



Factors controlling long-term changes in soil pools of exchangeable basic cations and stream acid neutralizing capacity in a northern hardwood forest ecosystem

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Abstract. Understanding the factors regulating the concentrations of basic cations in soils and surface waters is critical if rates of recovery are to be predicted in response to decreases in acidic deposition. Using a dynamic simulation model (PnET-BGC), we evaluated the extent to which atmospheric deposition of strong acids and associated leaching by strong anions, atmospheric deposition of basic cations through changes in emissions of particulate matter, and historical forest cutting have influenced soil pools of exchangeable basic cations and the acid-base status of stream water at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. Historical deposition of basic cations was reconstructed from regression relationships with particulate matter emissions. Simulation results indicate that the combination of these factors has resulted in changes in the percent soil base saturation, and stream pH and acid neutralizing capacity (ANC) from pre-industrial estimates of $\sim 20\%$, ~ 6.3 and $\sim 45 \mu\text{eq L}^{-1}$, respectively, to current values of $\sim 10\%$, ~ 5.0 and $\sim 5 \mu\text{eq L}^{-1}$, respectively. These current values fall within the critical thresholds at which forest vegetation and aquatic biotic are at risk from soil and surface water acidification due to acidic deposition. While the deposition of strong acid anions had the largest impact on the acid-base status of soil and stream water, the reduction in deposition of basic cations associated with reductions in particulate emissions was estimated to have contributed about 27% of the depletion in soil Ca^{2+} exchange pool and 15% of the decreases in stream water concentrations of basic cations. Decline in stream water concentrations of basic cation occurred under both increasing and decreasing exchangeable pools, depending on the process controlling the acid base status of the ecosystem. Model calculations suggest that historical forest cutting has resulted in only slight decreases in soil pools of exchangeable basic cations, and has had a limited effect on stream ANC over the long-term.

Introduction

The loss of basic cations (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+}) from forest soils can be accelerated by: 1) acidic deposition (Kirchner and Lydersen 1995; Likens et al. 1996; Johnson et al. 1999), 2) the declining inputs of basic cations from atmospheric deposition (Driscoll et al. 1989; Wesselink et al. 1995; Likens et al. 1996; Johnson

et al. 1999), and 3) forest clear-cutting (Likens et al. 1969; Federer et al. 1989; Dahlgren and Driscoll 1994). Acidification of soils and surface waters, and a decline in health of forest and aquatic biota may result from depletion of basic cations in available soil pools in forest ecosystems (Johnson et al. 1991; Driscoll et al. 2001). In soils, acidification leads to mobilization of trace metals, such as Al, and the displacement of basic cation with acid cations (H^+ and Al^{n+}) on soil cation exchange sites. The mobilization of Al in the soil may increase Al to Ca^{2+} ratios inhibiting plant Ca^{2+} uptake (Shortle and Smith 1988; Cronan and Grigal 1995). Critical chemical thresholds that appear to coincide with the onset of deleterious effects to biotic resources, include: 1) the molar Ca/Al ratio of soil water < 1.0 and soil percent base saturation $< 20\%$, which indicate that forest vegetation is at risk with respect to soil acidification from acidic deposition (Cronan and Schofield 1990; Cronan and Grigal 1995), and 2) surface water pH < 6.0 , acid neutralizing capacity (ANC) $< 50 \mu eq L^{-1}$ and inorganic monomeric Al concentrations $> 2 \mu mol L^{-1}$, which indicate that aquatic biota are at risk from surface water acidification due to acidic deposition (MacAvoy and Bulger 1995).

Following the 1970 Amendments of the Clean Air Act (CAAA) there has been a decline in the concentrations of SO_4^{2-} and basic cations in bulk precipitation and stream water in northeastern US (Driscoll et al. 1989; Stoddard et al. 1999; Driscoll et al. 2001). While the decline of SO_4^{2-} in precipitation is due to reductions in SO_2 emissions, the process(es) responsible for the decline in precipitation concentrations of basic cations is not evident. Sources of basic cation inputs to the atmosphere have not been quantified and as a result, detailed emission inventories are not available (Driscoll et al. 1989). However, the US Environmental Protection Agency (EPA) has estimated a large decline in anthropogenic emissions of total suspended particulates since 1970 (Nizich et al. 1996). This decline has been ascribed to: i) installation of control technology at coal-fired utilities and industrial boilers, ii) prohibition of open burning of solid waste (Nizich et al. 1996), and iii) decreases in atmospheric entrainment of soil particles (Stensland and Semonin 1982; Butler et al. 1984).

