

## Chapter 7

# ACIDIFICATION AND NUTRIENT CYCLING

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### 1. INTRODUCTION

Additions of acid anions can alter the cycling of other nutrients and elements within an ecosystem. As strong acid ions move through a forest, they may increase the concentrations of nitrogen (N) and sulfur (S) in the soil solution and stream water. Such treatments also may increase or decrease the availability of other anions, cations and metal ions in the soil. A number of studies in Europe and North America have documented increases in base cation concentrations such as calcium (Ca) and magnesium (Mg) with increased N and S deposition (Foster and Nicolson 1988, Feger 1992, Norton et al. 1994, Adams et al. 1997, Currie et al. 1999, Fernandez et al. 2003). Experiments in Europe also have evaluated the response of forested watersheds to decreased deposition (Tietema et al. 1998, Lamersdorf and Borken 2004). In this chapter, we evaluate the effects of the watershed acidification treatment on the cycling of N, S, Ca, Mg and potassium (K) on Fernow WS3.

To accomplish this goal, we primarily will examine trends in annual nutrient fluxes. For these analyses, inputs were calculated on a calendar year basis, using data from the Fernow Fork Mountain deposition monitoring site, located near the top of WS4, and from the Parsons NADP site located in the Nursery Bottom in Parsons, West Virginia. Both of these sites and methods are described in Adams et al. (1994) and Gilliam and Adams (1996). Briefly, precipitation samples were obtained using Aerochem Metric automated wet/dry collectors, and open bucket “bulk” collectors. Inputs for N and S were calculated as the sum of total wet and dry deposition (<http://www.epa.gov/castnet/data.html>). Estimates of dry deposition are not available for Ca, Mg,

and K, therefore inputs were calculated for these analytes based on bulk deposition (see Chapter 1). Bulk deposition samples were collected weekly and analyzed for pH, Ca, Mg, sodium (Na), K, ammonia-N ( $\text{NH}_3\text{-N}$ ), chloride (Cl), nitrate ( $\text{NO}_3$ ) and sulfate ( $\text{SO}_4$ ), according to NADP protocol as described in Stensland *et al.* (1980). Stream water exports were calculated using flow rates for the individual watersheds and weekly grab sample nutrient concentrations, summed over a calendar year. Further information on sampling methods and analytical techniques can be found in Chapter 2, Chapter 4, and Adams *et al.* (1994). The calculation of watershed-specific precipitation and loadings is described in Adams *et al.* (1994). Additional published sources also are used to describe internal cycling. We focus primarily on WS3 (treatment watershed), WS4 (reference watershed), although we use information from studies of other watersheds, most notably WS7 (vegetative reference). See Chapter 2 for a description of these watersheds.

## 2. NITROGEN CYCLING

### 2.1 Inputs

Sources of N inputs include both wet and dry deposition. Approximately 45% of N is deposited as wet  $\text{NO}_3$ , and approximately 26% as wet ammonium ( $\text{NH}_4$ ). Dry nitric acid ( $\text{HNO}_3$ ) makes up about 22% of N deposition, about 6% of N deposition occurs as dry  $\text{NH}_4$ , and less than 1% is dry  $\text{NO}_3$  (NADP 2004). Wet deposition of N has declined slightly since 1978, the first year of record for the Nursery Bottom NADP site, from an annual average of about  $8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  to about  $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Most of this decline is the result of decreases in wet  $\text{NO}_3$  deposition, since  $\text{NH}_4$  deposition has remained relatively constant on average, but with considerable inter-annual variability. Total N deposition (wet plus dry deposition) at the Fork Mountain monitoring station averaged  $10.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  between 1986 and 2002, the period of data used in the analyses of nutrient budgets (Fig. 7-1). Atmospheric inputs of N at Fernow vary with elevation, the result of both higher concentrations of  $\text{NH}_3$  and  $\text{NO}_3$  in wet deposition and higher amounts of precipitation at greater elevations (Gilliam and Adams 1996).

Nitrogen fixation is another possible source of N in eastern forested watersheds. The only native N-fixing tree, black locust, is relatively sparse on the study watersheds, 15 stems  $\text{ha}^{-1}$  on WS3 and 2.5 stems  $\text{ha}^{-1}$  on WS4 (Gilliam *et al.* 1995, see Chapter 2). Because of the scattered nature of the locust trees, the closed canopy on both watersheds and the acidic soils, the N fixed is likely to be minimal on a watershed scale (Boring *et al.* 1988).

Presence of leguminous herbs is also negligible (Aulick 1993, Hockenberry 1996).

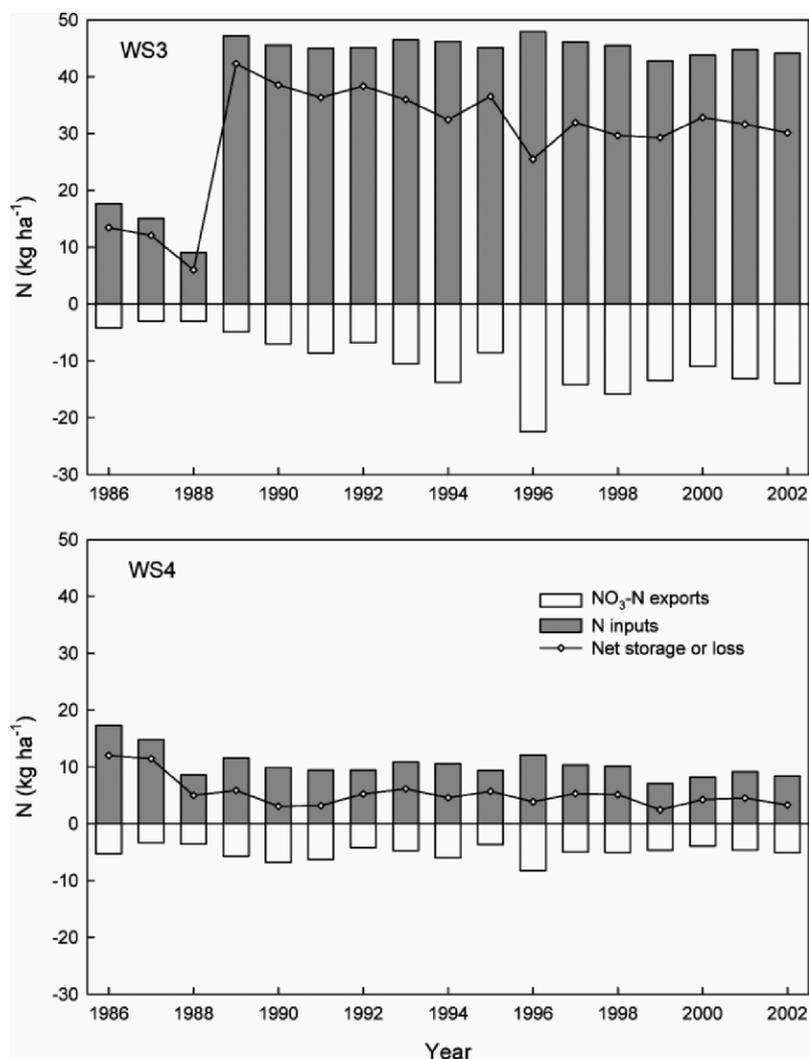


Figure 7-1. Inputs, exports and storage of N from WS3 and WS4. Treatments were initiated in 1989.

## 2.2 Outputs

Nitrogen outputs from the watersheds include ammonium, nitrate, and dissolved organic N (DON) in stream water, and gaseous losses of N (Fig. 7-2). Ammonium concentrations are consistently low, generally near the detection limits of our equipment, and so exports are generally negligible. Most of the N exported from the watersheds is in the form of  $\text{NO}_3^-$ . Pretreatment  $\text{NO}_3^-$ -N exports from WS3 (1986-1988) averaged about  $3.3 \text{ kg ha}^{-1}$ , and WS4 exports averaged  $3.9 \text{ kg ha}^{-1}$ . Exports on WS3 increased quickly after treatments began, to an average of  $12.5 \text{ kg ha}^{-1}$  during the treatment period. Exports from WS4 averaged  $5.3 \text{ kg ha}^{-1}$  during the same time period.

