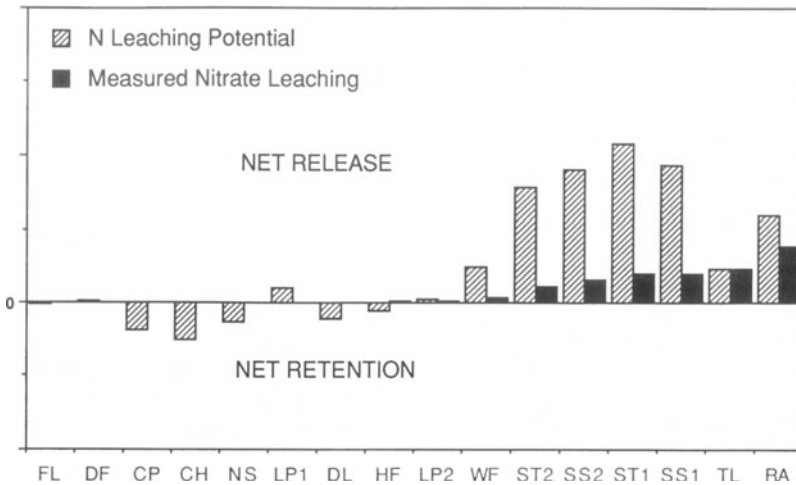


Figure 6.21. Comparison of estimated  $\text{NO}_3^-$  leaching potential based on atmospheric N inputs, soil N mineralization, and tree N uptake with measured  $\text{NO}_3^-$  leaching rates at IFS sites (see text for explanation of leaching potential).

increase in positive charges in solution, exchange reactions between the soil water and the cation exchange complex largely determine the relative abundance of the different cations in solution (Reuss and Johnson 1986). The equations most commonly used to describe such exchange reactions are those of Gaines and Thomas (1953) and Gapon (1933). According to these theoretical exchange relationships, which are discussed more extensively in Chapter 8, any increase in ionic strength of the solution will mostly displace multivalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from soils with medium to high base saturation, whereas Al will be preferentially mobilized from more acid soils (i.e., soils with low base saturation). Elevated Al concentrations in solution or accelerated cation loss through  $\text{NO}_3^-$ -mediated leaching may cause nutrient imbalances or deficiencies of essential nutrients, which in turn may negatively impact forest productivity (e.g., Thornton et al. 1987; Shortle and Smith 1988; Kelly et al. 1990; Raynal et al. 1990).

#### *Cation Loss and Base Saturation*

The weighted average ion concentrations of B horizon solutions collected at the various IFS sites are given in Figure 6.22, and illustrate the role of natural and anthropogenic anion loading in soil solution chemistry. This section focuses mainly on the contribution of  $\text{NO}_3^-$  to the overall leaching process.

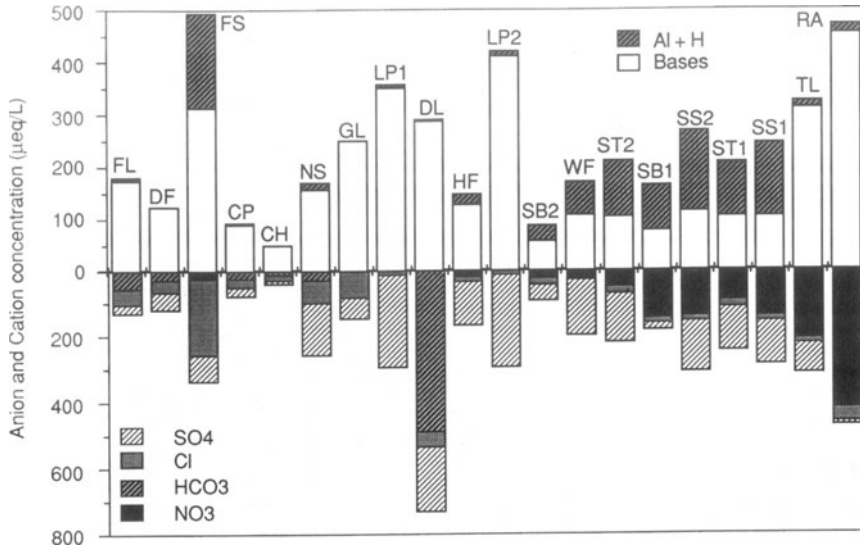


Figure 6.22. Weighted average anion and cation concentrations of B horizon solutions collected in IFS sites.

At the TL and RA sites, soil solution chemistry is largely dominated by  $\text{NO}_3^-$  leaching. High  $\text{NO}_3^-$  concentrations in solution cause accelerated cation leaching, predominantly of  $\text{Ca}^{2+}$  and to a lesser extent of  $\text{Mg}^{2+}$  (Van Miegroet and Cole 1984; Foster and Nicolson 1988). Calculations for the RA site show that as much as 14% of the exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  are exported annually below the 40-cm soil depth through  $\text{NO}_3^-$ -mediated leaching. This accelerated leaching has caused a striking redistribution of exchangeable  $\text{Ca}^{2+}$  from the upper parts of the A horizon to the B horizon, with a similar but less pronounced downward shift for  $\text{Mg}^{2+}$  and  $\text{K}^+$ . Such relative cation depletion of the upper soil horizons could at least in part account for the decline in percent base saturation of the A horizon under alder (Van Miegroet and Cole 1984; Van Miegroet et al. 1989). However, despite high annual cation leaching rates, no measurable decline in the total exchangeable cation pool has occurred, suggesting some base replenishment possibly from increased mineral weathering. Indications of differences in weathering rates between the DF and RA sites, which are established on the same soil, are further discussed in Chapter 10.