Some researchers (Henriksen 1984; Wright et al. 1986; Kulp 1987; Linthurst 1984) have assumed that historic and future trends in acidity of surface waters occur primarily through changes in S deposition. Although elevated S loadings clearly have had effects on water quality (Smith et al. 1987; Schindler et al. 1985; Kirchner and Lydersen 1995), including the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (Driscoll and Likens 1982; Lawrence et al. 1986; Driscoll et al. 2001) it has been suggested that atmospheric deposition of basic cations may also alter the acid-base status of surface waters (Driscoll et al. 1989; Wesselink et al. 1995; Johnson et al. 1999). Using a mass balance approach, Driscoll et al. (1989) estimated that up to 77–85% of the decline in stream base cations could be explained by the decreases in the atmospheric deposition of basic cations at the HBEF. Likewise Likens et al. (1998) estimated that about 20% of the depletion of exchangeable Ca^{2+} that has occurred in soil over the past 40 years was due to reductions in atmospheric Ca^{2+} deposition. Therefore, if decreases in atmospheric S deposition decreases the leaching of basic cations from the soil exchange complex

and increase the base saturation of the soil (Galloway et al. 1983; Reuss and Johnson 1986) and reductions in atmospheric deposition of basic cations decreases the supply of basic cations to the soil exchange complex (Driscoll et al. 1989; Weselink et al. 1995; Johnson et al. 1999), then it follows that decreases in basic cation deposition can offset the recovery of surface waters from acidification associated with reductions in atmospheric S deposition.

Another important disturbance to forest ecosystems and surface waters is clear-cutting. Repeated clear-cutting may have deleterious effects on site productivity and soil fertility through elevated losses of available nutrients (Kimmins 1977; Bormann and Likens 1979; Federer et al. 1989; Hendrickson et al. 1989). Nutrient cations, including Ca^{2+} , Mg^{2+} , and K^{+} are lost from forest ecosystems by harvesting via biomass removal (Mann et al. 1988; Ferrier et al. 1995; Johnson et al. 1995), vegetation uptake (Richter et al. 1994; Huntington et al. 2000), and enhanced leaching (Neal et al. 1992; Dahlgren and Driscoll 1994).

One method used to understand the factors regulating the biogeochemistry of basic cations is the application of biogeochemical models, which simulates both biotic and abiotic processes. The objective of this research was to use an integrated biogeochemical model (PnET-BGC; Gbondo-Tugbawa et al. (2001)) to evaluate the relative contribution of historical disturbances including: 1) atmospheric deposition of strong acids and associated leaching by strong anions, 2) atmospheric deposition of basic cations through changes in emissions of particulate matter, and 3) historical forest disturbance, to changes in soil pools of exchangeable basic cations and stream ANC at the HBEF.

Methods

PnET-BGC model

The integrated biogeochemical model PnET-BGC (Gbondo-Tugbawa et al. 2001; Figure 1), was used to understand the historical changes in base cation pools and surface water chemistry at the HBEF. This model, which has been described in detail elsewhere (Gbondo-Tugbawa et al. 2001), was formulated by linking two submodels to simulate major elements cycles in forest and interconnected aquatic ecosystems. These submodels include: 1) PnET, (PnET-CN; Aber et al. (1997) and Aber and Driscoll (1997)) a simple generalized model of monthly carbon (C), water and N balances, which provides estimates of net primary productivity, N uptake and water balances; and 2) BGC, a submodel which expands PnET, to include vegetation and organic matter interactions of other elements (Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , Si, S, P, Al^{3+} , Cl^{-} , F^{-}), abiotic soil processes, solution speciation and surface water processes.