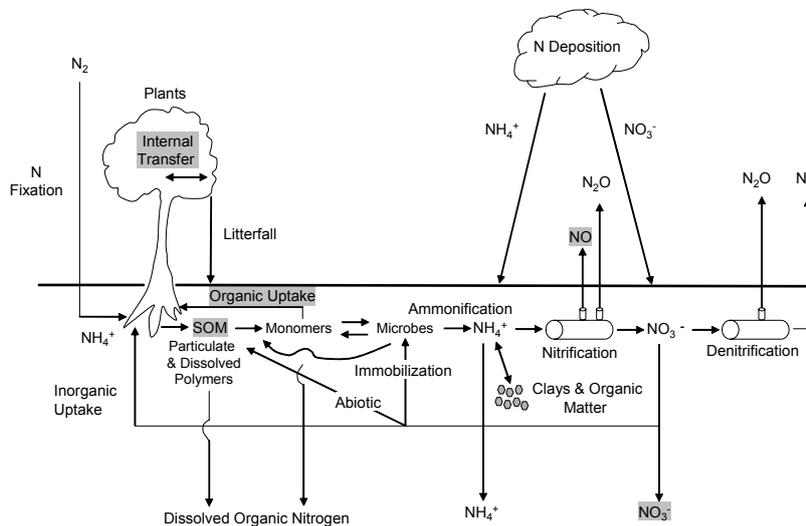


Figure 7-2. N cycle. Highlighted fluxes or pools are those which were affected by the watershed acidification treatment.

Although estimates of dissolved organic N (DON) exports are not available for WS3, DON is not expected to contribute a dominant portion of total annual N exports. DON is mostly retained in soils even when it is present in reasonably high levels (Davidson *et al.* 2003). Foster (1997) estimated that DON exports from Fernow WS10 and WS4 ranged from 0-50% of total N exports, and averaged 23% for WS10 and 13% from WS4. She attributed the difference between the two watersheds to differences in organic matter content of the soil, particularly the forest floor (see Chapter 3).

Therefore, based on soil organic matter concentrations in WS3 ( $91 \text{ g kg}^{-1}$ ) compared with WS4 and WS10 ( $112$  and  $62 \text{ g kg}^{-1}$ , respectively), we may conclude that DON export does not contribute greatly to N leaching losses.

Some N is exported from the watersheds in gaseous emissions, although this flux is estimated to be relatively small. Soil emissions of nitric oxide (NO) were higher in WS3 relative to WS7, the vegetative reference watershed containing similar soils and a stand of hardwoods the same age as WS3 (Venterea et al. 2004). Increased NO emissions also were observed for the N-amended West Bear Brook watershed in Maine, providing evidence that increased soil NO emissions are a characteristic response in forests subjected to elevated N inputs. Venterea et al. (2004) estimated that NO emissions represented  $<1.6\%$  of total inputs to Fernow WS3 and to West Bear Brook (both receiving ammonium sulfate fertilizer). Assuming all NO produced is released to the atmosphere, these emissions represent a flux of less than  $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ .

Nitrous oxide ( $\text{N}_2\text{O}$ ) production was measured in WS3 and WS4 by Peterjohn et al. (1998). Although  $\text{N}_2\text{O}$  production was 22% greater for WS3 than WS4, these differences were not significantly different. Mean monthly rates of  $\text{N}_2\text{O}$  production ( $3.41\text{-}11.42 \text{ } \mu\text{g N m}^{-2} \text{ hr}^{-1}$ ) were consistent with measurements from other well drained forest soils but were much lower than those of N-rich sites with poorly drained soils, and probably represents a flux of less than  $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Peterjohn et al. 1998, Bowden et al. 1990, 1991). Thus, increases in gaseous emissions in response to elevated N additions are not likely to contribute significantly to losses from the system.

### 2.3 Budgets

Nitrogen inputs to WS3 prior to the start of fertilization averaged approximately  $8\text{-}10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , including dry deposition of approximately  $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . The significant increase in inputs to WS3 after 1989 reflects the addition of  $35.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the fertilization treatment (Fig. 7-1). Stream water exports of  $\text{NO}_3\text{-N}$  began increasing shortly after the first fertilizer applications. By contrast, WS4, receiving only ambient N and S inputs, experienced relatively little annual variation in N inputs or exports (Fig. 7-1). Since the treatments began, 53% to 89% (average of 73%) of the added inorganic N has been retained on WS3. Between 1989 and 2002, WS3 has retained, either through uptake, immobilization, or abiotic fixation (Fig. 7-2), approximately  $470 \text{ kg N ha}^{-1}$ . Pretreatment retention (1986-1988) of N by WS3 was around 65%; immediately after treatment began, almost 90% of the N inputs were retained. Percent N retained has declined steadily with continued treatment to around 70% in 2002, approaching pretreatment levels.

During this same time period, WS4 retained from 30% to 60% (average = 45%) of the total inorganic N deposited in deposition. Two other Fernow reference watersheds, WS10 and WS13, retained 85% and 44% of inorganic N, respectively (Campbell *et al.* 2004). It is notable that in a study of inorganic N budgets for 24 undisturbed forested watersheds across the northeastern United States, Fernow WS4 was the only watershed exhibiting a net loss (of  $0.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ; Campbell *et al.* 2004). Note however, that those estimates do not include dry deposition, thus do not incorporate all inputs to the watershed. Nonetheless, WS4 does demonstrate some of the lowest retention of N in the northeastern U.S.

The addition of N to WS3 via the ammonium sulfate fertilizer clearly increased the  $\text{NO}_3\text{-N}$  export from the watershed (Adams *et al.* 1997, Edwards *et al.* 2002, see Chapter 4). However, there was no detectable effect on  $\text{NH}_4$  concentrations in stream water; indeed,  $\text{NH}_4$  remains at very low levels in the stream water draining both WS3 and WS4. Apparent net storage of inorganic N on WS3 has declined over time, suggesting that less of the fertilizer N is being taken up and/or retained by the watershed, in response to continuing elevated N inputs. Conversely, during the period of analysis, in response to ambient deposition only, WS4 exports and apparent net retention have remained nearly constant.

## 2.4 Internal Cycling

Studies of N dynamics in the soils of the Fernow watersheds have shown that rates of net mineralization and net nitrification are high on both WS3 and WS4, compared with other forested ecosystems (Gilliam *et al.* 2001b). Net nitrification on WS3, WS4, and WS7 was 141, 114, and 115  $\text{kg N ha}^{-1} \text{ yr}^{-1}$ , respectively (Gilliam *et al.* 2001b, Christ *et al.* 2002), and essentially equal to 100% of net mineralization for these watersheds. These rates do not differ significantly among watersheds. Thus,  $\text{NH}_4$  deposited via precipitation or fertilizer is mineralized and nitrified equally rapidly on WS3, WS4 and WS7. However, the lack of statistically significant differences may be due to high spatial variability, which may mask an important source of N available for export. The difference in mean net nitrification rates between WS3 and WS7 ( $26 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) is more than 2.5 times the amount needed to account for the approximately  $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  increase in stream water N output observed due to fertilizer treatment on WS3.

Soil emissions of NO were higher in WS3 relative to WS7 (Venterea *et al.* 2004), with nitrification hypothesized as the dominant source of NO. However, there were no significant differences in nitrification rates between WS3 and WS7 (Venterea *et al.* 2004), similar to the results of Gilliam *et al.* (2001b). Therefore, Venterea *et al.* (2004) speculated that a slight decrease in the pH of the upper soil horizon on WS3 (this was also noted in Chapter 3, a

decrease of 4.34 to 4.20 in the 0-10 cm horizon during 1994-2002) may have caused increased protonation of nitrification-derived  $\text{NO}_3^-$ , and the subsequent abiotic formation of  $\text{NO}$ , which contributed to the differences in  $\text{NO}$  emissions between WS3 and WS7.

Nitrous oxide production, as measured in WS3 and WS4 by Peterjohn et al. (1998), was also found to be related to soil N processing. The mean rate of  $\text{N}_2\text{O}$  production was greater for WS3 than WS4, but these differences were not significantly different. Again, chemoautotrophic nitrification was important in both watersheds, accounting for 60% and 40% (WS3, WS4 respectively) of total  $\text{N}_2\text{O}$  production.

Evidence for effects of the fertilization treatment on N uptake by vegetation is equivocal. Differences in foliar nutrient concentrations were observed (Adams et al. 1995, May et al. 2005), which suggests there may have been differences in N uptake by the vegetation. Specifically, N concentrations of foliage collected in 1992 from WS3 were generally higher than from WS7 for four tree species: red maple, black cherry, yellow-poplar, and sweet birch – but were only significantly greater on WS3 relative to WS7 for black cherry and red maple. In 1997, foliar N concentrations were significantly greater on WS7 for red maple, relative to WS3. No other significant differences in foliar N concentrations were detected between the watersheds (Fig. 7-3). Foliar N concentrations generally decreased slightly or remained the same over the course of the study (Fig. 7-3), with the exception of yellow-poplar foliage, which showed a slight increase in N concentration over time. A sustained increase in foliar N concentrations would have provided support for the idea of continued high rates of N uptake as availability continued to increase.