At TL, base cations are taken up by the hardwood forest from the effective rooting zone between 0- and 60-cm soil depth. Net base retention in this old-growth forest is small relative to the recycling of bases to the soil by litterfall, canopy leaching, and tree mortality. Some  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are removed from decomposing organic matter in the forest floor layers by  $\text{NO}_3^-$ . Additional  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  leached from the organic layers in association

with organic anions are exchanged in the the B horizon with  $H^+$  produced by nitrification. Hence, at TL the large annual  $Ca^{2+}$  and  $Mg^{2+}$  leaching losses from the rooting zone are primarily induced by nitrification in the soil. Strong acids from the atmosphere are not retained by the vegetation or soil, further increasing leaching of bases from the rooting zone. At TL, leaching removes as much as 5% of the exchangeable  $Ca^{2+}$  and 10% of the exchangeable  $Mg^{2+}$  in the soil annually. Although weathering currently replaces some of the cation loss, the base saturation of the soil is likely declining and the soil acidity increasing.

### *Al Mobilization*

In extremely acid soils [such as those in the spruce forests (ST and SS) of the Smokies] or soil horizons (e.g., A horizon under RA) with an exchange complex largely dominated by exchangeable acidity (i.e., in soils with low base saturation), the  $NO_3^-$ -induced increase in ionic strength of the solution causes significant Al mobilization (Figure 6.23), which is in agreement with the soil-solution equilibrium reactions discussed earlier (see also Chapter 8). Seasonal  $NO_3^-$  peaks are particularly important in displacing Al from the exchange complex, as illustrated for the Smokies spruce site by Johnson et al. (1991) and demonstrated by Reuss (1989) for selected leachates collected at the RA site. As shown in Figure 6.22 for the ST site, Al concentrations in the A horizon leachates mostly range between 30 and 100  $\mu\text{mol L}^{-1}$ , but peak values (associated with  $NO_3^-$  or  $SO_4^{2-}$  peak levels) occasionally approach threshold toxicity levels reported for red spruce seedlings (Hutchinson et al. 1986; Thornton et al. 1987; Joslin and Wolfe 1988).

It has been hypothesized that increases in Al concentrations induced by atmospheric deposition ( $SO_4^{2-}$  as well as  $NO_3^-$ ) may cause an imbalance in the Ca or Mg nutrition of the trees, which may ultimately result in a reduction in forest productivity (e.g., Shortle and Smith 1988; Schulze 1989). Such causal relationship between soil solution chemistry and productivity decline in high-elevation spruce forests has not been conclusively established, however. It further needs to be pointed out that part of the increase in  $NO_3^-$  leaching that has been observed in the spruce forests of the Smoky Mountains is caused by internal N sources (i.e., mineralization) in addition to atmospheric N deposition. The large N pools with a small C:N ratio that currently lead to those large  $NO_3^-$  releases via mineralization, are, of course, the reflection of accumulation of atmospherically derived N over a period of perhaps several millennia. Indeed, if these sites have been receiving 25  $\text{kg N ha}^{-1} \text{ yr}^{-1}$  for 30 years (which is an upper-limit assumption), then that accumulated N would represent only 6% of the total N capital of the site. Thus, while high N inputs over the last decades have undoubtedly accelerated the N saturation process, past site history has also significantly contributed to the high  $NO_3^-$  leaching losses currently observed.

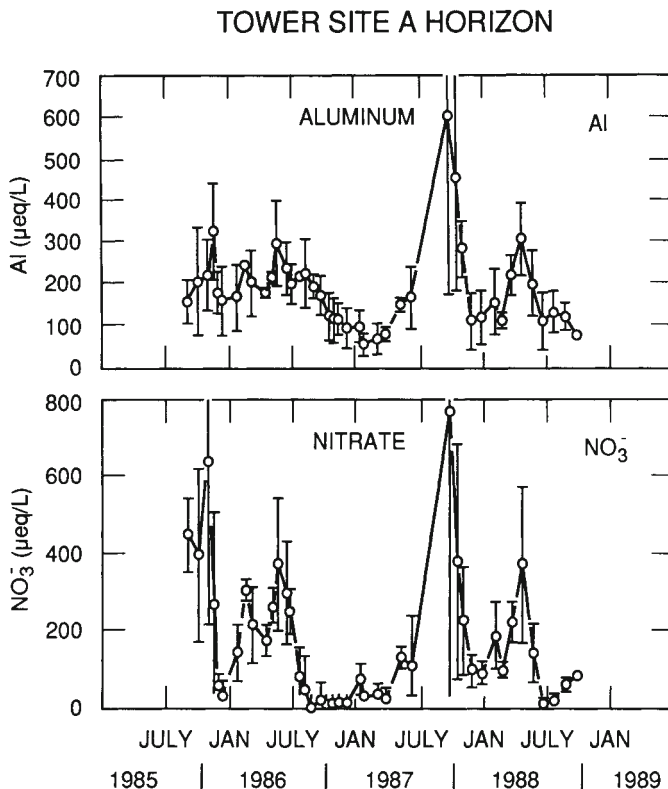


Figure 6.23. Nitrate and aluminum concentrations over time in A horizon solutions at spruce Tower site in Great Smoky Mountains National Park (From Johnson et al., 1991).

### Recovery

Nitrification can lead to a series of changes in soil and soil solution properties including a decrease in soil solution pH (caused by proton generation during the nitrification process), an increase in the exchangeable acidity, decrease in soil pH and base saturation, and an increase in the Al concentration in soil solution and on the exchange sites. Consequently it is critical to determine if systems subjected to nitrification can recover and, if so, how long such a process will take. While this subject is discussed further in Chapter 12 (this volume), some aspects of recovery specific to N saturation are discussed here.