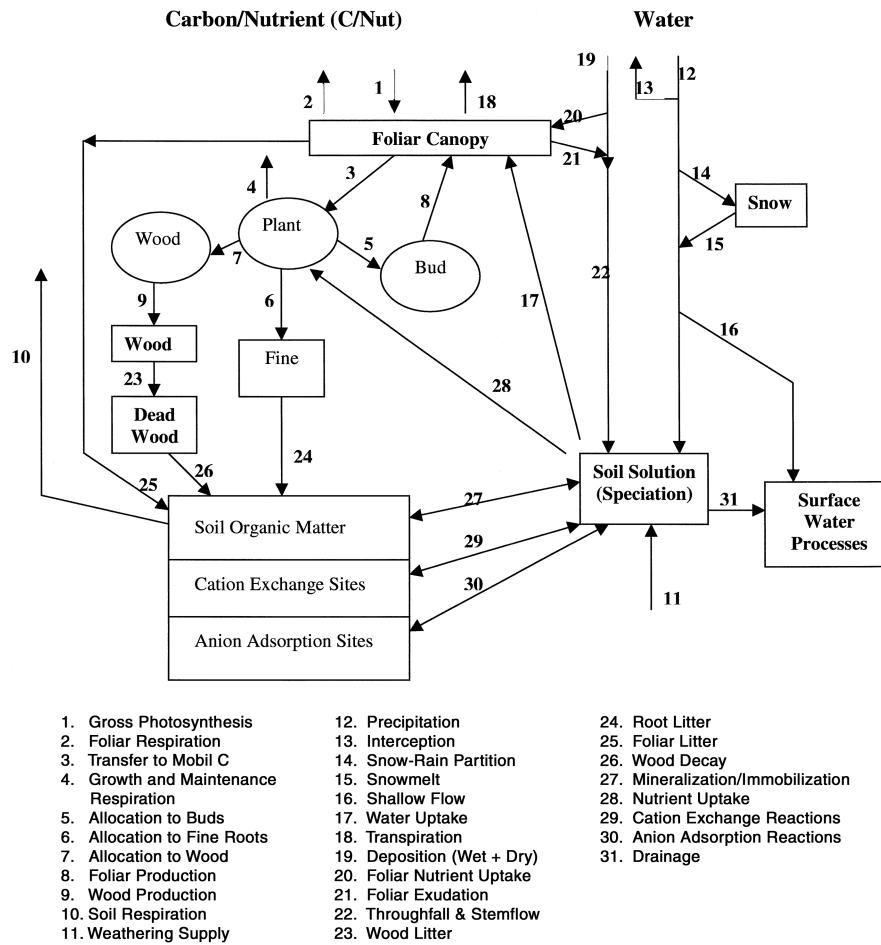


Figure 1. Structure of PnET-BGC illustrating the compartments and transfers of carbon and nutrients (C/Nut) within the model.

Study site and model scenarios

The HBEF has been described in detailed elsewhere (Likens and Bormann 1995). Watershed 6 (W6; 13.2 ha) is the biogeochemical reference watershed of the HBEF. It was logged intensively from 1910–1917 and experienced some salvage removals following the hurricane of 1938. We applied PnET-BGC to this watershed and considered the following scenarios: 1) a Reference Scenario, in which we assumed no human influence and pre-industrial deposition levels for model constituents throughout the simulation period for W6, 2) a business as usual or Ambient scenario, using actual deposition of all chemical constituents, land disturbance and climate history for W6, 3) a Background Basic Cation Scenario in which we assumed the pre-industrial deposition for basic cations (Ca^{2+} , Na^+ , Mg^{2+} and K^+) through-

out the simulation period for W6, 4) a Background Strong Acid Scenario in which we assumed the pre-industrial deposition for strong acid anions (SO_4^{2-} , NO_3^- , and Cl^-) throughout the simulation period for W6, and 5) a No Forest Disturbance Scenario in which we used actual atmospheric deposition for all chemical constituents species but excluded historical forest disturbances (i.e., no forest cutting in 1910–1917 and no salvage removal in 1938). For the Background Basic Cation and Strong Acid scenarios, we modified the deposition of H^+ to account for the fact that cations and anions in precipitation are charged balanced. Model parameter values given in Gbondo-Tugbawa et al. (2001) were used in these simulations.

Reconstructing atmospheric deposition

A critical component of this analysis is the reconstruction of historical atmospheric deposition trends for basic cations and strong acid anions. Cations and anions in deposition originate from a variety of sources, including oceanic spray, terrestrial dust, gaseous pollutants, and volcanic emissions. The HBEF is approximately 110 km to the east and 300 km to the south of the Atlantic Ocean, and even though the prevailing wind directions in the northeastern US are from the west and southwest, some marine influence can be expected (Likens et al. 1990). Bulk deposition of chemical constituents has been measured at the HBEF since 1964 (<http://www.hbrook.sr.unh.edu/data/atmos/atmos.htm>). Prior to about 1980, the $\text{Na}^+:\text{Cl}^-$ in deposition was roughly double the value anticipated from transported sea salt. In addition, the $\text{Ca}^{2+}:\text{Mg}^{2+}$ is representative of continental precipitation (Eaton et al. 1973; Likens and Bormann 1995). A recent study conducted on the origin of SO_4^{2-} deposition at the HBEF using stable S isotopes indicates a maximum marine contribution of 13% (Alewell et al. 2000). Therefore prior to 1980, deposition was probably dominated by continental sources. We explored linear regressions relationships between bulk deposition and anthropogenic emissions to reconstruct historical atmospheric deposition. Data on the long-term emissions of SO_2 , NO_x for the US are available from 1900, while data on the national emissions of particulate matter (PM-10) are available from 1940, from the US EPA (Nizich et al. 1996).

