Monitoring the Deposition and Effects of Air Pollution in the Hudson Valley, NY

Final Report 05 -01
February 2005

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PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish "Monitoring the Deposition and Effects of Air Pollution in the Hudson Valley, NY." This report was prepared by the Institute of Ecosystem Studies, located in Millbrook, NY. This project was funded as part of the **New York Energy $mart**[SM] Environmental Monitoring, Evaluation and Protection (EMEP) program and represents one of several studies focusing on ecosystem response to pollutants associated with the generation of electricity. More information on the EMEP program may be found on NYSERDA's website at: www.nyserda.org/programs/environment/emep.asp .

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ABSTRACT

At the Institute of Ecosystem Studies research site in rural, southeastern New York State, atmospheric deposition of both sulfur (S) and nitrogen (N) declined during the 15 years of our measurements (1988-2002) due to reductions in emissions of these pollutants in the eastern US. Reported here is a 10-year record from a mixed-oak forest that illustrates some of the biogeochemical consequences of the changing emissions and deposition. Nitrate leaching from the lower soil horizons is rarely above detection limits and has not changed during the period of record, indicating that the site retains nearly 100% of the N deposition it receives. Sulfur leaching from this site in soil solution is on average 70% greater than atmospheric deposition input, probably because of mineral weathering of S derived from the shale/slate bedrock. Despite this mineral weathering source of S in the ecosystem, the decline in S deposition has been accompanied by a decline in S leaching from the site. Interannual variability in S leaching is largely explained by variation in precipitation amount and S deposition. There is a strong correlation between S and base cations in soil solution. The decline in S leaching between 1992 and 2002 was accompanied by substantial declines in Ca^{2+}, Mg^{2+}, and K^{+} leaching. The greatest absolute decline in cation leaching was observed for Ca^{2+}, but the greatest relative response was observed in K^{+} leaching. Addition of nitrogen fertilizer to forest plots showed that these forest ecosystems are quite sensitive to excess nitrogen, responding with increases in foliar nitrogen concentration, soil microbial nitrogen transformations, and soil nitrate leaching.

KEY WORDS

Acid deposition, acid rain, nitrogen, sulfur, soil leaching, foliar leaching, base cations, oak forest, *Quercus*

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SUMMARY

Ecosystems of the northeastern US are exposed to elevated levels of sulfur and nitrogen oxides, air pollutants that are derived primarily from fossil fuel combustion. We have been tracking the fate of these pollutants in an upland oak-hickory forest near Millbrook in the mid-Hudson Valley of New York. The site is typical of upland forests in the Hudson Valley—second-growth forest on thin, acidic soils derived primarily from shale/slate bedrock. We measure the inputs of sulfur and nitrogen to the forest by atmospheric deposition (that is, delivery of these pollutants to the ground and vegetation in rain, snow, gases and particles) and the outputs through leaching of soil water below the rooting depth of the trees, as well as several indices of forest growth and nitrogen cycling.

Over the last 15 years, atmospheric deposition of sulfur has been decreasing at this site. The output of sulfur from the ecosystem through leaching of the sulfate ion exceeds the atmospheric deposition input, indicating a source of sulfur in the system, probably from weathering of sulfur-containing minerals in the bedrock. Despite this internal source of sulfur in the system, the trend in sulfur leaching parallels the declining trend in atmospheric deposition, suggesting that reductions in sulfur emissions are having a measurable effect on this forest. When sulfur is leached from the ecosystem as sulfate, it takes with it nutrient ions such as calcium and magnesium. We found a very strong relationship between the leaching of calcium and the leaching of sulfate, indicating that the depletion of soil calcium from the soils is declining in concert with the reduced sulfur deposition.

Although the atmospheric deposition of nitrogen has also declined over the last 15 years, we observed a much different behavior of nitrogen in the ecosystem. There is very little leaching of nitrogen from these plots in soil water, suggesting that nearly all of the pollutant nitrogen that is deposited to the forests is retained in the vegetation and soils. This lack of movement of nitrogen out of the forest means that (1) the groundwater and streams are being protected from the deleterious effects of nitrogen, and (2) the nitrogen is accumulating in the forest soils or vegetation. In the last decade, however, there has been no trend in our indices of internal nitrogen cycling in the ecosystem, such as foliar or soil nitrogen concentrations.

We have begun a nitrogen fertilization experiment to assess the susceptibility of these forests to "nitrogen saturation," a condition in which oversupply of nitrogen can alter the normal patterns of nitrogen cycling, produce leaching of excess nitrogen to groundwater, and potentially harm the trees. Preliminary results of this experiment suggest that the trees respond quickly to nitrogen fertilization by increases in nitrogen in foliage, while the soils respond after a delay of several years through increased microbial production of nitrate. Unlike oak stands that have been studied elsewhere, fertilization dramatically increases the nitrogen leaching from these stands.

From a policy perspective, these results indicate the following:

(1) Reductions in sulfur deposition have reduced the drain of calcium, magnesium, and potassium from the soils, and further reductions are likely to further reduce that drain. This will probably be beneficial to calcium- and magnesium- demanding species such as sugar maple, flowering dogwood, and white oak. However, further reductions in sulfur emissions will not reduce sulfur leaching proportionately, because the leaching will reach a lower limit set by the natural leaching of sulfur from the bedrock.

(2) Changes in nitrogen deposition will have little immediate effect on the leaching of nitrogen to surface water or groundwater in this ecosystem, because essentially all the nitrogen deposited is retained in the forest. We do not yet know the consequences of the nitrogen accumulation in the forest. However, our experiments with relatively high levels of nitrogen fertilization indicate that these forests are susceptible to nitrogen saturation. Further research is needed to determine the amount of N deposition or accumulation that triggers the onset of nitrogen saturation.

1. INTRODUCTION

Atmospheric deposition of sulfur (S) and nitrogen (N) can have significant and long-lasting effects on the biogeochemistry of forest ecosystems (Driscoll et al. 2001). The nature and significance of these effects is mediated by the inherent biological and geochemical characteristics of the ecosystem, particularly its ability to retain deposited S and N within the system and its ability to buffer the acidity often associated with these pollutants. If sulfate (SO_4^{2-}) is deposited with a cation that is retained in the canopy (e.g., H^+, NH_4^+), cation exchange reactions in or on canopy surfaces can cause leaching of nutrient cations (e.g., Ca^{2+}, Mg^{2+}) (Lovett and Hubbell 1991). For some tree species this loss of nutrients can have negative effects on frost-hardiness (DeHayes et al. 1999). Deposited nitrate (NO_3^-) can cause the same effect, but NO_3^- itself is often retained to some extent by canopies, mitigating the canopy leaching loss of cations (Lovett and Lindberg 1993).