Ideally, an experiment on recovery from the effects of nitrification should be conducted on systems that have reached N saturation from atmospheric deposition, but within the timeframe of the IFS program such examination of recovery was not feasible. However, we were able to follow the recovery process in a system where N saturation had been achieved through N inputs

Table 6.5, Average Soil Solution  $\text{NO}_3^-$  Concentrations ( $\mu\text{mol/L}$ ) Collected beneath Forest Floor, A and B Horizons, from the 55-Year-Old Red Alder and Douglas Fir Forest Sites at Thompson Research Center

Horizon	Forest Type	
	Red Alder	Douglas Fir
Forest floor (0 cm)	315	1.7
A (0–10 cm)	273	0.5
B (10–40 cm)	229	0.5

via a symbiotic N fixation associated with the red alder. It has been well documented through previous research (Van Miegroet and Cole 1984; Reuss 1989; Van Miegroet et al. 1989; Van Miegroet et al. 1990) that such N additions in the red alder stand result in a number of soil and soil solution properties changes, including increased  $\text{NO}_3^-$  leaching (Table 6.5), a decline in soil pH (see Figure 6.24), and Al mobilization (Figure 6.25). The “control” or reference used in this study to evaluate these changes was an adjacent stand of Douglas fir established at approximately the same time (55 years ago) on the same soil series.

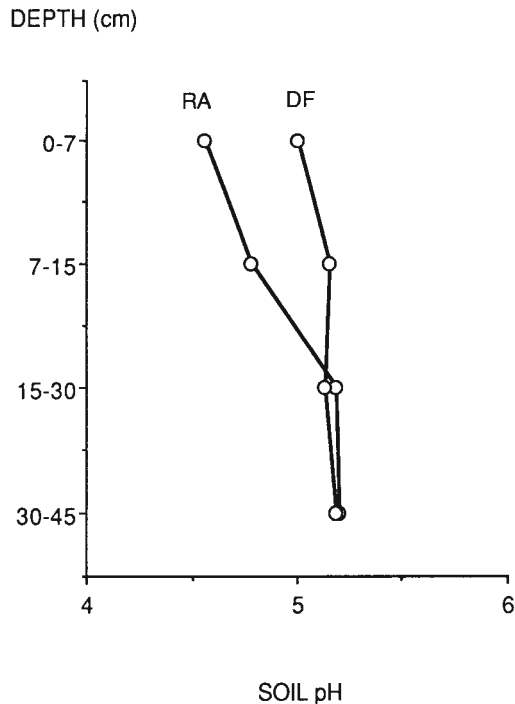


Figure 6.24. Soil pH (water) under mature stand of alder and Douglas fir at Thompson Research Center.

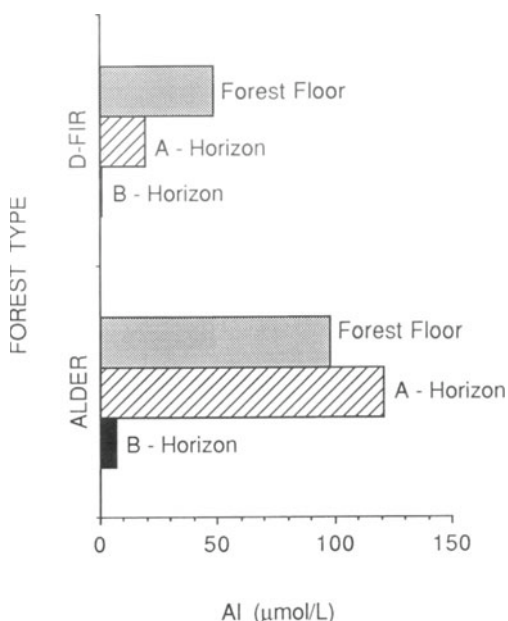


Figure 6.25. Average soil solution Al concentrations ( $\mu\text{mol L}^{-1}$ ) collected beneath forest floor (FF), A and B horizons from 55-year-old red alder and Douglas fir forest sites at Thompson Research Center.

An experiment was carried out to determine the effect of removing the input of N, in this case through the fixation process. To that end, the alder was harvested in a 1-ha area and 0.5-ha plots of both alder and Douglas fir were subsequently established. The first indication that a site could recover from N saturation was observed approximately 1 year after the removal of the red alder when soil solution  $\text{NO}_3^-$  concentrations dropped below levels in the uncut control area. Total  $\text{NO}_3^-$  leaching loss dramatically decreased (Figure 6.26) in both conversion plots. Nitrate solution concentrations reached levels as low as 1 to 2  $\mu\text{mol L}^{-1}$  in the fourth year following harvesting, which were similar to those found under the adjacent Douglas fir stand. This decrease in the  $\text{NO}_3^-$  leaching was accompanied with an equivalent decrease in the leaching of base cations. We have not, however, seen any corresponding shift in soil solution acidity nor decrease in soil solution Al concentration, nor have we resampled the site to see if there has been any cation replacement on the exchange sites through mineralization and mineral weathering. We believe that recovery of these soil properties will be a long-term process that could not have occurred within this short time period.

While this evidence for recovery from N saturation in terms of soil solution chemistry is only one example, that is, N fixation associated with alder, the processes involved should be similar to those triggered from de-

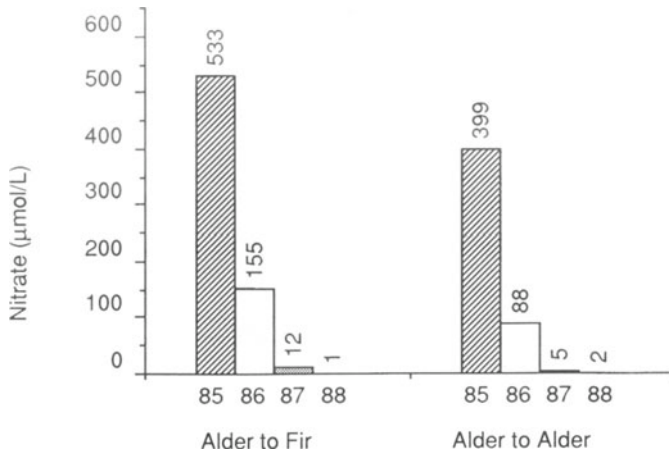


Figure 6.26. Reduction in soil solution  $\text{NO}_3^-$  concentrations from 1985 to 1988 following harvesting of alder with subsequent establishment of alder and Douglas fir conversion plots. (Expanded from Van Miegroet et al., 1990.)

position. Consequently, we believe that this study of alder provides a preliminary assessment of recovery potential from N saturation caused by atmospheric N deposition.