May et al. (2005) also evaluated three of the same tree species in 1992 and 2001. In 1992, foliar N concentrations for red maple, yellow-poplar and black cherry were approximately 11% greater in WS3 relative to WS7. However, by 2001 mean foliar N was greater in WS7 for all three of these species for the trees that were sampled. Such a shift in foliar concentrations implies a change in the N uptake and/or allocation by these trees. This could be due to an increase in uptake by trees on WS7, decreased uptake by trees on WS3, or both, or could be due to changes in nutrient use and retranslocation of N once within the tree.

Mean foliar N values of all of the tree species examined fell within the range of values observed across the northeastern United States for these species (Northeastern Ecosystem Research Cooperative 2004), pointing to no obvious N deficiencies. Note however that in the 1970s, Auchmoody and Smith (1977) reported a 47% increase in basal area of small sawlog-sized yellow-poplar in response to N fertilization, which suggests the trees may have been N limited. We may further theorize that N availability, as reflected in foliar concentrations, has changed over time.

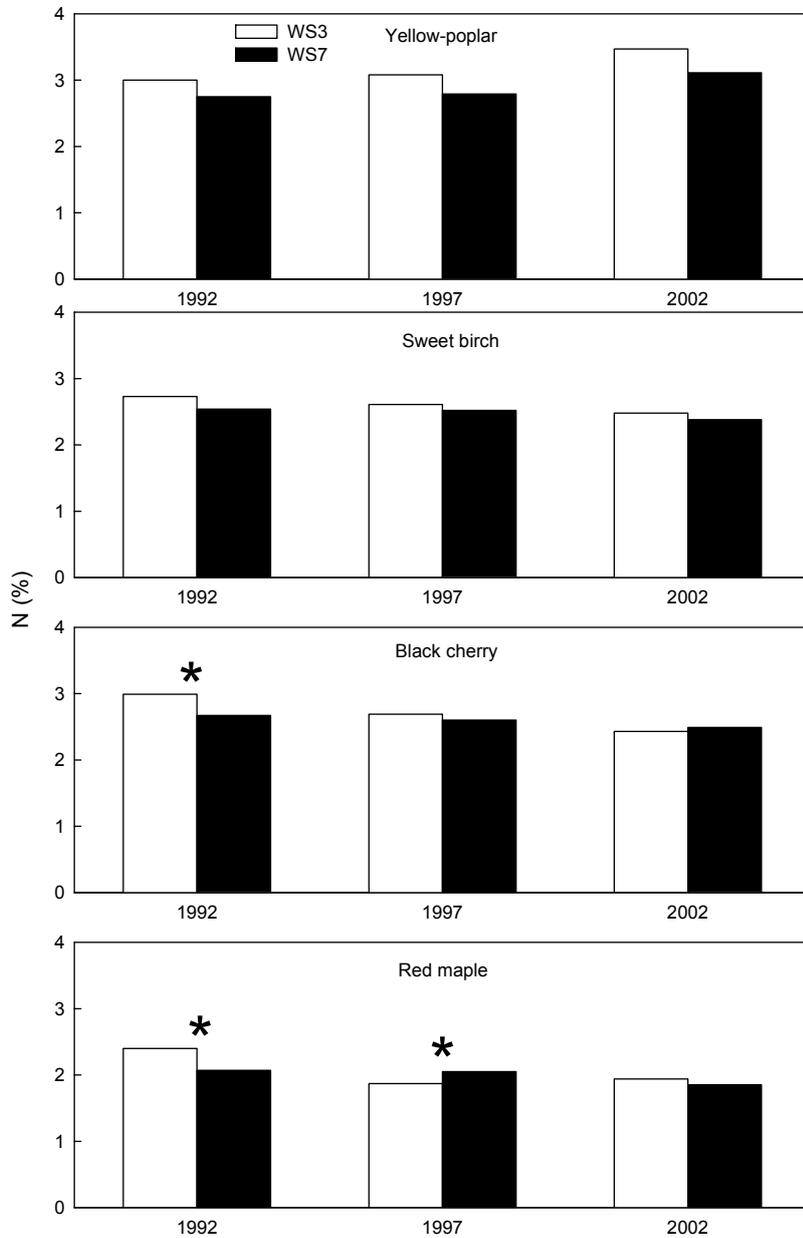


Figure 7-3. Mean foliar N concentrations for four tree species on WS3 and WS7, over time. \* indicates statistically significant differences between watersheds ( $p < 0.10$ ).

A comparison of concentrations of other foliar nutrients with the regional foliar data base suggests that phosphorus (P) may be limiting to black cherry, sweet birch and red maple, on both WS3 and WS7. Most forests are considered to be N-limited. However, once the demand for N has been met or exceeded, then another nutrient, most often P, becomes the nutrient limiting productivity. Data from fertilized root ingrowth core assays on WS4 (Foster 1997) and from phosphomonoesterase activity assays in roots of violets from WS3, WS4, WS10 and WS13 (W.T. Peterjohn, unpublished data) provide some support for this hypothesis. Thus, it may be long-term elevated ambient N deposition has led to a limitation by P, which could lead ultimately to decreased uptake of N.

Changes in nutrient allocation within the trees could also reflect altered nutrient availability. May et al. (2005) reported that the acidification treatment decreased nutrient resorption efficiencies on WS3. The resorption of N averaged 30% lower in WS3 for red maple and black cherry than in WS7, but there were no significant differences in N resorption efficiency between watersheds for yellow-poplar. For WS7, resorption efficiencies remained within the high end of published values, averaging 73-81% for N. Decreases in N reabsorption could be indicative of excess N uptake, with the tree decreasing retranslocation as a means to balance internal nutrient concentrations. Such changes in nutrient reabsorption and translocation may have significant implications for nutrient cycling in the forest floor and soil.

Changes in N uptake or nutrient resorption also could result in changes in litter quality. Although litter from yellow-poplar, black cherry, and sweet birch on WS3 decayed more slowly than on WS7, N loss rates from the leaf litter did not vary between the two watersheds after 3 years of treatment (Adams and Angradi 1996). Increases in total soil N concentrations over time were observed on WS3 (Chapter 3) and provide some support for the idea of increased uptake of N by the vegetation. The O horizon was the most responsive of the soil horizons to the fertilizer treatment, which could be partly explained by the application of fertilizer to the ground where the topmost horizon would receive and capture the additional N, but it could also be due to increased N uptake by vegetation leading to higher N foliar concentrations, ultimately resulting in greater N content of the litter layer.

After 3 years of the acidification treatment, aboveground N content of WS3 was slightly higher than WS7, except in the herb layer (Adams et al. 1995), although this difference was not statistically significant. WS3 contained 255 kg N ha<sup>-1</sup> aboveground, compared with 233 kg N ha<sup>-1</sup> for WS7. To some extent, this reflects greater aboveground biomass on WS3, which could not be attributed to treatment due to lack of pretreatment information (Adams et al. 1995).

All of these observations suggest that while vegetation on WS3 has responded to the N fertilization through increased uptake and some changes

in allocation of nutrients, the response is highly variable, temporally, spatially within the watersheds, and among plant species. Chapter 5 details the responses of vegetation, some of which support the idea that uptake of N was increased, at least early on in the experiment.

Important and unresolved questions regarding N cycling remain. In particular, what accounts for the apparent storage of ~70% of N inputs? This was unexpected, particularly in a system that has many of the symptoms of N saturation (Peterjohn *et al.* 1996, Fenn *et al.* 1998). Other studies suggest incorporation into soil organic matter (Magill *et al.* 2000), but the mechanism by which this occurs is still unclear. Specifically, the role of abiotic immobilization of N (Fitzhugh *et al.* 2003) in forest soils requires further consideration.