Similar processes occur in the soil. If SO_4^{2-} and NO_3^- move through the soil and are lost in leachate, they cause equivalent leaching of cations from the ecosystem. The cations leached include nutrients such as Ca^{2+} and Mg^{2+} as well as acidic cations such as H^+ and Al^{3+}. Loss of $Ca^{2+}$and Mg^{2+} can reduce soil fertility, while leaching of Al^{3+} and H^+ can be toxic to organisms in downstream surface waters. The relative amounts of these cations leached depend on the acid/base status of the soil (Reuss and Johnson 1986). Sulfur can be retained in the ecosystem by three principal processes: geochemical adsorption onto Fe and Al sesquioxides, plant uptake, and incorporation into soil organic matter (Johnson et al. 1982). For most forests in the glaciated region of the northeastern US, S adsorption capacity is small, and S incorporation into soils and vegetation is minimal, so most deposited SO_4^{2-} passes through the ecosystem and is lost in leachate. Nitrogen is more strongly retained in plant biomass and soil organic matter, however, and forests of the northeastern US generally retain between 50 and 99% of the nitrogen they receive from atmospheric deposition (Boyer et al. 2002, Lovett et al. 2000, Lawrence et al. 2000). Nitrogen accumulated in the ecosystem may cause changes in biogeochemistry, including increases in foliar and litter N (Magill et al. 1997), changes in decomposition rates (Carreiro et al. 2000), stimulation of nitrification (Magill et al. 1997), altered resistance to pests (Latty et al. 2003), and changes in species composition (Driscoll et al. 2003).

The US Clean Air Act of 1970 has resulted in a general decline in S emissions in the eastern US in the last three decades and that trend has continued after the Clean Air Act Amendments of 1990 (Lynch et al. 2000). At our research site in southeastern New York State, we have seen a decline in S deposition resulting from the reduced emissions (Kelly et al. 2002). Nitrogen deposition has also declined, although less than S. To determine the effects of atmospheric deposition on the forest ecosystems of this region, we have been tracking some key biogeochemical indicators in long-term research plots. This paper reports the first 10 years of results from this long-term study, and examines the effects of the changes in atmospheric deposition we have observed in those 10 years. In addition, we report the preliminary results from a nitrogen amendment experiment in the same forest.

2. LONG-TERM TRENDS IN NUTRIENT CYCLING AND LOSS

METHODS

Site Description

All samples were collected at the Institute of Ecosystem Studies (IES) in Millbrook, NY, (41° 50' N, 73° 45' W) between January 1993 and December 2002. Precipitation and dry deposition samples were collected in an open field on IES property beginning in 1988. For the 1993-2002 time period, mean annual precipitation was 1074 mm, mean annual temperature was 9.6 °C, January mean temperature was –3.1 °C and July mean temperature was 21.9°C. Annual precipitation was 78% rain, 11% snow and 11% rain/snow mix. Precipitation at this site is distributed relatively evenly throughout the year.

Soil solution, throughfall and soil samples were collected at two sites located in the Cannoo Hills, approximately one kilometer northeast of the location where precipitation is measured. The sites are located in second growth forest with a canopy of mixed oak, maple and pine, and records indicate a history of use as woodlots that were abandoned in the 1890s (Glitzenstein et al. 1990). The sites are underlain by late Cambrian–early Ordovician shales and slates, covered by a mantle of glacial till of variable depth (Glitzenstein et al. 1990). Soils are classified as lithic dystrochrepts of the Nassau series, described as a slaty silt loam on glacial till, consisting of shallow, well-drained soils on uplands and derived from the acidic shales and slates (Secor et al. 1955). Soil depth varies from 0 on the bedrock outcrops to approximately 50 cm.

Research Methods

Daily total precipitation amounts were determined using a universal recording rain gauge (Belfort Instrument Co. Series 5-780). Precipitation amounts were also determined on an event basis by weighing the collecting bucket used for precipitation chemistry and dividing by the area of the bucket opening. To reduce the effect of wind, the bucket was surrounded by Alter shields. Amount of precipitation that falls as snow was determined by a rain and snow gauge (National Weather Service Specification No. D040-SP001). Atmospheric particles, SO_2, and HNO_3 were collected by drawing air at 3.0 L/min through a three-stage filter pack mounted on a 10-m tower (Kelly et al. 2002). Dry deposition was estimated using weekly mean air concentrations and dry deposition velocities calculated from a dry deposition model parameterized with meteorological data from the site (Kelly et al. 2002).

Each of the two 15 x 15 m forest sites contained ten throughfall collectors consisting of a 20 cm diameter plastic funnel seated in the mouth of a 4 L plastic jug. The jug and funnel assembly was set 1 m above the ground in a plastic crate. The collection jugs were covered with a fitted cover of opaque plastic to prevent sunlight-induced algal growth in the sample, and a plug of polyester fiber was inserted into the neck of the funnel to filter out debris. Throughfall was collected on an event basis during the period 1993-1999 and each collector bulked by month. Each time an event was collected, the funnels were rinsed with deionized water and the polyester fiber plug was replaced.

Snow throughfall was collected using two different methods. From 1993-1995, snow was collected in buckets, (660.5 cm^2 collection area) and from 1996-1999, PVC pipes 20 cm in diameter were used to support the heavy plastic bags in which snow was collected. Samples were brought inside, thawed, filtered and composited by month.

In each plot ten Soil Moisture 1900 suction lysimeters were installed 30-60 cm deep and connected to a hanging-column, constant-tension vacuum system, which maintains a constant suction of 0.1 atm. Lysimeters were collected weekly until 2000, when collection switched to bi-weekly. Samples were bulked on a monthly basis. Using a hand-held piston pump, the sample was drawn out of the lysimeter into a collection flask, which was rinsed with deionized water between samples. To calculate fluxes of ions in the soil solution, we used the Brook90 v. 3.25 model to generate monthly values for soil water flow (Federer 1995).

Potential nitrogen mineralization and nitrification were measured in two depth horizons, 0-3 cm (roughly equivalent to the forest floor) and 3 – 10 cm (corresponding to the top layer of the mineral soil). The measurements were made in July using a 14-day lab incubation and extracting with 2 M KCl. Exchangeable cations were measured by extracting soil samples with 2 M $BaCl_2$ and analyzing the extracts for pH, Ca^{2+}, Mg^{2+}, Na^+, K^+ and Al.

Sample Analysis

After bulking, all samples were preserved with 100 µL chloroform / 100 mL sample and stored at 4°C until chemical analysis could be performed. Hydrogen ion concentration was measured on a Fisher/Accumet AR 20 pH meter with Fisher glass and calomel electrodes. Ammonium concentration was measured on an Alpkem Total Flow Solutions III Autoanalyzer using the indophenol blue method. This instrument was also used to measure ammonium and nitrate concentrations in the extracts from the N-mineralization soils. Calcium and magnesium concentrations were measured with a Perkin-Elmer inductively coupled plasma emission spectrometer (ICP). Potassium and sodium concentrations were measured on a Perkin-Elmer Atomic Absorption Spectrometer (AA). Nitrate, sulfate and chloride concentrations were measured with a Dionex DX-500 ion chromatograph. Total nitrogen was measured using a persulfate digestion method to digest an aliquot of the bulked sample. The digested samples were then run on the Alpkem Autoanalyzer using the cadmium reduction method for nitrate. All the soil exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and Al^{3+}) were measured with the ICP. All analyses were performed in the IES analytical laboratory.