### Retention or Loss of N in IFS Sites and Evaluation of Relative Importance of Processes

D.W. Cole, H. Van Miegroet, and N.W. Foster

#### Summary of Pathways and Processes

As discussed earlier in Chapter 6, there is a striking difference between the IFS sites in their relative capacity to retain N: some sites are clearly N saturated (ST, SS, TL, RA) as indicated by the consistently high solution  $\text{NO}_3^-$  level, while there are a few sites (e.g., WF, HF) that appear to be at a transition stage, as suggested by a combination of total soil N content and C:N ratio, N mineralization potential, and measured  $\text{NO}_3^-$  leaching. The majority of the sites within the IFS network, however, are not yet saturated: they consistently retain incoming atmospheric N inputs and no traces of  $\text{NO}_3^-$  leaching could be detected.

It also became clear from our analysis that atmospheric N deposition, as a single factor, is insufficient to explain all of these differences in  $\text{NO}_3^-$  leaching. Other sources and sinks of N within the forest ecosystems must also be considered if we are to explain adequately the differences in N leaching rates between sites. For those sites with measurable  $\text{NO}_3^-$  leaching there is a stronger positive correlation between atmospheric N input and  $\text{NO}_3^-$



leaching rates than across all the sites, indicating that the  $\text{NO}_3^-$  output from sites that approach or have reached N saturation is more directly influenced by changes in atmospheric N deposition. In the IFS program, a number of sources and sinks were studied and their contribution to the retention or loss of N evaluated. Besides deposition inputs, the factors analyzed included total N content of the soil and forest floor, N mineralization rate in the upper soil layer, C:N ratio of the soil (as an index of N immobilization), and the age, vigor, and species composition of the stand resulting in differences in N uptake. As a single factor, N mineralization potential explains best the variation in  $\text{NO}_3^-$  leaching between sites (see Table 6.4). Recognizing the difficulty in estimating actual field N mineralization rates accurately, the best practical index of N loss was found to be the C:N ratio of the soil with total soil N. Sites with a narrow C:N ratios ( $\text{C:N} < 20$ ) and with a total soil N content greater than  $350 \text{ kmol ha}^{-1}$  ( $5000 \text{ kg ha}^{-1}$ ) also appear to be the sites most susceptible to nitrification and  $\text{NO}_3^-$  leaching. Atmospheric N deposition and N mineralization potential together are the two major sources of N that can explain almost two-thirds of the variation in  $\text{NO}_3^-$  leaching observed, underscoring the equally important role of current and past N deposition history in the degree of N saturation reached by a particular forest ecosystem.

### Comparison of Net Losses between Sites

As illustrated in Figure 6.16, there is a major disparity between sites in the extent of  $\text{NO}_3^-$  leaching taking place. The greatest leaching loss amongst the 17 sites is associated with red alder. Here, additions from N fixation are an order of magnitude larger than those via atmospheric N deposition at the site and exceed by at least a factor of four the total N deposition measured at the other sites of this program. Besides the red alder site (RA), annual N losses in excess of  $750 \text{ mol ha}^{-1}$  ( $\sim 10 \text{ kg ha}^{-1}$ ) are found only at the sites in the Smokies (SS, ST, SB) and at Turkey Lakes (TL). More than 50% of the sites experience annual leaching losses of less than  $100 \text{ mol ha}^{-1}$ , and 4 sites leach between  $100$  and  $200 \text{ mol ha}^{-1} \text{ yr}^{-1}$  of  $\text{NO}_3^-$ . These results raise the obvious questions: Why do such differences occur? To what extent are they regulated by internal processes and to what extent are they a function of inputs from external sources (e.g., deposition or fixation)? Nitrification results in the introduction of a mobile  $\text{NO}_3^-$  and  $\text{H}^+$  ions in the soil solution, which in turn can cause various changes to take place in the soil and soil solution, including:

- A decrease in the soil solution pH
- An increase in exchangeable acidity, a decrease in base saturation, and a decrease in soil pH
- An increase in Al activity in the soil solution
- Change in the nutrient availability (e.g., P).

It is imperative we understand the processes and environmental conditions that trigger elevated  $\text{NO}_3^-$  levels in the soil and  $\text{NO}_3^-$  leaching losses if we are to know when and how extensively these reactions occur in our forest ecosystems. Indeed, the occurrence and rate of  $\text{NO}_3^-$  leaching may have important implications for site fertility or water quality in these forested systems.