### 3. SULFUR CYCLING

#### 3.1 Inputs

West Virginia and western Pennsylvania receive some of the highest deposition of S in the eastern United States. However, S deposition has declined markedly since monitoring began in Parsons, from a high of >50 kg S ha<sup>-1</sup> yr<sup>-1</sup> in wet deposition to a current level of approximately 28 kg S ha<sup>-1</sup> yr<sup>-1</sup>, nearly a 45% decrease. Note that while such declines have been recorded at most monitoring stations in the northeastern United States (Hedin *et al.* 1994, Lynch *et al.* 2000), suggesting some success in regulating emissions, SO<sub>4</sub> deposition is still greater at the FEF than for either Hubbard Brook Experimental Forest, or Coweeta Hydrologic Laboratory, two other Appalachian sites (Fig. 7-4). Total S inputs to WS3 averaged approximately 23 kg S ha<sup>-1</sup> yr<sup>-1</sup> prior to the initiation of the acidification treatment. This increased to 71 kg S ha<sup>-1</sup> yr<sup>-1</sup> as a result of the acidification treatment. Sulfur inputs to WS4 averaged 29 kg S ha<sup>-1</sup> yr<sup>-1</sup> for the same period (Fig. 7-5).

The majority of the S deposition is delivered via wet SO<sub>4</sub> deposition (56%), with another 39% deposited as dry sulfur dioxide (SO<sub>2</sub>). The remainder is dry SO<sub>4</sub>. Helvey and Kunkle (1986) estimated average annual bulk deposition of 13.3 kg S ha<sup>-1</sup> yr<sup>-1</sup> with an additional 4.4 kg S ha<sup>-1</sup> yr<sup>-1</sup> delivered in throughfall. More recent estimates suggest that dry deposition contributes an average of 6.3 kg S ha<sup>-1</sup> yr<sup>-1</sup> to deposition, or approximately another 34%, to forest ecosystems above wet deposition (<http://www.epa.gov/castnet/data.html>).

Similar to wet deposition of N, wet deposition of S increases with elevation at the FEF, the result of higher concentrations of SO<sub>4</sub> combined with higher amounts of precipitation at greater elevations (Gilliam and

Adams 1996). Wet inputs of S also exhibit a distinct seasonal pattern at Fernow, increasing in late spring to a maximum during summer months (June to August). From 1983 to 1989, wet inputs of S from June to August averaged nearly twice that of the other months. This has important implications for impacts on these forests, which are more metabolically active during this time of the year. Also, because of the contribution of S inputs to deposition of acidity to the forest, there are also implications for inputs of  $H^+$ , which increased from a minimum of  $0.05 \text{ keq } H^+ \text{ ha}^{-1}$  in January to a maximum of  $0.14 \text{ keq } H^+ \text{ ha}^{-1}$  in July (Gilliam and Adams 1996).

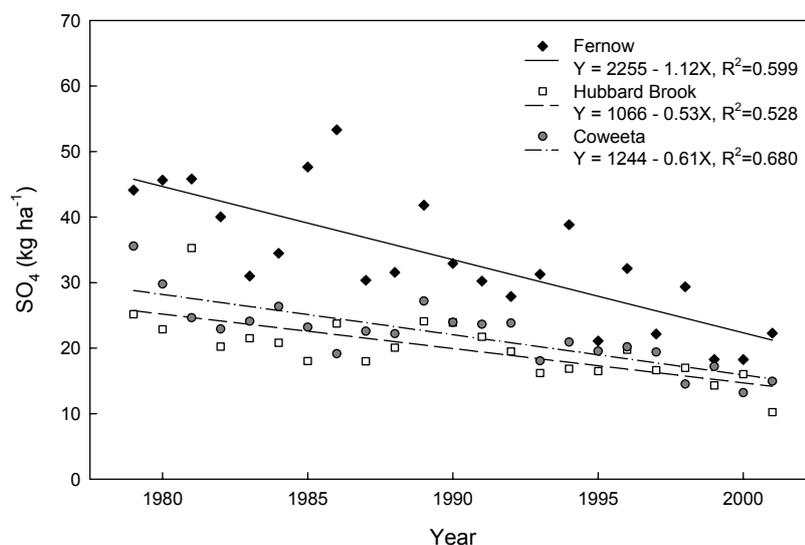


Figure 7-4. SO<sub>4</sub> deposition at three Appalachian monitoring stations, 1979-2001.

### 3.2 Outputs

Sulfur is usually exported from a watershed in the form of SO<sub>4</sub> in stream water, although there also may be some loss as hydrogen sulfide (H<sub>2</sub>S) from wet soils with anaerobic conditions. Hydrogen sulfide however, is uncommon in well-drained forest soils such as found on the FEF because it is rapidly oxidized to SO<sub>4</sub>. Exports of SO<sub>4</sub>-S from WS3 in the three years prior to the treatments were about  $6.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . Exports increased to an average of  $11.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$  during the treatment period. Exports from WS4 averaged  $8.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (pre-treatment years) and  $10.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$  during the treatment period. Baseflow SO<sub>4</sub> concentrations increased from 1986 to approximately 1996 (Chapter 4), then decreased through 2002, and these changes may be

attributable to the 1990 CAAA. The pattern of  $\text{SO}_4$  exports from WS4 follows a similar pattern (Fig. 7-5).

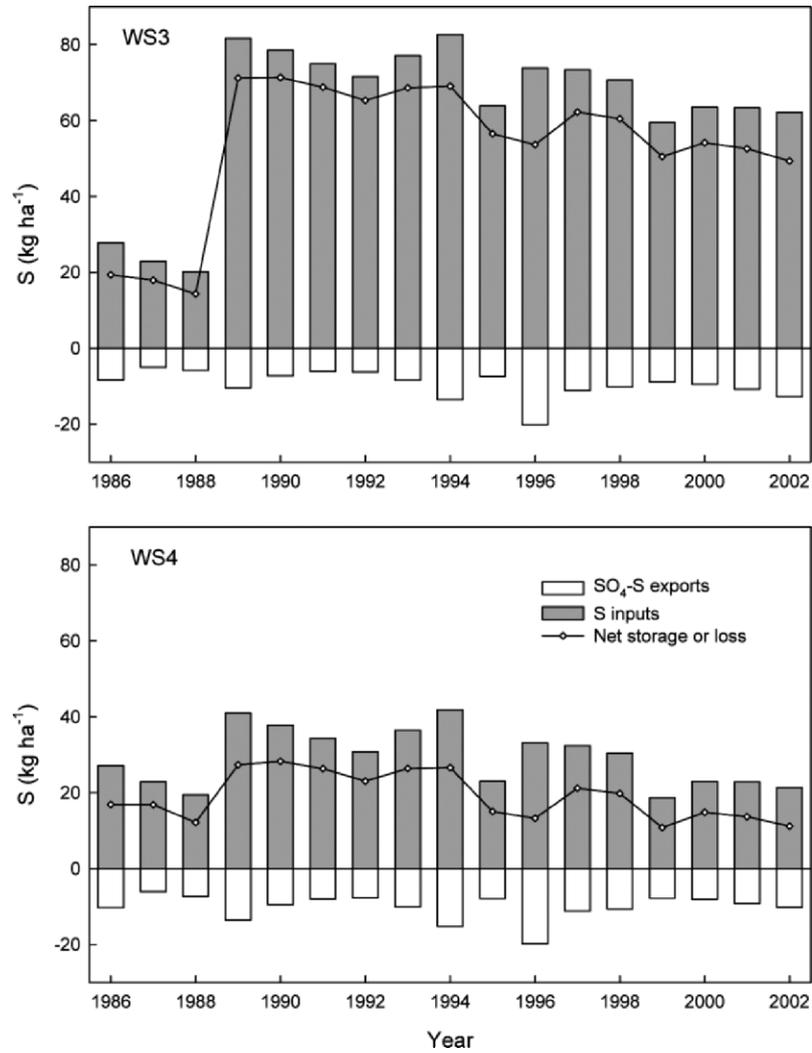


Figure 7-5. Inputs, exports and storage of S from WS3 and WS4. Treatments were initiated in 1989.

### 3.3 Budgets

Sulfate inputs, exports and net storage or loss for WS3 and WS4 are shown in Figure 7-5. Sulfate can be retained within a catchment through vegetative uptake, immobilization via microbial assimilation, incorporation into organic matter or through physical adsorption onto soil colloids (Fig. 7-6; Reuss and Johnson 1986, Edwards 1988). Early work by Helvey and Kunkle (1986) showed that during the mid-1980s, WS4 was retaining S. Total inputs were  $17.7 \text{ kg SO}_4\text{-S ha}^{-1} \text{ yr}^{-1}$  in bulk deposition, and exports in stream water were  $8.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  for an estimated retention of 47% of the  $\text{SO}_4\text{-S}$  inputs at the deposition levels occurring at that time. However, Polk (1991) suggested that the soils on Fork Mountain were no longer able to adsorb  $\text{SO}_4$ , although there were differences in adsorption capacity among soil horizons.