RESULTS

Precipitation amount averaged 1075 mm/yr during the 10-y period 1993-2002, ranging from 797mm in 2001 to 1426 mm in 1996 (Figure 2-1). Throughfall amount, which was only measured from 1993-1999, was somewhat less than precipitation amount because of evaporation in the canopy and diversion to stemflow. Modeled soil water drainage was roughly 50% of the precipitation, averaging 536 mm/y, and reflected the interannual pattern of precipitation.

Soils at this site are quite acidic, with a mean pH and base saturation of 3.66 and 22.8%, respectively, in the 3-10 cm layer (Table 2-1). Al^{3+} dominates the exchange sites and Ca^{2+} availability is quite low at 0.83 $cmol_c$/kg.

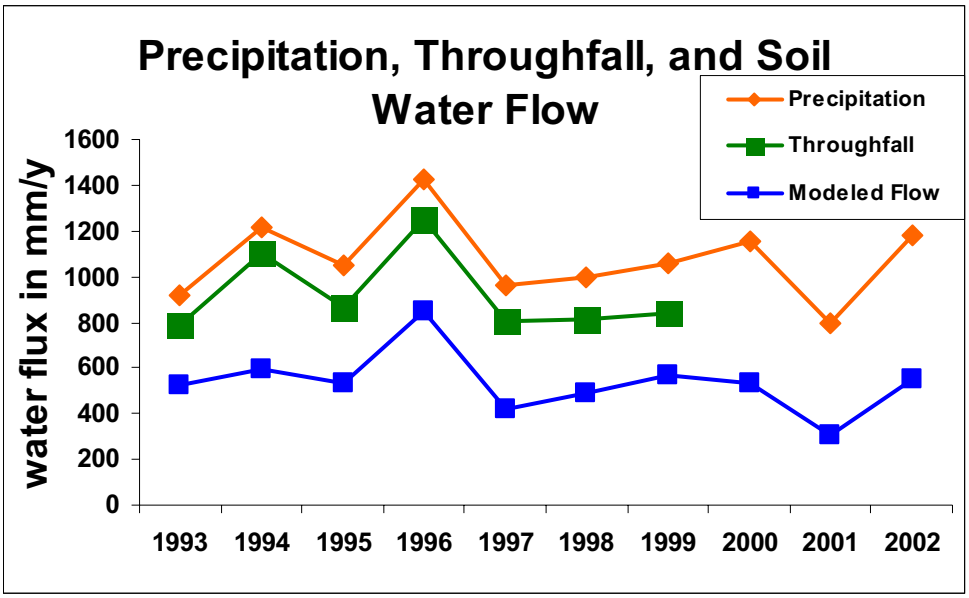

Figure 2-1. Trends in water flux in precipitation, throughfall, and modeled soil water drainage (B-horizon).

Table 2-1. Exchangeable cations in soils at the study site. Data in $cmol_c$/kg except base saturation (%) and pH. All variables measured in 0.1M $BaCl_2$ extraction.

	Depth from surface	
	0-3 cm	**3-10 cm**
Ca^{2+}	5.95	0.83
Mg^{2+}	1.17	0.28
K^{+}	0.42	0.14
Na^{+}	0.04	0.03
Al^{3+}	3.49	4.38
H^{+}	0.39	0.22
ECEC	11.47	5.88
Base saturation	66.6%	22.8%
pH	3.41	3.66

Total (wet + dry) S deposition has declined substantially since measurements at this site began, from 20.5 kg S/ha in 1988 to about 8 kg S/ha in 2001 (atmospheric deposition data for 2002 are not yet available) (Figure 2-2a). Much of this decline occurred prior to the 10-year period of biogeochemical measurement (1993-2002), but S deposition has continued to decline since the Clean Air Act Amendments went into effect in 1995. At this site, the S deposition is roughly 50% wet and 50% dry, with the dry deposition primarily from SO_2 (Kelly et al. 2002). Throughfall SO_4^{2-} flux was slightly less than total wet + dry deposition, probably because of diversion of S to stemflow, which was not measured. The near-equivalence of throughfall and wet +dry deposition of S supports the view that throughfall can be an effective measure of total S deposition (Lindberg and Garten 1988, Lindberg and Lovett 1992). Soil

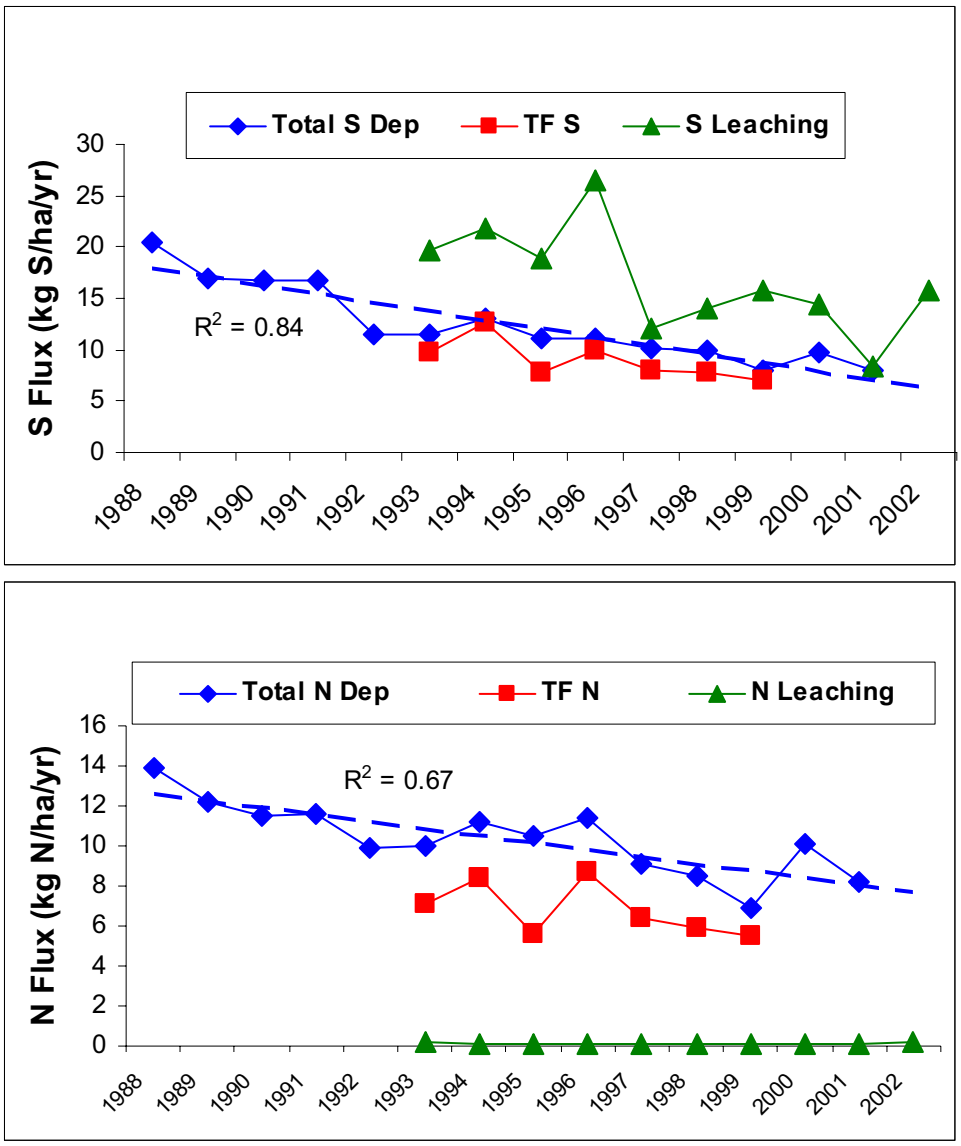

Figure 2-2. Trends in fluxes of sulfur (top panel) and nitrogen (bottom panel) in atmospheric deposition, throughfall and soil solution. Dashed lines are the regression lines for the deposition trends based on annual fluxes, with coefficients of determination (R^2) shown on the graph.