### Reasons for N Losses from Ecosystems

It is clear from this analysis that the loss of N from an ecosystem is not simply a function of some current event including atmospheric N deposition or additions through fertilization unless such events are drastic in their magnitude. Rather, the loss of N is regulated through the integration of a series of soil related processes, processes which could well be tempered or accentuated by events predating the current ecosystem occupying the site. For example, the accumulation of N and C at these sites undoubtedly reflects the cumulative history of these sites (temperature, disturbance, stand history, prior N deposition regime) far more than any current event. This is not to say that the deposition input of N is not important and does not lead or contribute to N saturation and  $\text{NO}_3^-$  leaching. As a matter of fact, deposition inputs can play critical roles in N loss in several ways:

- At sites with a long history of such additions, there undoubtedly will be a cumulative effect over time and N leaching will ultimately take place. With some sites experiencing additions in excess of  $1500 \text{ mol ha}^{-1}$  ( $\sim 20 \text{ kg ha}^{-1}$ ) annually, ultimately the C:N ratio will narrow through N accumulation in excess of organic C accumulation, triggering, in time, nitrification and  $\text{NO}_3^-$  leaching. The alder site in Washington illustrates this concept. Nitrogen addition through the fixation process has resulted in the accumulation of more than  $200 \text{ kmol ha}^{-1}$  of N during a 50-year period, increasing the storage of N in this ecosystem from approximately  $200 \text{ kmol ha}^{-1}$  (or  $3000 \text{ kg ha}^{-1}$ ) to  $400 \text{ kmol ha}^{-1}$  ( $5500 \text{ kg ha}^{-1}$ ). At some point in time predating our research at this site (before 1970 when the stand was only 35 years old),  $\text{NO}_3^-$  leaching began to take place, that is, N saturation was reached in less than 35 years of high N input levels. There is every reason to believe atmospheric additions will cause the same net effect. If the inputs are less than those caused by fixation (often  $>7000 \text{ mol ha}^{-1} \text{ yr}^{-1}$  or  $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ), then only the time function will differ. For sites receiving an annual deposition of  $1500 \text{ mol ha}^{-1}$  ( $\sim 20 \text{ kg ha}^{-1}$ ), N saturation and  $\text{NO}_3^-$  leaching should take about five times longer than that witnessed with alder, assuming of course that all other environmental and ecosystem factors are equal.
- At sites where  $\text{NO}_3^-$  leaching is already occurring, such as ST, SS, SB, RA, and TL, additional inputs of N, by deposition or any other source will further add to the  $\text{NO}_3^-$  losses currently taking place. This additional loss could certainly be larger than the N input through stimulation of N

mineralization in systems with already narrow C:N ratios (i.e., low N immobilization potential).

- A few sites, notably the high-elevation spruce forest at Whiteface Mountain and the mixed hardwood site at Huntington Forest in New York, appear to be at a transition stage. They show some, albeit still low, annual  $\text{NO}_3^-$  leaching loss indicative of periodic nitrification peaks. They can be classified as intermediate in terms of N mineralization potential based on field assays and the soil C:N ratio. Such systems will be particularly sensitive to atmospheric N deposition, especially as the stands further mature and the role of N uptake as a N sink decreases.

### **Analysis of N Cycles in Polluted versus Unpolluted Environment**

H. Van Miegroet, D.W. Johnson, and D.W. Cole

Figure 6.27 summarizes the N distribution and cycling patterns at the Findley Lake and the Smokies Tower sites, which represent high-elevation conifer systems subject to low and high atmospheric N inputs, respectively. Within the IFS network the total atmospheric N input is highest at the Smokies site ( $28 \text{ kg ha}^{-1} \text{ yr}^{-1}$  or  $2000 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ) which is more than sixfold higher than the estimated  $4 \text{ kg ha}^{-1} \text{ yr}^{-1}$  ( $300 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ) at Findley Lake.

Total ecosystem N content (biomass + soil to a depth of 60 cm) is somewhat higher at the ST sites ( $12,000 \text{ kg ha}^{-1}$  or  $900 \text{ kmol ha}^{-1}$  in plot 1 and  $9,000 \text{ kg ha}^{-1}$  or  $700 \text{ kmol ha}^{-1}$  in plot 2) than at the FL site ( $8,500 \text{ kg ha}^{-1}$  or  $600 \text{ kmol ha}^{-1}$ ), but in view of the observed within-site variability and compared to the range of values for the other IFS sites (see Figure 6.15) this difference can be considered inconsequential. Both systems generally rank at the higher end of total N content among the IFS sites. However, they show distinct differences in terms of N distribution and cycling patterns. The vegetation N content is 60% greater at FL than at the ST site, reflecting its greater aboveground standing biomass. Subordinate trees (such as birch) and understory vegetation account for 15% (plot 2) to 35% (plot 1) of total aboveground N at the ST site, a result of the opening of the stand following adelgid-caused Fraser fir mortality, which is also indicated by a sizable N pool as dead trunks. At the FL site with its dense old-growth subalpine fir forest, the understory component remains small. On the other hand, forest floor N is two- to fourfold higher at the ST sites, accounting for almost one-fifth of the total ecosystem N compared to less than 10% at FL. Soil N is slightly higher at the Smokies sites.

A comparison of the total N input to the ecosystem versus rate and form of N leaching below the rooting zone indicates that the FL site is still accumulating N (N output  $< 1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ). At the Smokies sites substantial  $\text{NO}_3^-$  leaching outputs are measured, which are similar to or in some years