Mineral dust in the atmosphere is generally alkaline, and is a source of basic cations in precipitation (Semb et al. 1995). Because there are no emission inventories for basic cations inputs to the atmosphere, we used linear regression relationships between the annual volume-weighted concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ in bulk deposition at the HBEF and PM-10 (Figure 2), to estimate historical patterns of atmospheric deposition of basic cations. Linear regression was conducted for annual volume-weighted concentrations of basic cations in bulk deposition and PM-10 emissions for the entire US, observed from 1964 to 1980, the period of significant continental influence. Strong regression relationships were obtained for Ca^{2+} ($r^2 = 0.74$; Figure 2a), and Na^+ ($r^2 = 0.77$; Figure 2b), a moderate relationship for Mg^{2+} ($r^2 = 0.55$; Figure 2c) and a weaker regression relationship for K^+ ($r^2 = 0.30$; Figure 2d). Assuming that industrial sources were the dominant source of Cl^- ions before 1980, we regressed the deposition of Cl^- and anthropogenic particulate emissions, and a strong relationship ($r^2 = 0.79$; Figure 2e) was

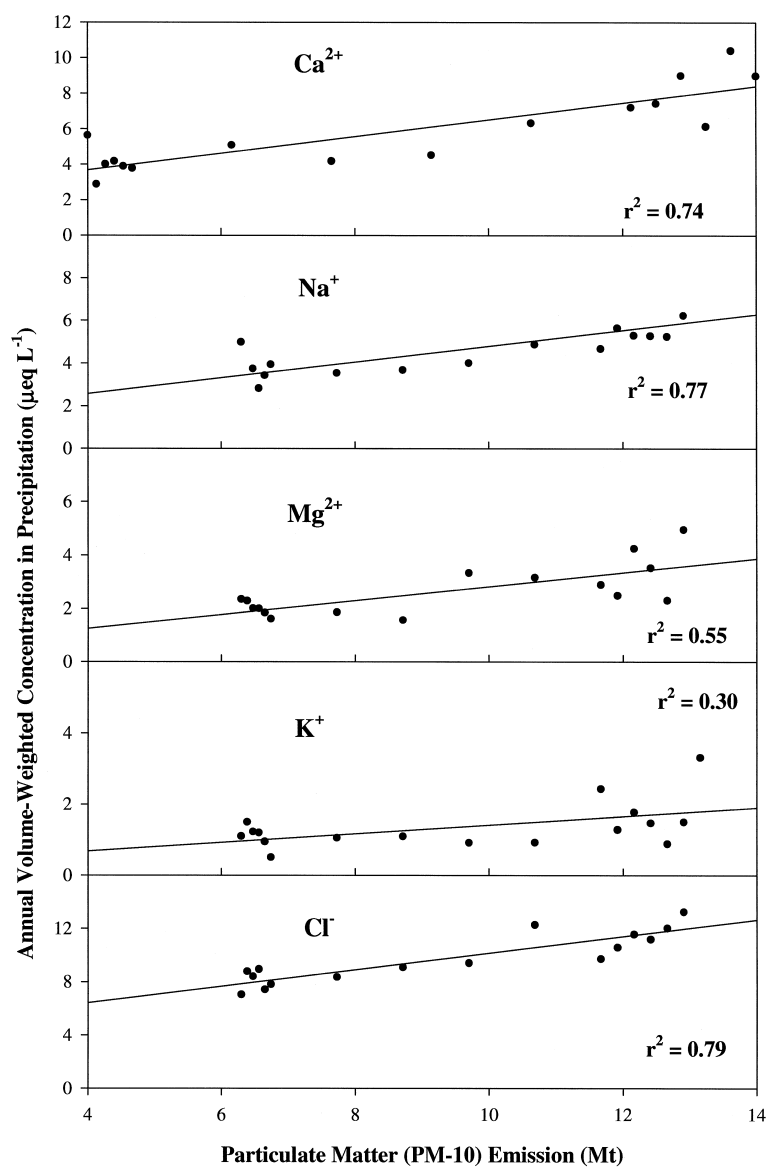


Figure 2. Annual volume-weighted concentrations of Ca^{2+} (a), Na^{+} (b), Mg^{2+} (c), K^{+} (d) and Cl^{-} (e) in bulk precipitation at the Hubbard Brook Experimental Forest, NH as a function of annual emissions of particulate matter (PM-10) in the US, between 1964–1980.

obtained. We used the above regression relationships to reconstruct the bulk deposition for each basic cation and Cl^{-} for the period 1940 to 1964.