solution SO_4^{2-}-S fluxes are consistently higher than deposition inputs to this site, in some years more than twice as high (e.g., 1996, Figure 2-2). Sulfate leaching has undergone a significant decline since the measurements began in 1993 (linear regression, $r^2 = 0.34$, $p = 0.046$), decreasing at an annual rate of approximately 1 kg S/ha/yr. However, Figure 2-2 shows much interannual variability in S leaching, primarily driven by differences in rainfall amount (Figure 2-1). A multiple regression of S leaching flux vs. atmospheric S deposition and rainfall amount explains 76% of the interannual variation in S leaching from the ecosystem ($n = 9$, $p = 0.008$).

Nitrogen deposition has also declined substantially since 1988 (Figure 2-2). Throughfall N fluxes were substantially lower than wet + dry deposition, indicating canopy uptake of inorganic N, a common occurrence in forests (Lovett and Lindberg 1993). Soil leaching fluxes of inorganic N were near zero throughout the entire period of record, indicating almost complete retention of deposited NO_3^- and NH_4^+ by this forest. Dissolved organic N (DON) was the main N species in soil solution, and the calculated export flux averaged 0.7 kg N ha^{-1} y^{-1} with no significant trend. The lack of nitrate leaching is consistent with the near-zero net nitrification rates measured in these soils (Figure 2-3). Net N mineralization was quite variable from year to year but was low compared to sites we have measured in the Catskill Mountains (Lovett et al. 2004). Extractable NH_4^+ averaged 22 µg N gdw^{-1}, and extractable NO_3^- was usually below our method detection limit of 0.2 µg N gdw^{-1}.

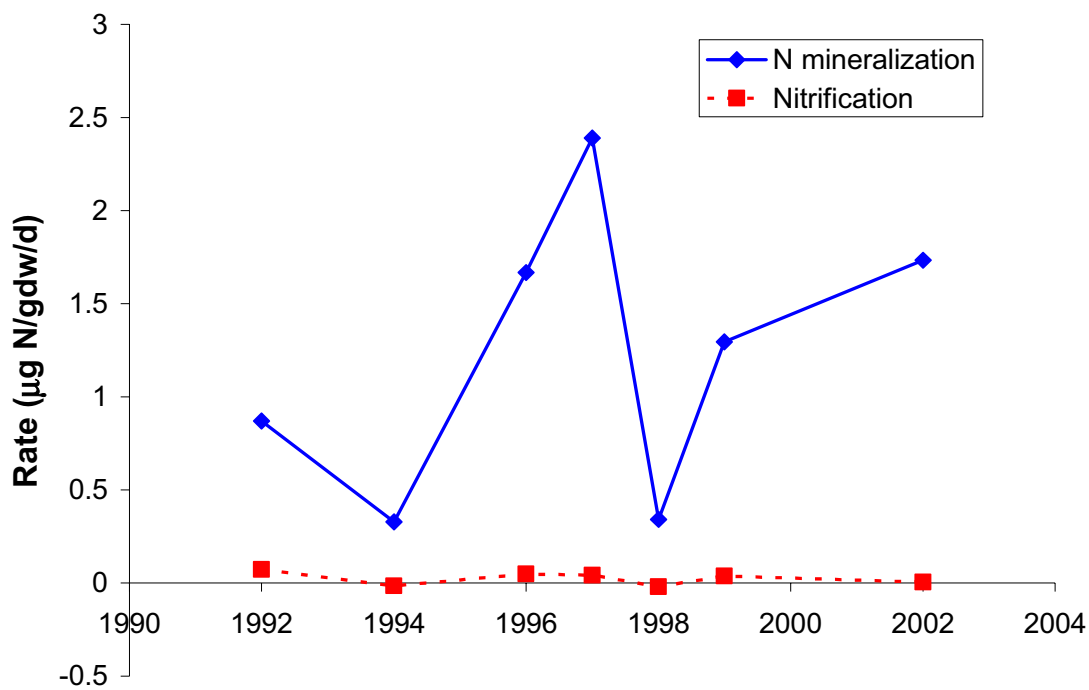

Figure 2-3. Trends in potential net N mineralization and nitrification in the top 10 cm of the soil.

Sulfate was the predominant anion in the solutions measured in this study, and it increased in concentration as precipitation percolated through the ecosystem as throughfall and then soil solution (Figure 2-4). Nitrate increased in concentration as precipitation passed through the canopy, but then decreased to near zero in the soil solution collected in the B-horizon. Both the canopy and the soil removed hydrogen ion from the solution, and part of the hydrogen ion consumption was exchange for the base cations Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}. All four of these ions increased as precipitation passed through the canopy, but K^{+} was consumed in the soil while the other three ions increased in concentration in soil solution relative to throughfall (Figure 2-4). Precipitation was nearly in ionic balance, but throughfall showed an anion deficit, likely resulting from the anionic charge of unmeasured organic acids leached from the canopy (Lovett et al. 1985, Lovett and Hubbell 1991). Soil solution, on the other hand, showed a cation deficit, suggesting that whatever anionic charge was present from organic acids was more than compensated by unmeasured cations. Much of this unmeasured cationic charge was most likely from Al^{3+}, which was important on the soil exchange sites (Table 2-1) but was not measured in soil solution.