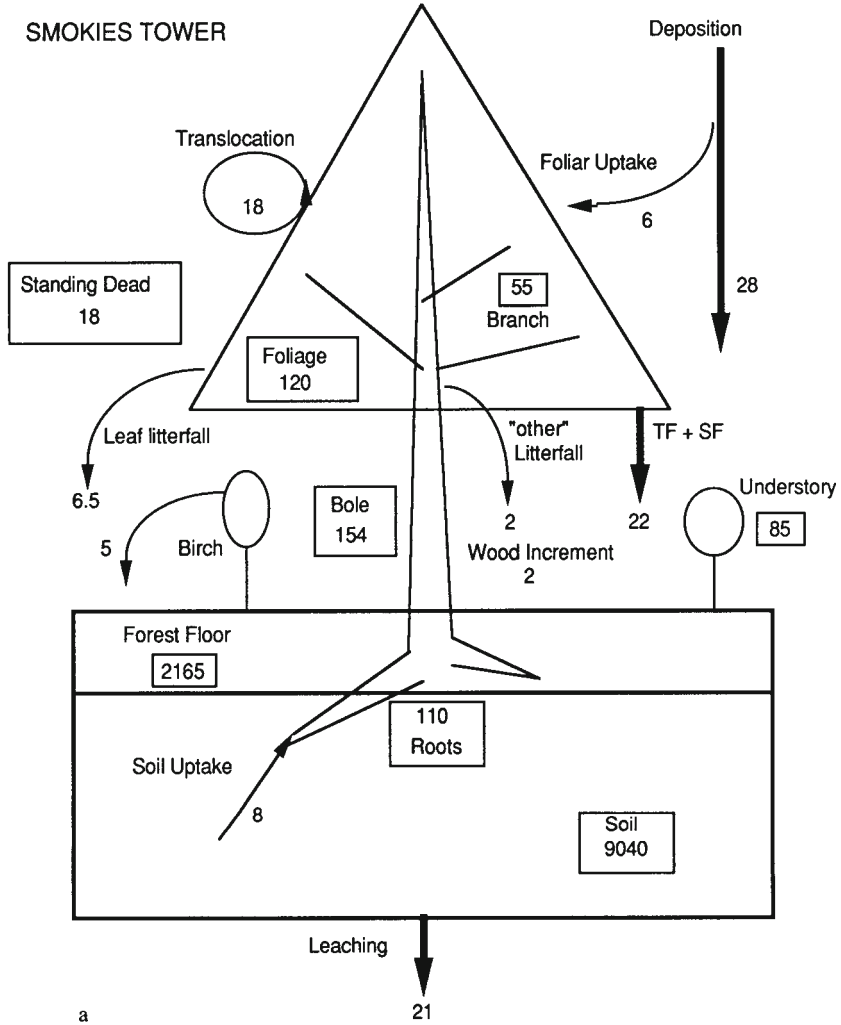


Figure 6.27. Nitrogen distribution and cycling patterns in spruce Tower site at Great Smoky Mountains National Park (a) and at Findley Lake site in Washington (b).

exceed total atmospheric N deposition, suggesting low N retention capacity, as discussed earlier in Chapter 6. This difference in ecosystem N retention cannot be accounted for by concurrent differences in vegetation uptake values. As a matter of fact, the N fluxes to and from the vegetation and internal cycling patterns within the vegetation are quite similar in both ecosystems, except for the somewhat greater role of the subordinate vegetation at the ST site. Wood increments are low (of the order of  $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$  or  $150 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ), and most of the N requirement ( $12 \text{ kg ha}^{-1} \text{ yr}^{-1}$  at FL and between 21 and  $30 \text{ kg ha}^{-1} \text{ yr}^{-1}$  at ST) is associated with new foliage production.



Annual N return with needle litterfall is similar in both sites ( $\sim 7 \text{ kg ha}^{-1} \text{ yr}^{-1}$  or  $500 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ). This, in association with the significantly larger foliar N pool at the FL site, suggests that needles are retained three to four times longer at that site than in the Smokies, which may be an indication of the less favorable nutrient (N) conditions at FL. As a result of the higher total N deposition at the ST sites, throughfall N input to the forest floor is significantly greater at the Smokies site. At FL, the N entering the belowground compartment via litterfall (needle and other) plus net throughfall is retained completely below ground and no measurable amounts of N leach below a 40-cm soil depth. Root uptake can account for approximately half of this N retention, while the remainder (about  $9 \text{ kg ha}^{-1} \text{ yr}^{-1}$  or  $700 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ) must be accumulation in the soil.

At the Smokies site, by contrast, N input to the soil (via litterfall and net throughfall) minus calculated root uptake of N is about  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (or  $1500 \text{ mol ha}^{-1} \text{ yr}^{-1}$ ), which is close to the average annual  $\text{NO}_3^-$  leaching value, indicating little or no net N immobilization in the soil. The greater N accumulation potential of the FL soil is further substantiated by the ratio C:N = 37 (see Figure 6.18) and by the insignificant net N mineralization rates measured during in situ incubation (see Figure 6.19 and discussion earlier in Chapter 6). The C:N value of the ST soil (11 for plot 1 and 18 for plot 2) and the results from the field mineralization assays suggest that the Smokies soils, on the other hand, are at a stage of minimum net N accumulation and large net release through nitrification and  $\text{NO}_3^-$  leaching. The high atmospheric N inputs undoubtedly contribute to the high  $\text{NO}_3^-$  leaching rates currently observed, but it is clear that past N accumulation and disturbance history (or lack thereof) and not the current N input regime have led to the present soil condition (i.e., N saturation).

Even though both systems have similar (high) total ecosystem N contents, they differ significantly in belowground N dynamics. The FL site exhibits the behavior of a site that is N limited. All incoming N is retained, N mineralization (N availability) is low, canopy N turnover is slow, and no excess N is available for  $\text{NO}_3^-$  production and leaching. The ST site behaves as a N saturated system: because of past N and C accumulation the soil C:N is such that N in excess of what can be immobilized via vegetation uptake can no longer be retained within the belowground compartment. In addition, fir dieback has opened up the stand, rendering the soil even more susceptible to the direct impact of external influences. This site condition, coupled with the high atmospheric N deposition rates, accounts for the high  $\text{NO}_3^-$  leaching losses observed at the site.