A strong empirical relationship has been observed between estimates of SO_2 emissions for the eastern US (including the Ohio Valley) and the annual-volume

weighted concentration of SO_4^{2-} in bulk precipitation at HBEF (Likens et al. 2001). Using the empirical relation between emissions and bulk precipitation, the bulk deposition of SO_4^{2-} was reconstructed for the period 1900–1963. In contrast, there is no relationship between emissions of NO_x for eastern US and volume-weighted concentrations of NO_3^- in precipitation. In general, NO_3^- concentrations in precipitation tend to be highest in areas with elevated emissions of NO_x , especially in areas with high population density, numerous motor vehicles, and many power plants or industrial boilers (NADP 2000). Based on these observations, we assumed that changes in NO_x emissions are proportional to changes in NO_3^- deposition, and used emission values of NO_x for the eastern US to reconstruct NO_3^- deposition from 1900 to 1963.

We also needed estimates of pre-industrial or natural background deposition for both basic cations and the strong acid anions. The pre-industrial or natural background deposition of SO_4^{2-} has been estimated as $1.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (Granat et al. 1976), and $0.7 - 1.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (Husar and Holloway 1982), and this is approximately 10% of the measured long-term average bulk deposition values at the HBEF. We therefore assumed the pre-industrial deposition for all the chemical constituents before 1850 to be 10% the long-term measured values at the HBEF. To complete the reconstruction of the atmospheric deposition of the chemical constituents, we ramped the deposition of SO_4^{2-} and NO_3^- linearly from this background value in 1850 to the regression estimate in 1900, while for the basic cations and Cl^- deposition was ramped linearly from the background deposition in 1850 to regression estimate in 1940. The background and ramped deposition values were adjusted to depict the month to month, and seasonal variations observed in the long-term HBEF deposition record (Likens and Bormann 1995). Likens and Bormann (1995) reported approximately 24% increase or decrease in deposition during extreme wet and dry years in 1964/65 and 1973/74, respectively. A review of the reconstructed climate at the HBEF from 1897 (<http://www.hbrook.sr.unh.edu/data/wea/wea.htm>), indicated a severe drought in 1930. Reconstructed deposition inputs were reduced by 24% to account for this climatic perturbation in 1930.

Uncertainty analysis

Although there may be some uncertainties associated with the background deposition estimates, the values provide a means of comparing the impact of anthropogenic deposition to natural inputs in forest and aquatic ecosystems. We evaluated the sensitivity of the background bulk deposition on model predicted soil and stream chemistry, using a range of background values from 5% to 20% of current deposition. For each modeled output, a sensitivity index defined as the ratio of the relative change in modeled output to the relative change in the acidification potential of background deposition, was estimated. Acidification potential of background atmospheric deposition was defined as the background deposition of strong acid anions less basic cations ($2\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- - 2\text{Ca}^{2+} - 2\text{Mg}^{2+} - \text{K}^+ - \text{Na}^+$). The higher the sensitivity index, the more sensitive a simulated output is to the assumed background deposition.

Results

Model simulations were started in 1700 using background atmospheric deposition inputs for all chemical constituents to allow all ecosystem pools to develop and come to steady state before the actual deposition inputs were applied in 1850. Although all the basic cations were simulated in each model scenario and changes in SO_2 , NO_x and PM-10 emissions affected the biogeochemistry of all the basic cations, we focused this analysis on Ca^{2+} because it is: 1) the dominant basic cation in the soil exchange complex, 2) an essential macronutrient, and 3) the principal basic cation in stream water at the HBEF.

Reconstructed deposition

National emissions of PM-10 peaked at ~ 17 Mt. in 1950, after which values declined by $\sim 45\%$ from 1970 to 1975 and by $\sim 30\%$ from 1984 to 1985 (Figure 3a). Emissions of SO_2 (Figure 3b) and NO_x (Figure 3c) increased rapidly after 1900. While the emissions of SO_2 decreased in the mid 1970s following the implementation of the 1970 CAAA, NO_x emissions remained elevated. The reconstructed atmospheric deposition of basic cations to the HBEF (Figure 3d) was estimated to have a background input of $0.12 \text{ keq ha}^{-1} \text{ yr}^{-1}$. From 1850 the estimated deposition of basic cations increased steadily to a maximum value of $0.66 \text{ keq ha}^{-1} \text{ yr}^{-1}$ in 1950 after which the deposition decreased. There was a decrease of $0.24 \text{ keq ha}^{-1} \text{ yr}^{-1}$ in basic cation deposition from 1964 to 1965. The reconstructed total atmospheric deposition of the sum of strong acid anions (SO_4^{2-} , NO_3^- and Cl^- , Figure 3e) was dominated by SO_4^{2-} , and the estimated background deposition in 1850 was about $0.19 \text{ keq ha}^{-1} \text{ yr}^{-1}$. Total deposition of the sum of strong acid anions increased rapidly from 1900 and values remained elevated until the late 1960s. Since the mid 1970s there has been significant decline in strong acid anion deposition in accordance with decreases in SO_2 emissions and declines in SO_4^{2-} deposition.