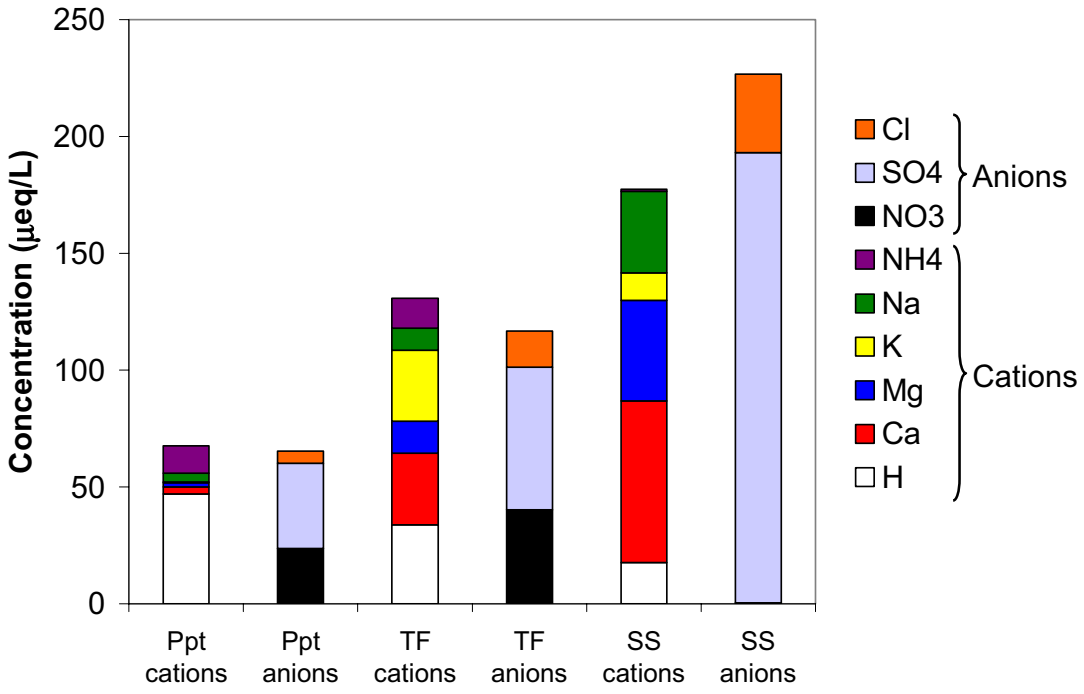

Figure 2-4. Volume-weighted mean concentrations of anions and cations in precipitation (PPT), throughfall (TF), and soil solution (SS) during the study.

Because of the very low NO_3^- concentration in soil solution, SO_4^{2-} is the principal mobile anion in the ecosystem. As a result, concentrations of base cations in soil solution and throughfall were strongly correlated with SO_4^{2-} concentrations (e.g., Ca^{2+}, Figure 2-5). (Figure 2-5 is plotted as concentrations, rather than fluxes, because fluxes of ions are partially self-correlated in that the same water flux term is used in the calculation of each ion flux.) Calcium, Mg^{2+}, and K^+ fluxes in soil solution have declined significantly over the period of record, but Na^+ flux has not (Figure 2-6). None of the base cations has shown a significant change in wet deposition over this period (Kelly et al. 2002).

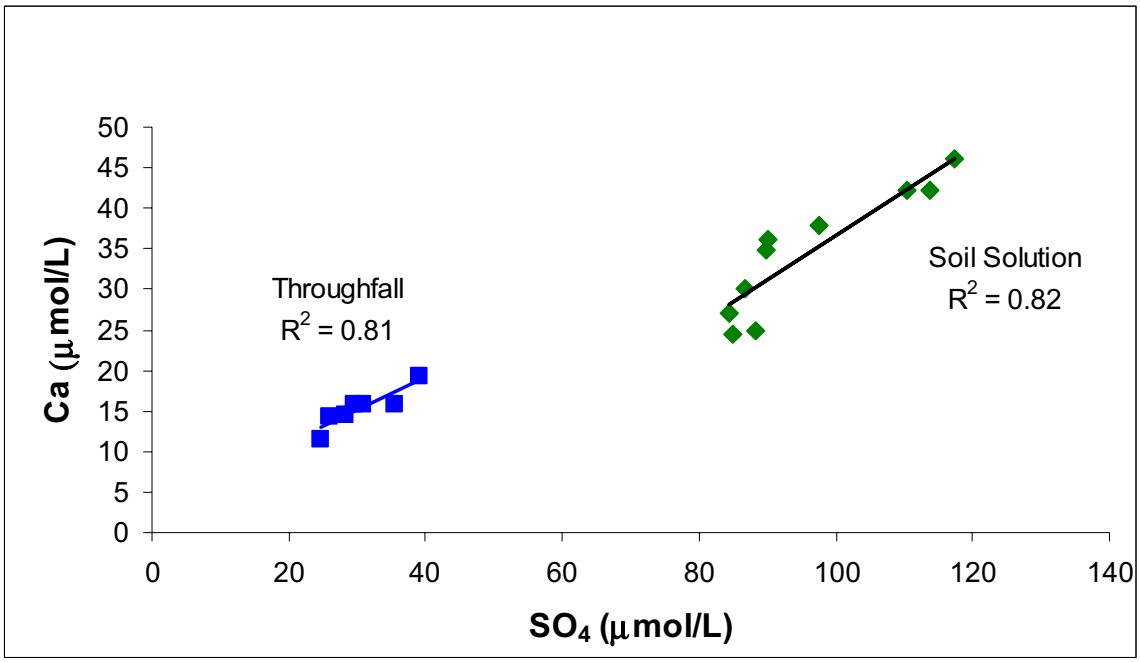

Figure 2-5. Plot of annual mean sulfate vs. calcium concentrations in throughfall and soil solution. Regression lines and coefficients of determination are shown.

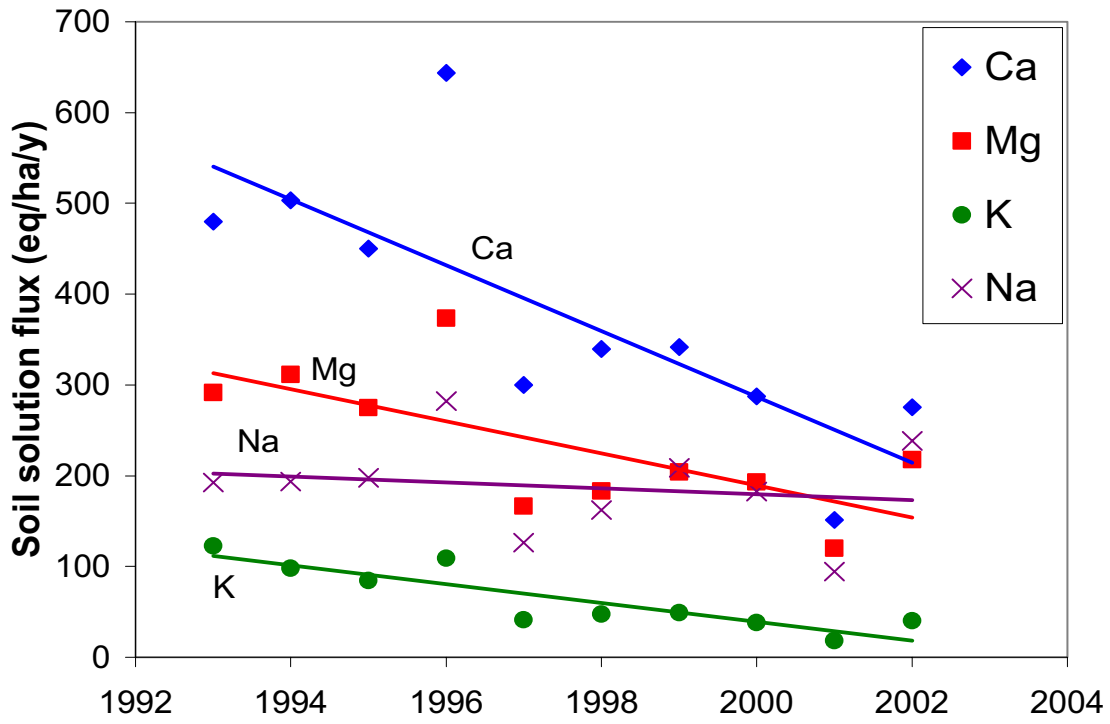

Figure 2-6. Trends in soil solution flux of base cations. Ca: adjusted r^2 = 0.55, p = 0.009; Mg: adjusted r^2 = 0.41, p = 0.03; K: adjusted r^2 = 0.75, p = 0.0008; Na: adjusted r^2 = -0.09, not significant (p = 0.6).