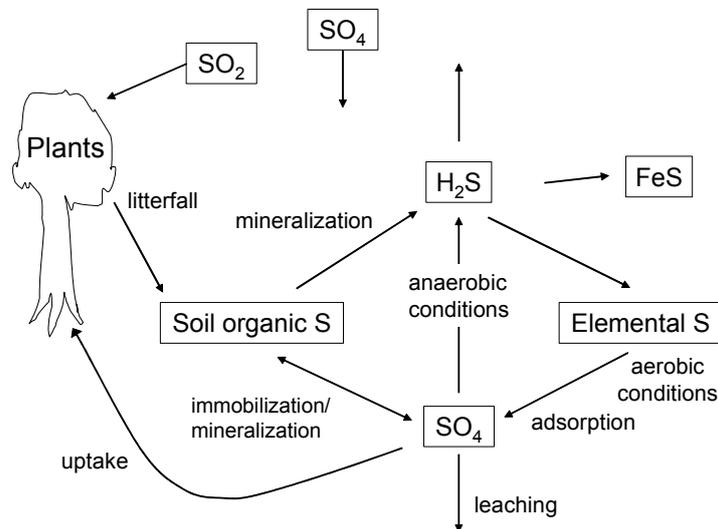


Figure 7-6. S cycle in forest ecosystems.

On an annual basis, both WS3 and WS4 were retaining  $\text{SO}_4\text{-S}$  prior to initiation of treatment in 1989, although net storage was slightly less for WS4 (66%) than for WS3 (73%). The application of ammonium sulfate increased inputs to WS3, without a concomitant increase in  $\text{SO}_4\text{-S}$  exports. Retention of  $\text{SO}_4\text{-S}$  by WS3 immediately after treatments began was high (about 90% of total inputs), but declined slightly, and by 2002 was around 80%. Baseflow  $\text{SO}_4$  concentrations have increased throughout the study (Chapter 4),

suggesting saturation of  $\text{SO}_4$  adsorption capacity, at least in the stream-side zone. WS3 soil water concentrations suggest that adsorption, perhaps via pH changes and/or increasing  $\text{SO}_4$  concentrations, is occurring in the majority of the watershed, but the concentrations in streamside areas do not suggest significant retention (Chapter 4). The streamside areas act as repositories for materials leached from the uplands over longer time periods, such that soils in the streamside areas have no more ability to retain S even through there still appears to be retention ability in the uplands. Note a similar pattern of retention occurring on WS4 (Fig. 7-5) and WS7 (Fig. 7-7), despite the absence of fertilizer additions. This provides some support for our hypothesis of desorption due to decreased atmospheric inputs and, ultimately, effects on solution concentrations.

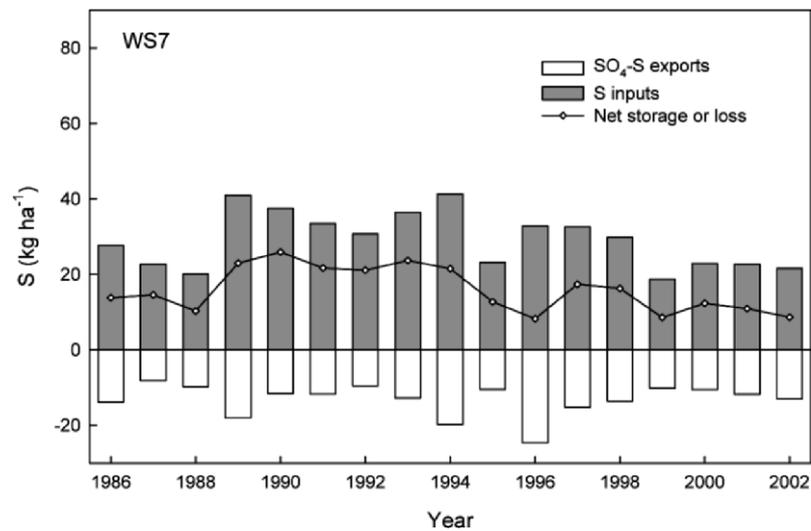


Figure 7-7. Inputs, exports and storage of  $\text{SO}_4$ -S from WS7.

### 3.4 Internal Cycling

Sulfur deposition usually exceeds the S uptake requirements for a forest (Reuss and Johnson 1986); therefore large changes in uptake, even with increasing N uptake, are not likely to account for significant changes in retention. As  $\text{SO}_4$ -S inputs have decreased to WS4, we may be seeing release of S in recent years due to lower concentrations in deposition, as hypothesized by Rochelle and Church (1987) and Reuss and Johnson (1986). Sulfate adsorption can be induced by increasing  $\text{SO}_4$  concentration and

decreasing pH. Because  $\text{SO}_4$  adsorption capacity is concentration dependent, increasing concentration results in further adsorption until a new equilibrium is reached. Conversely, decreased inputs could lead to  $\text{SO}_4$  desorption and increased leaching from the soil as a new equilibrium is established.

Some of the apparent retention of S by these watersheds may also be related to stream channel characteristics and hydrology. The watersheds in part may have net storage because the stream channels are intercepting less water during storms and higher base flows than the other watersheds, and exporting less S. Net S budgets are not strongly related to annual discharge, except when streamflows are unusually high, such as 1996, a year of record annual streamflow (P.J. Edwards, unpublished data).

## 4. CALCIUM CYCLING

### 4.1 Inputs

Calcium concentrations in wet deposition have declined considerably over the last 25 years, representing fluxes ranging from a high about  $3.5 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$  to around  $1.5 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$  currently. This decline is attributed to improved scrubber technology on power plants, which has not only significantly reduced S emissions (see above), but also has reduced emissions of ash and particulates, which often included constituents composed of basic components, e.g., Ca and Mg (Hedin et al. 1994). Calcium inputs to WS3 and WS4, as measured in bulk deposition, averaged less than  $3.5 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$  over the period of study.

### 4.2 Outputs

Ca exports in stream water increased on WS3 from an average of  $6 \text{ kg ha}^{-1} \text{ yr}^{-1}$  to an average of  $13.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$  after treatment began in 1989. Increasing exports were also observed in WS4, from  $7.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$  to about  $10.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , although the rate of increase was not as steep as for WS3.

### 4.3 Budgets

Inputs, exports and net losses of Ca are shown in Figure 7-8. Note that for both WS3 and WS4, exports of Ca exceeded inputs prior to initiation of the study. Net losses on WS3 (inputs minus outputs) ranged from 3 to  $25 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$ , and net losses from WS4 ranged from 3 to about  $15 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$ . While exports were greatest during the wettest years (1996, record

annual streamflow) increases in stream Ca concentrations after treatment began were also observed (see Chapter 4), suggesting that these changes reflect treatment effects, not just changes in flow volumes. Between 1989 and 2002, 188 kg Ca ha<sup>-1</sup> was exported from WS3, and 147 kg Ca ha<sup>-1</sup> from WS4 over the same period.