Pre-industrial soil and stream chemistry

The simulated pre-industrial pool of soil exchangeable Ca^{2+} at the HBEF was estimated to be about 37 keq ha^{-1} (Figure 3f) and the corresponding soil base saturation was 22% (Figure 3g). In stream water, pre-industrial Ca^{2+} concentration, pH and ANC were hindcast to be of $32 \mu\text{eq L}^{-1}$ (Figure 3h), 6.3 pH units (Figure 3i), and $45 \mu\text{eq L}^{-1}$ (Figure 3j), respectively.

Reference scenario

Under the Reference Scenario, there were no significant changes to the soil and stream water chemistry compared to the pre-industrial levels throughout the simulation (Figure 3). Soil base saturation slightly decreased from 22% to 20% in the

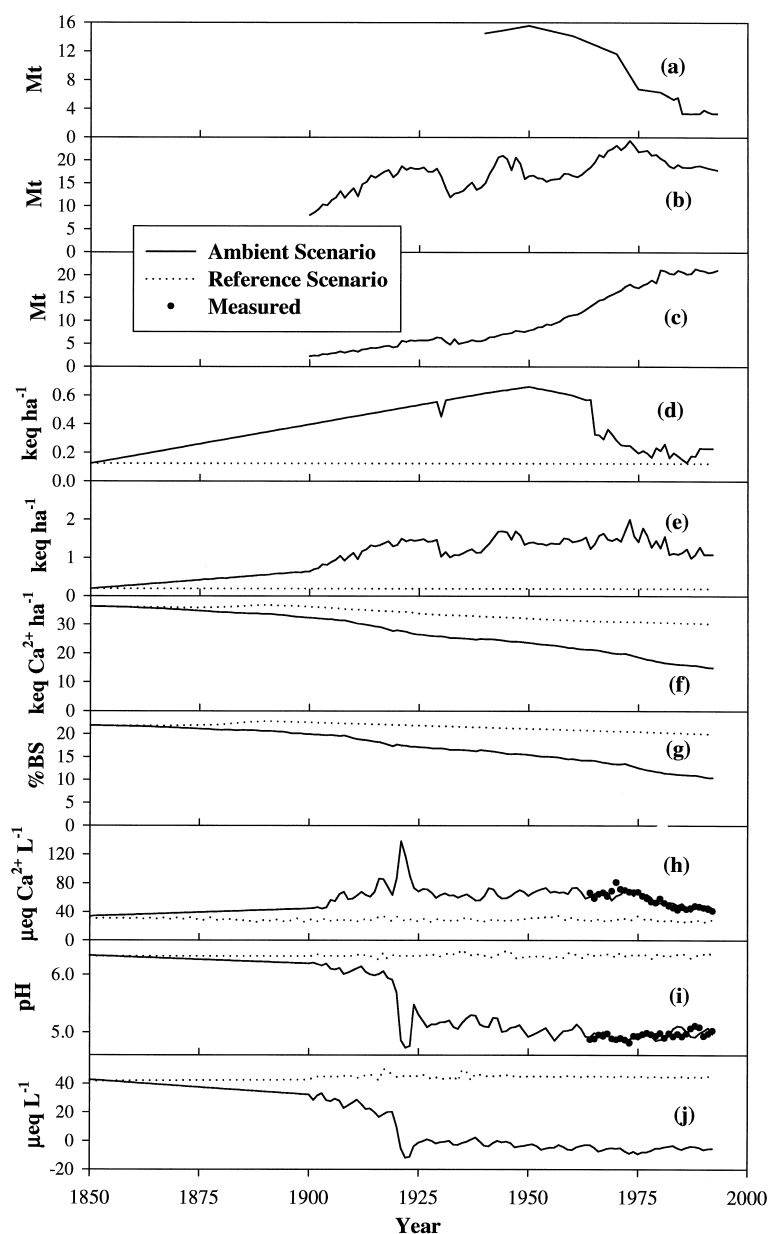


Figure 3. Particulate matter (PM-10) emissions (a), emissions of SO_2 (b) and NO_x (c), total estimated deposition of basic cations (d), total estimated deposition of strong acids (e), model simulated soil exchangeable Ca^{2+} (f), soil base saturation (g), stream Ca^{2+} concentration (h), stream pH (i) and ANC (j) for watershed 6 at the Hubbard Brook Experimental Forest, NH under two scenarios 1) estimated actual deposition (Ambient Scenario) and 2) background deposition of all constituents and no forest disturbances (Reference Scenario), for the period 1850 to 1995. Measured stream concentrations of Ca^{2+} and pH are included for comparisons.