DISCUSSION

This site showed unusual biogeochemical characteristics but it nonetheless responded to changes in atmospheric deposition. Deposited nitrogen was almost completely consumed by the forest ecosystem. Nitrogen retention in temperate forests is primarily in vegetation and soil organic matter (Johnson 1992, Magill et al. 1997), and the incorporation into soil can be either biotic or abiotic (Johnson 1992, Dail et al. 2001, Fitzhugh et al. 2003). Oak forests have been shown to be very retentive of N in other studies (Lovett et al. 2004, Lewis and Likens 2000), even under heavy loads of N fertilizer (Magill et al. 1997).

Sulfur, on the other hand, was exported from this system in soil solution at a rate that is on average 70% higher than the rate of input via wet and dry deposition. Atmospheric deposition contributed on average about 59% of the S exported via soil leaching, and the remaining 41% was the net result of sources and sinks within the system (mineral weathering + S desorption + organic S mineralization – plant and microbial sequestration). Other forested ecosystems in the northeastern US have shown an excess of S outputs over inputs, but these excesses are generally more modest (and are usually attributed to desorption of SO_4^{2-} from the soil or remineralization of S stored in SOM (Driscoll et al. 1998). For instance, at Hubbard Brook, NH, in recent years exports of S exceeded inputs by about 4 kg S/ha/y (Likens et al. 2002). In our study, exports exceeded imports by amounts that averaged 6.6 kg S/ha/y and ranged up to 15.4 kg S/ha/y (Fig 2-2). The net source of S in our ecosystem is large enough that we believe it to

include weathering of S from minerals derived from the shale bedrock as well as net release from soil and microbial pools. While there are no data on chemical or mineralogical composition of the bedrock at this site, slates and shales often contain substantial quantities of S, and ecosystems on shale have been observed to leach excess S (Giusti 1999). At our site, high S content of the bedrock is suggested by the fact that several of the bedrock wells used for drinking water in the surrounding area have a strong sulfide odor and require sulfide treatment prior to use. At some sites, the leaching of S from bedrock masks the effects of changes in atmospheric deposition (Turk et al. 1993, Giusti 1999), but at this site the trend in atmospheric deposition of S is evident despite the S weathering. Reduction in atmospheric S deposition has resulted in reduced S export in soil solution, and this has in turn reduced the base cation leaching from the site.

However, the reduction in base cation leaching has not been distributed evenly among the four cations. While S leaching declined by 46% (614 eq/ha/y decrease) between 1993 and 2002 (calculated from the regression of S leaching vs. year), Ca^{2+} leaching declined by 60% (326 eq/ha/y), Mg^{2+} by 51% (159 eq/ha/y), K^{+} by 84% (93 eq/ha/yr), and Na^{+} by 14% (29 eq/ha/yr) during the same period. The greatest absolute decline in cation leaching was observed for Ca^{2+}, but the greatest relative response was observed in K^{+} leaching. The absolute declines are in the relative order ($Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$) that would be predicted from soil cation exchange theory, given the valences and relative abundances on cation exchange sites in these soils (Reuss and Johnson 1986). We have not measured base cation pools in vegetation or soils or mineral weathering rates at this site so we cannot calculate the complete cation budget. Nonetheless, it would seem that these substantial reductions in the leaching of Ca^{2+}, Mg^{2+} and K^{+}, apparently due to declining S deposition, must certainly constitute a significant amelioration of base cation depletion at a site with such acidic soils. The reduction in base cation loss is very nearly proportionate to the reduction in sulfate (fig. 2-5), which does not suggest any major depletion of soil exchangeable cation pools during the time course of this study. If the soil exchangeable pool were being substantially depleted, we would expect less Ca^{2+} leaching per equivalent of SO_4^{2-} leaching as time progressed, but that was not observed.

Uncertainty in Flux Measurements

Measurement of ecosystem fluxes is always subject to considerable uncertainty. The estimates of two principal fluxes in this ecosystem input-output budget—atmospheric deposition and soil leaching—both rely on a combination of measurements and models. In the case of atmospheric deposition, measurement is made of chemical concentration of ions in precipitation, amount of precipitation, and chemical concentration in air. All of these measurements are routine and the chemistry is done by standard techniques, so we estimate the uncertainty at no more than 5%. It is more difficult to estimate the dry deposition flux, which is calculated as the product of concentration of the substance in the air and a modeled deposition velocity. The models, which use site-specific meteorological data, are widely used but their uncertainty has not been well evaluated. Nonetheless, as we point out above, the modeled estimates of total atmospheric deposition of sulfur agree well with the flux of sulfur in throughfall (Figure 2-2), which serves as a check on the deposition estimates. The throughfall sulfur fluxes are expected to be somewhat lower that atmospheric deposition because stemflow was not measured. Because of the

agreement with throughfall, we estimate that our sulfur deposition fluxes are probably accurate to within 20%. For nitrogen, the same deposition models are used, but we cannot use throughfall as a check because nitrogen is taken up in the canopy. Therefore we cannot estimate the uncertainty in nitrogen deposition, but we expect about the same uncertainty as for sulfur.

For the soil leaching fluxes, again the measurement of concentration is straightforward and probably accurate to <5%. We have two sites, and the mean fluxes are very similar, indicating that our sampling intensity is adequate. Fluxes are calculated as the product of the concentrations and monthly water flux, and the water flux is calculated from a model. The BROOK90 model (Federer 1995) that estimates the water flux is widely used in the Northeast, and has been tested at other sites but not at our site. We cannot test the model against stream flow because we do not have a gauged watershed. Nonetheless, the results appear reasonable, as the pattern of soil water flow follows the pattern of precipitation inputs, and the total water loss is about half of the precipitation amount (Figure 2-1) as is typical of Northeastern forests. Again, we expect this estimate to have an uncertainty of no more than 20%, but we have no way to confirm this.

3. NITROGEN ADDITION EXPERIMENT

Our input and output data from our long-term monitoring plots indicate that the plots are accumulating nearly all the nitrogen that is deposited to them from atmospheric deposition. To explore more fully the consequences of N accumulation in these forests, we began in 1996 an N addition experiment in ridgetop oak-hickory plots near the long-term plots discussed above. This section of the report discusses the preliminary results of that experiment.