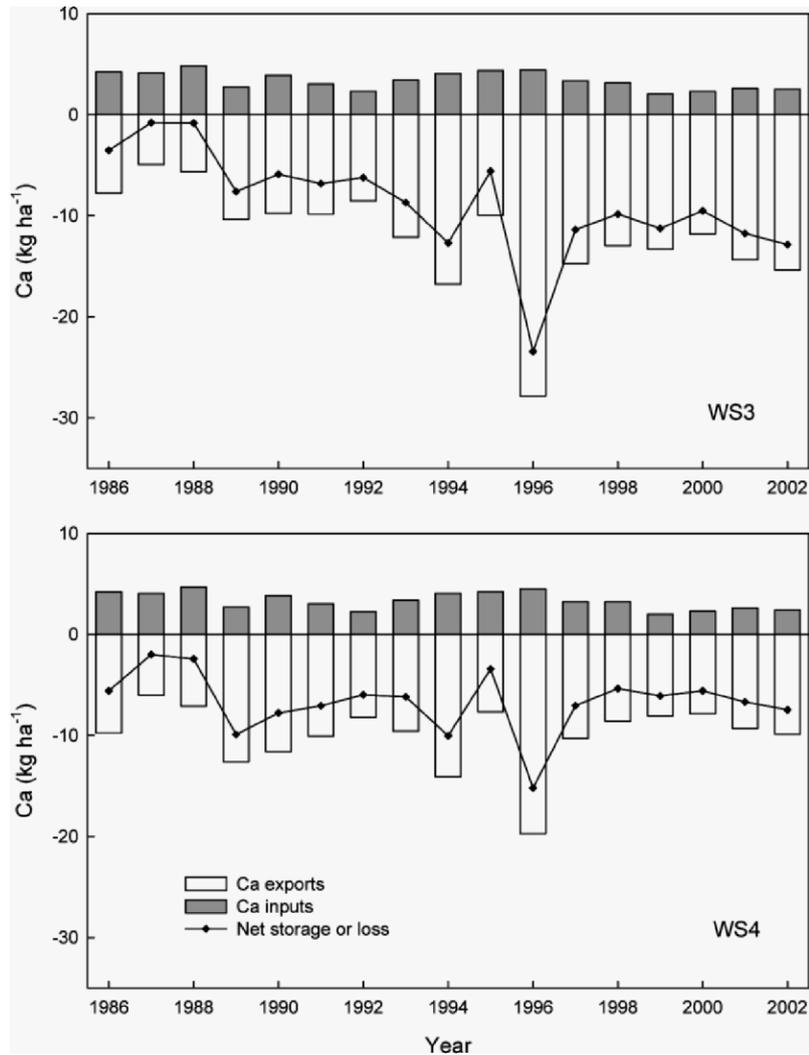


Figure 7-8. Inputs, exports and storage of Ca from WS3 and WS4. Treatments were initiated in 1989.

#### 4.4 Internal Cycling

Important Ca cycling processes in forest ecosystems include plant uptake, litterfall and decomposition, weathering from primary minerals, soil exchange processes, and leaching via soil solution to stream water and groundwater. Some of these processes, notably weathering, have not been quantified for this study. However, we can make some observations.

Because Ca is not retranslocated from the leaves to other parts of the tree, foliar Ca levels can provide us with information about uptake by the vegetation. Foliar Ca concentrations on WS3 were lower than those on WS7 for sweet birch, yellow-poplar, and red maple in 1992 (Fig. 7-9). Concentrations of Ca in the tree boles of sweet birch, black cherry and red maple did not differ between the two watersheds, but significantly higher concentrations of Ca were detected in the bolewood of yellow-poplar on WS7 (Adams et al. 1995). These results suggest greater uptake of Ca by vegetation on WS7 relative to WS3. This could be due to greater availability of Ca on WS7 or to decreased availability on WS3.

The stands on WS3 and WS7 are of the same age, originating with the growing season of 1970 as natural regeneration. However, portions of WS7 were maintained barren of vegetation for 2 to 5 years through the use of herbicides (see Chapter 2). As a result, the litter layer quickly decomposed, and soil organic matter decreased in the upper horizons of the soil (Troendle et al. 1974). In addition to increased decomposition of the litter layer, large amounts of dead wood and slash were left on the site, and were available for rapid decomposition. This could have resulted in greater mineralization of nutrients stored in organic matter and down wood, therefore greater availability of nutrients in the medium term. This is reflected in greater soil exchangeable Ca in WS7 (1677 kg Ca ha<sup>-1</sup>) than WS3 (905 kg Ca ha<sup>-1</sup>) and WS4 (428 kg Ca ha<sup>-1</sup>), as measured in 1991 (Adams et al. 1995). Aboveground Ca content was also greater on WS7 (169 kg Ca ha<sup>-1</sup>) than on WS3 (155 kg Ca ha<sup>-1</sup>), despite greater average aboveground biomass on WS3 (Adams et al. 1995).

Lower Ca contents on WS3 could also be due to decreased uptake. As soil acidification proceeds, base cations such as Ca are stripped from soil exchange sites, and leached from the soil to streams and groundwater, resulting in decreased availability over time. Soil solution data (Chapter 4) suggest such a mobilization and depletion of Ca from soil exchange sites. Dendrochemistry data also show this pattern (Chapter 5). Because

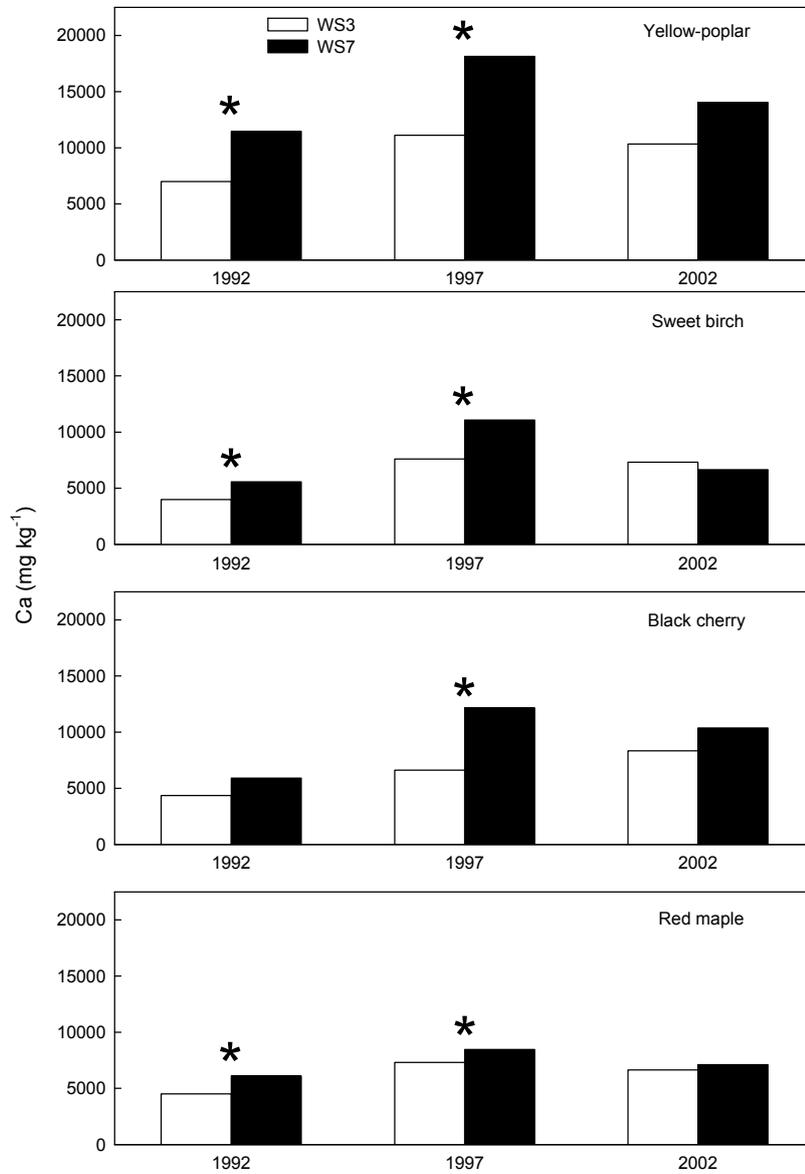


Figure 7-9. Mean foliar Ca concentrations for four tree species on WS3 and WS7 over time. \* indicates statistically significant differences between watersheds ( $p < 0.10$ ).

yellow poplar is a Ca-demanding tree species (Raynal *et al.* 1992), and because Ca is not retranslocated within an individual tree, this difference in bolewood

concentration, along with significantly lower concentrations of Ca in foliage of yellow-poplar from WS3 supports the hypothesis that less Ca may be available for tree uptake on WS3, at least for yellow-poplar. Such a decrease in exchangeable soil Ca is not clearly indicated for WS3, however (Chapter 3).

As soil acidifies (pH decreases), soil aluminum (Al) becomes more available and may compete with Ca at the soil-root interface, inhibiting uptake of Ca (Schaberg et al. 2001). Such interactions between soil Ca and Al have been identified as a concern for root growth and aboveground productivity of some trees (Lawrence et al. 1995, Cronan and Grigal 1996), therefore, Al should also be considered when considering Ca cycling. For example, Lux and Cumming (1999) demonstrated that yellow-poplar seedlings were very sensitive to high Al concentrations in soil solution. The authors also reported that soil solution Al concentrations from WS3 were significantly greater than those from WS4 (107  $\mu\text{M}$  vs. 26  $\mu\text{M}$ , respectively); these high levels were considered to be toxic to yellow-poplar (Lux 1999). Foliar Al concentrations did not differ significantly between WS3 and WS7 in 1992, but bolewood Al concentrations were significantly lower for black cherry and yellow-poplar on WS7 relative to WS3 (Adams et al. 1995). However, foliar Al concentrations were significantly greater in 1997 and 2002 for black cherry and red maple on WS3. White et al. (1999) reported a similar pattern of decreases in foliar Ca and increases in foliar Al for the similarly treated West Bear Brook watershed in Maine. Thus, for some tree species on WS3, soil Al levels may be affecting Ca uptake and cycling.