1990s (Figure 3g). Stream pH and ANC remained above 6 and 40 $\mu\text{eq L}^{-1}$, respectively (Figure 3i,j).

Ambient scenario

The results of our Ambient Scenario includes calculations presented in our model evaluation study (1964 to 1992; Gbondo-Tugbawa et al. (2001)) and the hindcast simulations. Both the soil pool of exchangeable Ca and the soil base saturation, decreased slowly from 1850 to 1900 under ambient conditions. As the deposition of strong acid anions increased after 1900, the decline of the soil exchangeable Ca^{2+} (Figure 3f) and base saturation increased (Figure 3g). The soil pool of exchangeable Ca^{2+} before the forest cutting in 1919 was simulated as 27 keq ha^{-1} . The modeled value increased slightly by about 1.5% in 1920 and 1921 in response to the forest cutting. The decline in both the soil exchangeable Ca^{2+} and base saturation continued after 1921, with the pool of soil exchangeable Ca^{2+} and soil base saturation reaching ~ 22 keq ha^{-1} and $\sim 14\%$, respectively, in 1960. From 1960 to 1992, the simulated soil exchangeable Ca^{2+} pool and base saturation decreased to values of ~ 15 keq ha^{-1} and $\sim 10\%$, respectively. Note the steep declines in the predicted soil exchangeable pool of Ca^{2+} around the 1920s and mid 1970s under the Ambient Scenario (Figure 3f).

The simulated concentrations of Ca^{2+} in stream water (Figure 3g) increased steadily as deposition of basic cations and strong acid anions increased. Enhanced leaching of Ca^{2+} from the soil followed the forest cutting in 1919, with the simulated stream concentrations of Ca^{2+} increasing to a peak value of about 140 $\mu\text{eq L}^{-1}$ in 1921. Model prediction showed some year-to-year variations in stream concentrations of Ca^{2+} after 1920, but the concentrations remained elevated until the 1960s. Concentrations then decreased after 1960 from about 74 $\mu\text{eq L}^{-1}$ to about 46 $\mu\text{eq L}^{-1}$ in 1992. The model simulated concentrations of Ca^{2+} in stream water closely agreed with observed values reported for W6 at the HBEF from 1964 to 1992 (Gbondo-Tugbawa et al. 2001).

Under the Ambient Scenario, the stream ANC (Figure 3j) decreased to negative values after 1920 and the corresponding stream pH (Figure 3i) decreased to values below 5. The simulated stream ANC remained negative after 1920, showing some year-to-year variation. The model predicted ANC values in 1992 was ~ -6 $\mu\text{eq L}^{-1}$. The simulated stream pH also showed some year-to-year variations after 1920, with values remaining generally below 5 until the late 1980s when pH increased slightly above 5.

Background basic cation scenario

When the atmospheric deposition of all basic cations was maintained at the pre-industrial levels throughout the simulation period, the model predicted soil pool of exchangeable Ca^{2+} and the soil base saturation started deviating from the values predicted under the Ambient Scenario in 1875, with the rate depletion greatly increasing after 1900. (Figure 4b, 4c). From 1970 to 1992, both the soil exchange-