RESEARCH SITE AND METHODS

This experiment was conducted in six pairs of oak-hickory plots within 1 km of the long-term monitoring plots discussed above. The plots were selected to be typical of the ridgetop forest type in this area, and were chosen to be on relatively flat terrain to simplify the N additions. Each plot was 20 m in diameter, with an inner core plot 10 m diameter in which the nutrient cycling measurements were made. The two plots in a pair are separated by <20 m, and one plot of each pair is fertilized and the other left unfertilized as a control. Nitrogen was added to these plots as granular NH_4NO_3 four times per year (May, June, July and August) beginning in 1996. The application rate initially was 100 kg N/ha/y, but in 2000 the rate was lowered to 50 kg N/ha/y and it has remained at that level. The entire 20 m diameter plot was fertilized, but all biogeochemical measurements were made in the inner 10 m diameter plot to avoid edge effects.

Response variables measured in the plots were foliar N concentration, soil N mineralization and nitrification, N concentration in B-horizon soil solution, and C:N ratio of the soil. Field and analytical methods were identical to those used the long-term plots discussed above, except soil solution was measured with Prenart Teflon lysimeters rather than the Soil Moisture, Inc. ceramic cup lysimeters used in the long-term plots. Constant tension was applied to the Prenart lysimeters with the same hanging column system described above. Four lysimeters were installed in each plot. Except for the fertilization, control and fertilized plots were treated identically.

RESULTS

Foliar N concentration responded quickly to the N fertilization. Prior to the beginning of the fertilization in 1996, the mean foliar N concentrations in the control and fertilized plots were not significantly different (Fig. 3-1). In 1997 the N concentrations in foliage in the fertilized plots was significantly higher than in the control plots, and that pattern has continued.

In the soil, both nitrogen mineralization and nitrification rates have shown a response to fertilization, but the response was delayed. In 1996 (prior to the beginning of the fertilization), there was no difference between the fertilized and unfertilized plots. This was also true for the first 3 years after the fertilization began (1997-1999). We

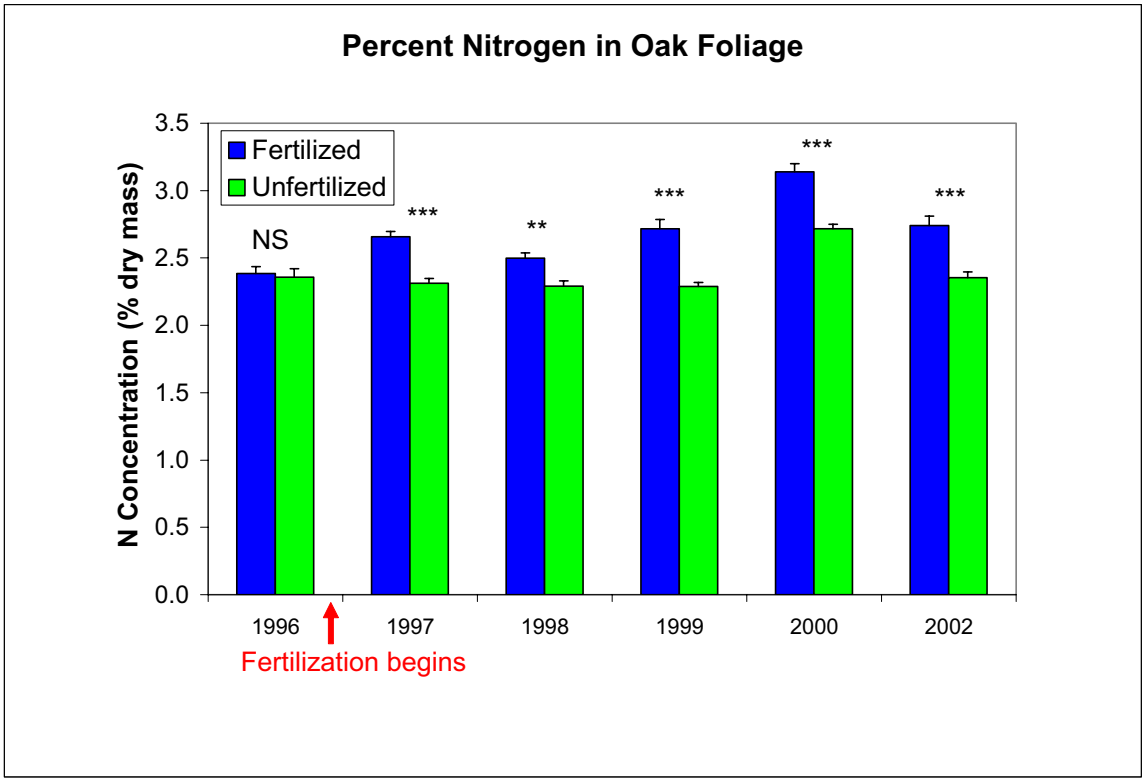

Figure 3-1. Concentration of N in oak foliage (% dry mass) on the fertilized and unfertilized plots. Each bar represents the mean of 6 plots; the error bar is one standard error. Fertilization began after the 1996 samples were taken. NS = not significant, ** p<0.01, *** p<0.001

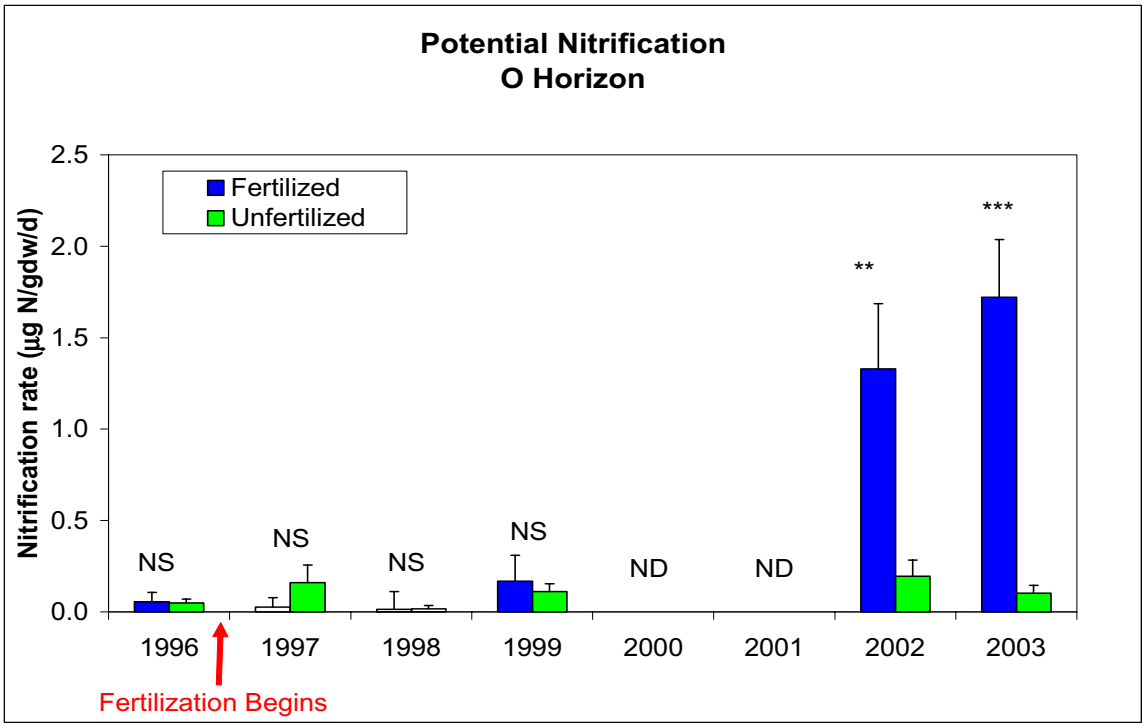

Figure 3-2. Potential nitrification (14-d lab incubation) in the fertilized and unfertilized plots. Bars represent means of 6 plots, error bars are one standard error. Fertilization began after the 1996 data were taken. NS = not significant, ND=No data, ** p<0.01, *** p<0.001

do not have data for 2000 and 2001, but in 2002 and 2003 both N mineralization and nitrification rate in fertilized plots were significantly higher than in control plots. Nitrification (Fig. 3-2) showed the greatest response.