Weathering rates of primary minerals are difficult to estimate (Laudelout and Robert 1994, Bailey et al. 2003), and weathering rates have not been determined for the FEF soils. However, reported rates of Ca weathering range from 2 to 5  $\text{kg Ca ha}^{-1} \text{ yr}^{-1}$  (Laudelout and Robert 1994, Bailey et al. 2003), approximately equal to or slightly less than deposition inputs. Total Ca pools in high elevation forest soils in West Virginia derived from acid sandstone and shale ranged from 400 to 1096  $\text{kg Ca ha}^{-1}$ , with corresponding exchangeable values from 156 to 350  $\text{kg Ca ha}^{-1}$  (Jenkins et al. 1998). Bailey et al. (2003) hypothesized that sources of Ca which have been previously unstudied in most forest ecosystems, such as calcium oxalate, may contribute significant amounts of Ca to an ecosystem, particularly in response to disturbance. Yanai et al. (2005) presented evidence that apatite provides a previously unappreciated Ca source in some forest ecosystems. Finally, Grigal and Ohmann (2005) demonstrated that diffusion from deep sources provides a plausible mechanism to replenish Ca levels in near-surface zones. Thus determining accurate weathering/mineralization rates could do much to improve our budgets and address concerns about Ca depletion of soils.

## 5. MAGNESIUM CYCLING

### 5.1 Inputs

Magnesium inputs are low, ranging from  $0.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$  to about  $0.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$  at the most, and deposition has declined since the 1970s. Deposition has remained consistently low since the mid 1980s, similar to the pattern observed for Ca, and for the same reasons (Hedin *et al.* 1994).

### 5.2 Outputs

Magnesium exports from WS3 have increased during the course of the experiment from about  $4 \text{ kg ha}^{-1} \text{ yr}^{-1}$  to an average of  $7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , similar to the pattern of Ca exports. Exports of Mg in WS4 stream water have increased from pretreatment levels of  $3.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$  to  $5.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$ .

### 5.3 Budgets

Annual exports of Mg from WS3 and WS4 exceed inputs, by as much as a factor of 10 (Fig. 7-10). Both watersheds show a significant net loss of Mg over the period of study. Between 1989 and 2002, nearly  $100 \text{ kg Mg ha}^{-1}$  was exported from WS3 and  $70 \text{ kg Mg ha}^{-1}$  from WS4. Over this same period of time, total inputs were around  $6.7 \text{ kg Mg ha}^{-1}$ .

### 5.4 Internal Cycling

The cycling of Mg within forest ecosystems is similar to that of Ca. Plant uptake, litterfall and decomposition, weathering and soil cation exchange are important processes. Foliar Mg for sweet birch and black cherry were at the lower end of the regional mean (Northeastern Ecosystem Research Cooperative 2004), but did not differ significantly between watersheds for most of the species and sampling dates. This suggests that Mg uptake has, for the most part, not been affected by the acidification treatment. There are exceptions: In 1992, foliar Mg concentrations were significantly less on WS3 for yellow-poplar relative to WS7 mean values, and were also significantly less for red maple on WS3 in the 1997 sampling (see Chapter 5). Also, soil exchangeable Mg levels are relatively low in all the watersheds, and did not differ between watersheds. Although we cannot rule out changes in Mg cycling due to the acidification treatment, the magnitude of the effect is sufficiently less than for Ca to be undetectable. More information on weathering and mineralization of Mg from organic matter is needed to better understand the importance of Mg on these forested watersheds.

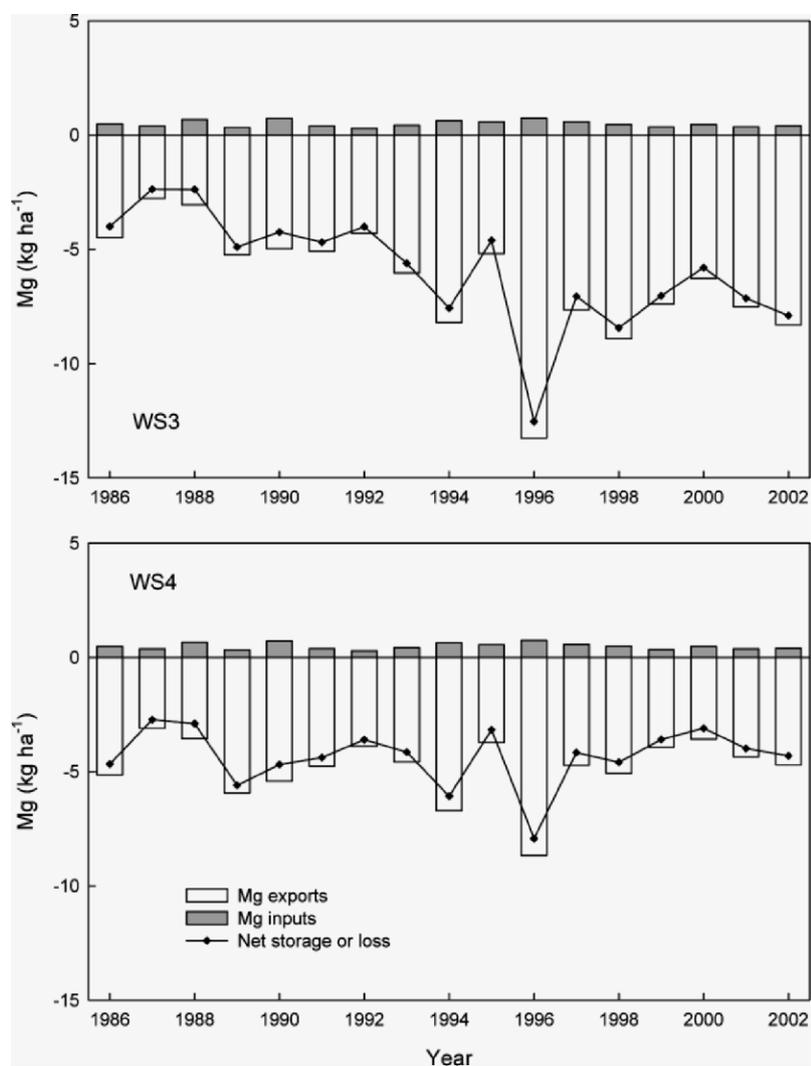


Figure 7-10. Inputs, exports and storage of Mg from WS3 and WS4. Treatments were initiated in 1989.

## 6. POTASSIUM CYCLING

### 6.1 Inputs

Measured in bulk deposition, annual K inputs ranged from less than 1 kg ha<sup>-1</sup> yr<sup>-1</sup> to a high of about 4.5 kg ha<sup>-1</sup> yr<sup>-1</sup>. Interannual variability is related to variability in annual precipitation amount. Wet deposition of K decreased from 1978 to 1988 and has remained relatively constant at around 0.2 to 0.4 kg ha<sup>-1</sup> yr<sup>-1</sup> since that time.

### 6.2 Outputs

Pretreatment exports of K in WS3 steamwater averaged 4 kg ha<sup>-1</sup> yr<sup>-1</sup>, and 6 kg ha<sup>-1</sup> yr<sup>-1</sup> during treatments. Average exports from WS4 during the same time periods were 3.5 and 4.5 kg ha<sup>-1</sup> yr<sup>-1</sup>. Initially exports from the two watersheds were identical, but in later years, exports increased from WS3.

### 6.3 Budgets

There were no immediate obvious effects of the fertilizer on K cycling (Fig. 7-11) and WS3 exports slightly exceeded inputs for a net loss of ~3 kg ha<sup>-1</sup> yr<sup>-1</sup>. However, WS3 K exports have increased significantly relative to those of WS4, starting in about 1993 (Fig. 7-12). Average net K export from WS3 during 1993-2002 was almost 4 kg ha<sup>-1</sup> yr<sup>-1</sup>. A similar increase in K concentrations in soil solution, and to a lesser extent in stream water, around 1991 is also documented in Chapter 4.