## Summary and Conclusions

H. Van Miegroet, G.M. Lovett, and D.W. Cole

In the course of the IFS project, we have been able to answer some of the research questions that were posed at the onset of the project with respect

to the form and amount of atmospheric N input to forested ecosystems, the occurrence and predictability of N saturation, and the role of atmospheric N deposition and internal ecosystem properties in causing or exacerbating N saturation and excess  $\text{NO}_3^-$  leaching. Nitrogen saturation is defined as that ecosystem condition where N flux density, that is, the N input from N mineralization plus atmospheric N deposition, exceeds the ecosystem's retention capacity and is expressed by measurable  $\text{NO}_3^-$  leaching out of the tree rooting zone.

### Atmospheric N Input and Canopy Interactions of N

In 13 sites of the IFS network, which covered a wide array of forest types, elevations, climatic conditions, and atmospheric deposition regimes, total atmospheric input of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  via wet and dry deposition and through cloud water input was estimated using methods described in Chapter 2.

Despite the dominance of aerosol  $\text{NH}_4^+$  in the air (50% to 70% of the atmospheric N concentrations),  $\text{HNO}_3$  is the dominant N species contributing to dry deposition because of its more reactive nature and ready absorption to surfaces. Coarse-particle  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can also add substantially to dry deposition fluxes. Deposition of  $\text{NO}_2$ , while not directly measured at most IFS sites, was investigated in laboratory experiments and found to be potentially important for sites close to urban areas. Particularly high rates of  $\text{NO}_2$  deposition were noted for forest floor surfaces, as opposed to leaves and bark, and the deposition to leaves occurred mainly through the stomates. Deposition velocities of  $\text{HNO}_3$  are much higher than those of  $\text{NO}_2$ , and the  $\text{HNO}_3$  deposits primarily to the exterior surfaces of the plant although a small amount of deposition does occur through the stomates.

Nitrogen input data suggest that wet and dry deposition contribute roughly equally to total N input to the low-elevation sites in the United States, implying that total atmospheric N input may be approximated by doubling wet deposition measurements at these sites. This generalization does not hold, however, for the high-elevation sites, where cloud water deposition can add substantially to the total N loading, particularly in forests with high cloud immersion frequencies. Total atmospheric deposition of N ranges from 340 to 1900 mol  $\text{ha}^{-1} \text{yr}^{-1}$  (4.7 to 27 kg  $\text{ha}^{-1} \text{yr}^{-1}$ ) across the IFS network, with the highest values in the eastern high-elevation sites. Low-elevation sites in the southeastern United States also receive relatively high N loadings, presumably because of the close proximity of the field sites to urban areas. However, the character of the deposition at the low-elevation sites, being predominantly nitrogen oxide gases and precipitation of relatively low N concentration, is quite different from that of the high-elevation sites, which are exposed to highly concentrated cloud water.

A comparison between atmospheric N deposition (including  $\text{HNO}_3$ ) vapor and throughfall plus stemflow N indicates that the forest canopies in all intensive monitoring sites consistently act as sinks for inorganic N. Through-

fall N fluxes can therefore not be used as a substitute or simple measure for total atmospheric N deposition as is the case for sulfur. This inorganic N removal partially coincides with a net increase in organic N in the through-fall flux, but the exact nature or cause of this net canopy effect is still unclear. On the average, 40% of the incoming inorganic N is retained in or transformed at passage through the canopy, and in absolute terms the net canopy effect is greatest at those sites receiving the highest atmospheric N inputs. The indication of significant N retention by forest canopies, and the role of foliar N uptake implied by it, has required a modification of the traditional calculation methods for tree N uptake and N requirements (Johnson and Lindberg 1989; Johnson et al. 1991).

### Atmospheric N Deposition and N Saturation

Belowground solutions were monitored using fritted-glass lysimeters at 10-kPa tension placed underneath the forest floor and at two depths in the mineral soil. Annual N leaching losses below the rooting zone were calculated from weighted average solution concentrations and water fluxes based on a hydrologic model modified for site-specific climatic conditions (see Chapter 3).

No strong positive correlation was found between estimated total atmospheric N input and measured  $\text{NO}_3^-$  leaching below the rooting zone across all sites. No  $\text{NO}_3^-$  leaching below the rooting zone occurs in more than half the sites irrespective of atmospheric N input rates. The relationship between input and output fluxes is somewhat stronger when only those sites are considered that are currently leaching  $\text{NO}_3^-$  below the rooting zone. These results imply that N saturation is not simply the result of current environmental conditions including the N deposition regime. However, high N inputs tend to accelerate the course of events and exacerbate N saturation once it has been attained. Inherent ecosystem properties such as soil N content and N immobilization or mineralization potential (a reflection of the past C and N accumulation history) and stand composition and vigor (expressed by differences in N uptake) must also be considered.

In this study, atmospheric N deposition and N mineralization potential together explain more than 60% of the variation in  $\text{NO}_3^-$  leaching rates between the various IFS sites, underscoring the importance of both past and current conditions to the degree of N saturation in a forest ecosystem. As a single factor, differences in soil N mineralization rates accounted for most of the variation (~40%) in  $\text{NO}_3^-$  leaching between sites. Recognizing the difficulties in establishing field N mineralization or immobilization rates accurately, the soil C:N ratio and soil N content appear to be the best practical indices of internal N release.

Some sites within the IFS network, such as the high-elevation spruce site in the Smoky Mountains and the mixed hardwood forest in Ontario's Turkey Lakes watershed, are clearly N saturated as indicated by consistently high



solution  $\text{NO}_3^-$  levels. They are characterized by a combination of moderate to high atmospheric N deposition, large soil N pools with low C:N ratios, high internal N mineralization rates, and moderate to low tree uptake values. A few sites appear to be at a transition stage, as suggested by the combination of soil N content and C:N ratio, N mineralization rates, and soil solution  $\text{NO}_3^-$  concentrations that increase in the upper soil profile periodically when tree uptake is low. Such sites are particularly sensitive to increases in atmospheric N inputs; they include both the low-elevation hardwoods and the high-elevation spruce sites in New York. The majority of the IFS sites, however, have not yet reached N saturation: they consistently retain incoming N, have low mineralization and nitrification potentials, and show no traces of  $\text{NO}_3^-$  leaching.