NITROGEN LEACHING FROM THE SOIL

While the control plots had levels of NO_3^- and NH_4^+ that were usually below detection, measurable quantities of NH_4^+ and especially NO_3^- began to appear in soil solution in the fertilized plots soon after the fertilization began (Fig. 3-3). Leaching of NH_4^+ has remained relatively low, but the leaching of NO_3^- increased to almost 50 kg N/ha/y, which is nearly equal to current fertilizer inputs. Low amounts of leaching in 2001 were probably due to the low precipitation amount that year.

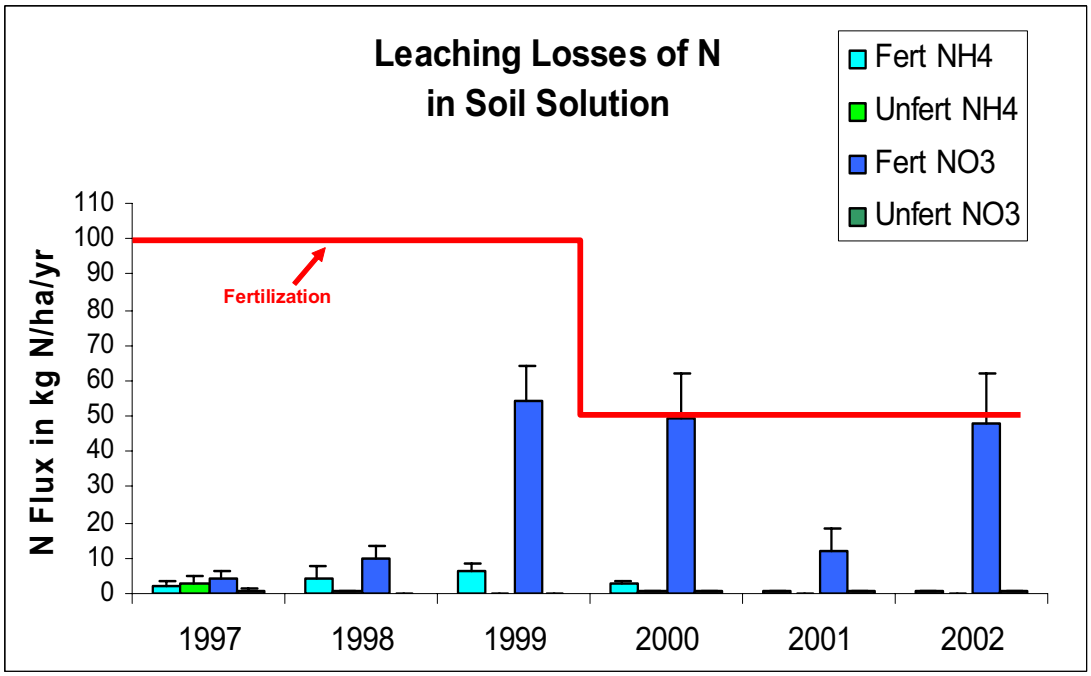

Figure 3-3. N leaching as calculated from B-horizon soil lysimeters. Each bar is the mean of 6 plots; the error bar represents one standard error. The red line shows the rate of application of fertilizer during the period. In addition, these sites (both fertilized and control) receive about 10-11 kg N/ha/y in atmospheric deposition of N (see Figure 2-2).

DISCUSSION

The response of these plots was somewhat surprising in that similar oak forests in Massachusetts showed little NO_3^- leaching, even after receiving as much as five times as much N fertilizer as was applied to our experimental plots (Magill et al 1997). Nitrate leaching in our plots began shortly after the initiation of fertilization and after six years was roughly equal to the rate of fertilization, indicating little retention of excess N in these fertilized plots. Both the plants and the soil microbes responded to the fertilization, as demonstrated by the increases in foliar nitrogen and nitrification rate, respectively.

We can only speculate why the response of these oak plots was so different from that of the Massachusetts plot studied by Magill et al. (1997). Both sites have a history of use as woodlots, but the harvesting could have differed in intensity between the two sites, and if the Massachusetts site had greater harvest removals of wood, it might subsequently have greater N retention capacity (Aber et al. 1998). Another possibility is that the forest is growing more rapidly at the Massachusetts site than at our site. Greater tree growth leads to greater retention of N in vegetation. While we have not directly measured forest age or growth rate at our site, it is a ridgetop forest with relatively mature trees whose growth could be limited by age or lack of water. Yet another explanation, which we consider most plausible, is that the soils at our site are thinner and rockier than those at the Massachusetts site, leading to less N retention capacity in the soil.

Fertilization of these plots produced increases in nitrate leaching before any increases in net nitrification were observed (Figures 3-2 and 3-3). There are several reasons why this could occur. First, the leaching could represent a direct pass-through of the nitrate in fertilizer, although this seems unlikely because it did not appear to occur in 1997, the first year after fertilization began, and it increased steadily after that. Alternatively, there could have been an increase in nitrification in the field before we observed it in the laboratory, but we consider this unlikely because the nitrifiers are more likely to respond in the optimal temperature and moisture conditions of the laboratory assay. Finally, we believe the most likely reason is that the N fertilization could have impeded the ability of the soils and vegetation to retain added N, for instance by inhibiting microbial N immobilization or abiotic nitrate retention in the soil, before there was a stimulation of soil nitrifiers.

The high level of nitrogen leaching at our sites after fertilization presents a paradox— while the forests are extremely retentive of nitrogen from ambient nitrogen deposition, allowing almost no nitrogen to leach below the rooting zone, addition of excess nitrogen cause a rapid and dramatic N saturation response, with leaching of nitrogen nearly equal to the fertilizer inputs. The dose of N in the fertilizer treatments, 100 kg N/ha/y in the first three years, followed by 50 kg N/ha/y in the next three years, was moderate by fertilization standards but high by atmospheric deposition standards. With atmospheric deposition at this site averaging about 10 kg N/ha/y, the fertilization levels were 5-10 times the ambient deposition rates. It remains to be seen how intermediate doses of N fertilizer would effect the N saturation response. Creating a dose response curve for N deposition would be very helpful for modeling the N saturation response and for evaluating policy options regarding N emissions.

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