### 6.4 Internal Cycling

Most K available to plants comes from weathering of K containing minerals, and is found in soil solution and exchange sites. K<sup>+</sup> is a highly mobile cation, and there is evidence of active uptake by plants (Mengel and Kirby 1982). There are no obvious effects of the acidification treatment on nutrient uptake, based on foliar K concentrations, but there do appear to be effects on soil concentrations. Exchangeable K concentrations in the O horizon increased almost threefold between 1994 and 2002 (Chapter 3). Soil solution concentrations also increased after about 6 years of treatment (Chapter 4). The cause of this increased availability of K in soil solution is unknown, and requires further investigation.

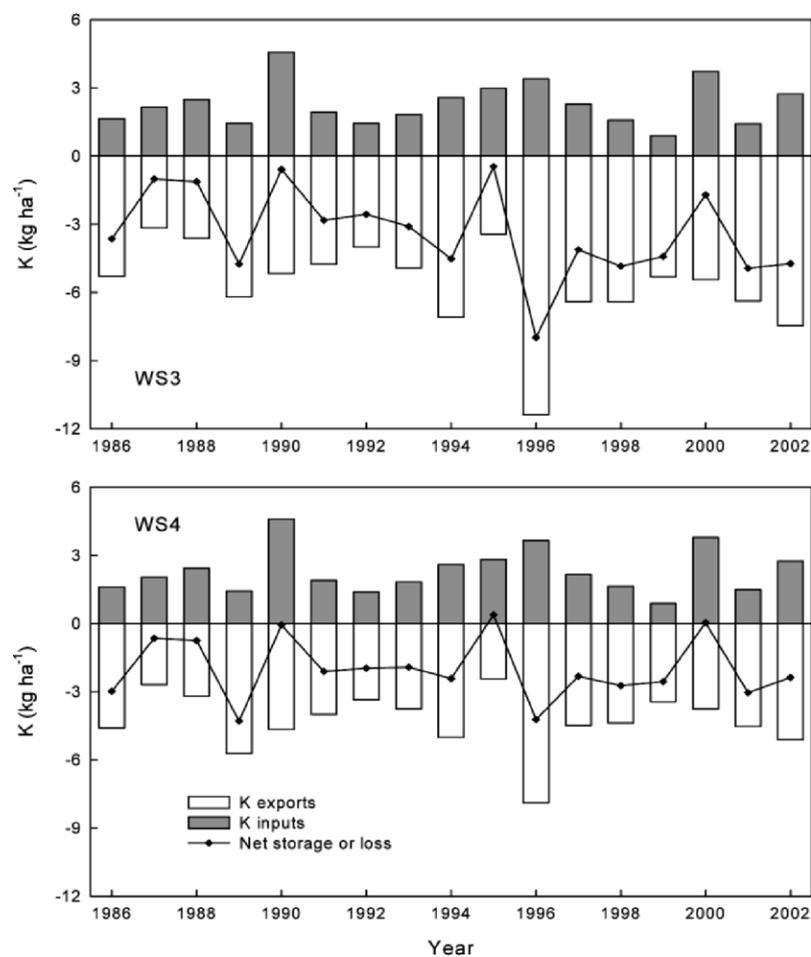


Figure 7-11. Inputs, exports and storage of K from WS3 and WS4. Treatments were initiated in 1989.

## 7. CONCLUSIONS

We have documented a number of significant effects of elevated N and S deposition on nutrient cycling within forested watersheds on the FEF. We have the most detailed information on N and have observed elevated stream water exports of N from the system, apparent short-term increases in plant uptake of N, and increased gaseous fluxes of N. Nitrogen mineralization and nitrification rates appear unaffected by the additional N, although that may

be due in part to already high N processing rates prior to treatment. We also have documented considerable spatial variability in N cycling among, as well as within, watersheds. Some of this small-scale spatial variability may be linked to vegetation (Peterjohn *et al.* 1999, Gilliam *et al.* 2001a, b), while variability across larger scales may be due to bedrock geology (Williard *et al.* 2003).

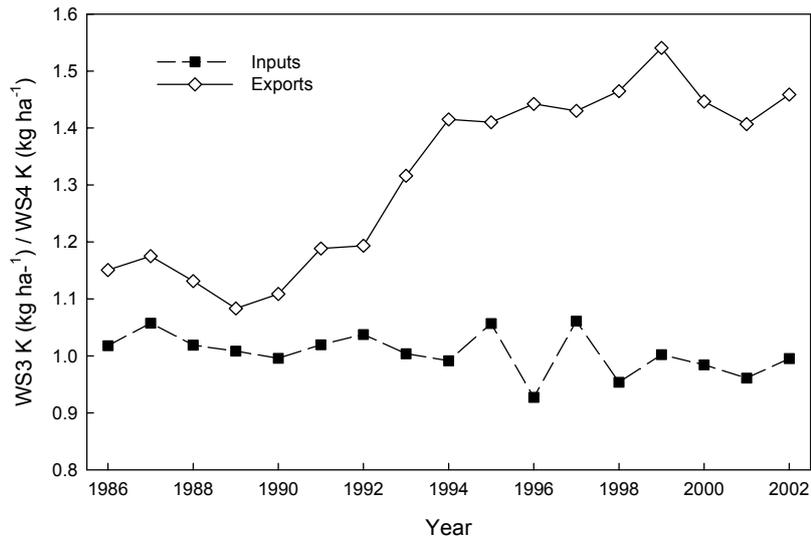


Figure 7-12. WS3:WS4 K ratio for inputs and exports over time. Treatments were initiated in 1989.

Stoddard (1994) described WS4 as being at Stage II of nitrogen saturation. Since then, a number of publications have explored the symptoms of N saturation, as described by Aber *et al.* (1998), on the FEF (Peterjohn *et al.* 1996, Fenn *et al.* 1998, Fernandez and Adams 2000). Additional research at FEF has focused on the possible effects of N saturation on plants (Gilliam *et al.* 2001a, Christ *et al.* 2002) and soils (Peterjohn *et al.* 1998; 1999; Gilliam *et al.* 2001a, b) of these hardwood stands. These studies have provided compelling evidence to corroborate Stoddard's earlier conclusions based on stream chemistry from WS4 — some of the forest stands of FEF are demonstrating symptoms of N saturation, including WS3 and possibly WS7. The implications of N saturation for other nutrients are further considered below. However, retention of N is still almost 70% of inputs, despite many years of elevated N inputs.

Sulfate export appears to be increasing from most of the gaged watersheds on the FEF, not just those receiving fertilizer additions. The rate

of  $\text{SO}_4$  retention by WS3 has decreased over time, suggesting a significant treatment effect. Thus, while the acidification treatment appears to have accelerated  $\text{SO}_4$  leaching from WS3, changes in ambient deposition are also occurring which are probably contributing to the changes observed in WS4 and WS7.

Cycling of Ca, Mg, and K also have been affected by the acidification treatment on WS3. It is significant to note that both WS3 and WS4 export more Ca, Mg and K on an annual basis than is delivered in deposition. Unmeasured fluxes, such as weathering and decomposition of organic matter, no doubt provide some of the balance, but it also seems probable that base cations are being depleted from the soils of WS3 and WS4, although we could not detect such a change on soil exchangeable cation concentrations. WS7 has slightly higher Ca levels, perhaps due to a different treatment history, and thus may have more buffering capacity than WS3 and WS4. Further work is needed to quantify additional base cation cycling processes within these watersheds, and better address the question of base cation depletion.

Some effects of the acidification treatment were immediately obvious – N appeared to have an effect very early on – while the effects on other elements were more subtle or appeared later as acidification of the watershed progressed. We know that foliar nutrient concentrations have increased in some tree species, but not in all species, nor across all sampling periods, suggesting that uptake of some nutrients has been altered by acidification processes for some tree species. The acidification treatment has resulted in increased exports of N, S, Ca, Mg and K from WS3, and may be contributing to changes in Al availability as well. While we conceptually understand many of these nutrient cycling processes, we were only able to detect a few changes with any degree of certainty. Part of this difficulty is due to the problems of large spatial and temporal variability: in tree species composition and their differential sensitivity to acidification, and in nutrient cycling processes. The difficulty of sampling, with sufficiently rigorous techniques to detect differences within this large variability, also contribute to this uncertainty.

There are still important questions to be answered about the cycling of these nutrients and others in forest ecosystems and their responses to acidification and other chronic disturbances. At the Fernow the most intriguing of these are related to the high retention of N in a supposedly “saturated” watershed, and the cycling of base cations, in particular weathering and other sources of these cations.

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