Nitrogen saturation and excess  $\text{NO}_3^-$  leaching thus do not appear to be limited to special forest ecosystem types (such as those containing N fixers), but can in principle be reached in any forested ecosystem given sufficient time and the appropriate environmental conditions for N to accumulate until it is incompletely retained by the biological component of the ecosystem (i.e., vegetation and microorganisms). Forest management practices or the occurrence and frequency of site disturbances reducing the N pool or increasing the biological N retention capacity of the system will tend to delay the time to N saturation, whereas an increase in external N sources (e.g., atmospheric N deposition, N fixation, and anthropogenic N additions) tend to speed up the N saturation process.

### Effects of N Saturation on Biogeochemical Cycles

The most immediate impact of high  $\text{NO}_3^-$  production and leaching rates is the accelerated leaching of cations displaced from the exchange complex. In sites with medium base saturation this means increased export of nutrient bases from the rooting zone, potentially resulting in nutrient deficiencies if bases are insufficiently replenished through atmospheric inputs, organic matter decomposition, or mineral weathering. In more acid soils with low base saturation it also entails increased Al mobilization into the soil solution, which in turn may adversely affect root activity and uptake. The IFS network encompasses sites in both categories that illustrate the magnitude of soil intensity effects of N saturation, that is, changes in soil solution chemistry in response to periodic  $\text{NO}_3^-$  peaks.

Within the short timeframe of this study it would have been unrealistic to expect drastic changes in soil properties (i.e., capacity effects of N saturation and excess  $\text{NO}_3^-$  leaching) to have taken place. The extent of such changes could nevertheless be illustrated by a low-elevation site in the northwestern United States that is receiving low N inputs from pollution but where N fixation at an average rate in excess of  $7000 \text{ mol ha}^{-1} \text{ yr}^{-1}$  ( $>100 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) caused N saturation in an alder forest compared to an adjacent conifer stand containing no N fixers. Intensive  $\text{NO}_3^-$  production and leach-

ing under alder has caused a significant decrease in pH and an increase in Al activity in the shallow soil solutions, a downward redistribution of the exchangeable bases associated with a concomitant increase in exchangeable acidity in the upper soil. These changes have resulted in lower base saturation and lower soil pH in the upper part of the soil profile where most plant roots are located. The first indications of possible changes in nutrient availability (e.g., P limitations) under alder are starting to emerge (Compton and Cole 1989). If those changes result from soil acidification, N addition through pollution could eventually lead to similar end conditions, albeit over a different (longer) timeframe.

Biological flux patterns were also monitored in all IFS field sites, which allowed us to evaluate to what extent the degree of N saturation affects internal N cycling within forests. Estimated fluxes included annual N return from the canopy using throughfall collectors and litter traps; tree requirements and uptake of N calculated from periodic remeasurement of tree growth, mortality, and chemical composition of the tissues; and belowground N mineralization and nitrification rates through field incubation assays. Two high-elevation IFS sites at opposite ends of the N deposition and N saturation spectrum, namely the Findley Lake site in western Washington and the spruce-fir site in the Smoky Mountains, were used to illustrate the influence of N deposition and N saturation on N cycling patterns.

Under the condition of N saturation, N availability to plants and microorganisms is high and the need for N conservation is minimal. This is expressed by a faster turnover of the canopy N, net N release through mineralization in the soil and forest floor, and high nitrification potential. Non-N-saturated systems are more conservative with respect to N, expressed by canopy and belowground N dynamics: Needles are retained longer and foliar N turnover is slow, N input fluxes to the forest floor are immobilized, and there is little net N mineralization. These factors result in low N availability for plant uptake and no measurable nitrification.

At this point, a causal relationship between the soil and solution chemistry changes associated with N saturation and a decline in forest productivity and health (especially at the high-elevation, high-N-input spruce forests) has not been conclusively established. There is still lively debate on this topic. As to the question of a possible recovery of forest soils from changes induced by N saturation and excess  $\text{NO}_3^-$  leaching, there are some indications of a fairly rapid response of the soil solution chemistry to a decrease in nitrification and  $\text{NO}_3^-$  leaching. Chemical changes in the soil generally require a longer time to take place, and within the timeframe of this study it was not possible to evaluate the rate or extent of soil recovery in response to a decline in atmospheric N input. Moreover, it is expected that other factors such as site history, forest cover, and management actions will also greatly influence the rate and extent of the recovery process.

There are considerable uncertainties associated with the estimates of N deposition and  $\text{NO}_3^-$  leaching outputs and of some of the internal N fluxes,

particularly those that are derived from other (measured or estimated) N fluxes. Uncertainties in N input–N output budgets arise from the fact that a combination of field measurements and model outputs is needed to estimate both N deposition and  $\text{NO}_3^-$  leaching losses. Other fluxes, such as net canopy exchange, are calculated as a difference between two or more N fluxes, each estimated with their own level of uncertainty. For example, an error analysis in one of the high-elevation spruce sites in the Smoky Mountains using statistical methods (where possible) and logical constraints (e.g., soil water flux <90% of precipitation) led to the conclusion that only differences between inputs and outputs greater than 50% can be considered statistically significant and meaningful (Johnson et al. 1991). Despite this uncertainty regarding absolute values of N deposition and  $\text{NO}_3^-$  leaching losses and the magnitude of various internal N fluxes, however, the IFS network has offered a unique opportunity to compare biogeochemical cycling of N in forest ecosystems spanning a wide range of N deposition regimes and at various degrees of N saturation.

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