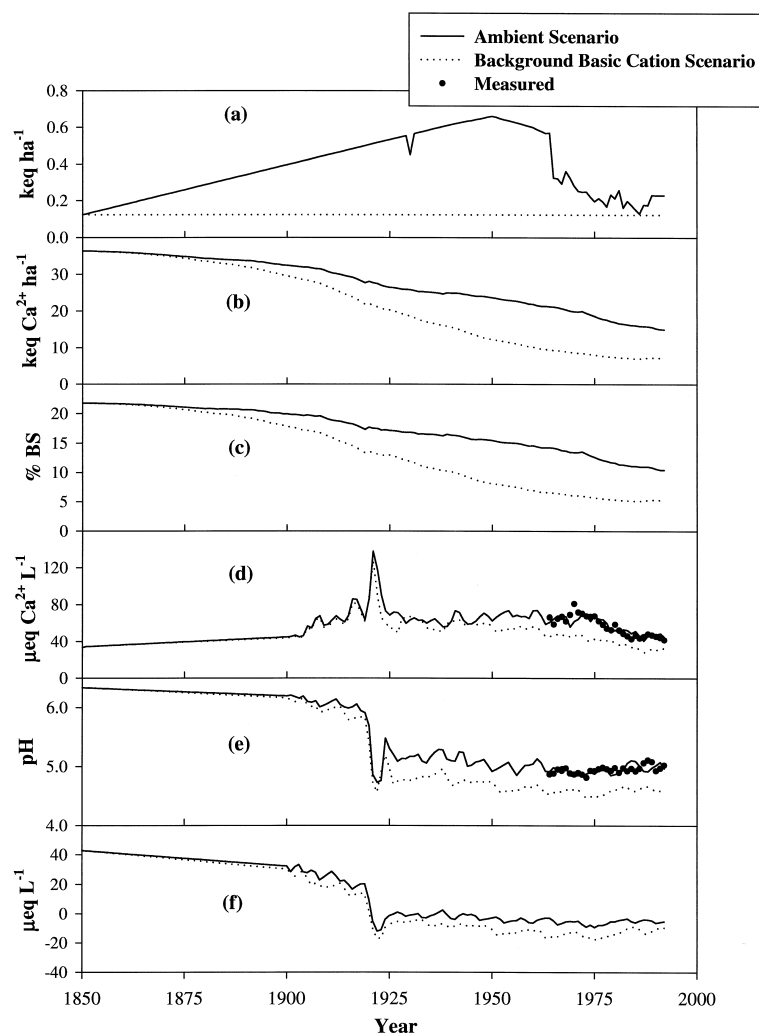


Figure 4. Total estimated deposition of basic cations (a), model simulated soil exchangeable Ca^{2+} (b), soil base saturation (c), stream Ca^{2+} concentration (d), stream pH (e) and ANC (f) for watershed 6 at the Hubbard Brook Experimental Forest, NH under two scenarios 1) estimated actual deposition (Ambient Scenario) and 2) background basic cation deposition scenario, for the period 1850 to 1995. Measured stream concentrations of Ca^{2+} and pH are included for comparisons.

able Ca^{2+} pool and base saturation under background basic cation deposition were about 50% lower than the corresponding predictions obtained under the Ambient Scenario. In the absence of anthropogenic deposition of basic cations, the predicted soil base saturation would be $\sim 5\%$ currently, which is considerably lower than model predictions for the Ambient Scenario.

Model prediction of stream water Ca^{2+} concentrations under Background Basic Cation deposition, initially followed the Ambient Scenario, but after the late 1940s

predicted concentrations of Ca^{2+} were lower than the Ambient Scenario (Figure 4d). From 1960 to 1992, model simulated stream Ca^{2+} concentrations were on average $\sim 25\%$ lower than stream Ca^{2+} concentrations for the Ambient Scenario scenario.

Our predicted stream pH decreased after 1920 and the simulated pH remained lower than under the Ambient Scenario from 1925 to 1992, by an average of about 0.4 pH units (Figure 4e). The stream ANC, also showed a significant difference compared to the Ambient Scenario after 1925, with the Ambient Scenario stream ANC $\sim 7 \mu\text{eq L}^{-1}$ higher on average (Figure 4f).

Background strong acid scenario

Under background deposition of strong acid anions, model predictions of the soil exchangeable Ca^{2+} pool and base saturation increased slowly after 1875 to about 40 keq ha^{-1} and 25% respectively in the 1920s (Figure 5b and 5c). A slight decrease in both values was evident in 1920 and 1921, after the forest cutting. Subsequently model predictions of both soil exchangeable Ca^{2+} pool and soil base saturation increased to 50 keq ha^{-1} and 32% , respectively in 1970, after which values leveled off. Thus, model simulations suggest that without historical anthropogenic deposition of strong acids from the atmosphere, the current soil exchangeable Ca^{2+} pool and base saturation would have been considerably higher compared to the values simulated for the Ambient Scenario.

Simulated stream Ca^{2+} concentrations did not vary much from pre-industrial levels, with the exception of the enhanced leaching associated with the cutting in 1920 (Figure 5d). Both the stream pH (Figure 5e) and stream ANC (Figure 5f) remained approximately at the pre-industrial values for most of the simulation period with the exception of the decreases that occurred following the forest cutting in 1919.

No forest disturbance scenario

Model simulation showed that forest cutting in 1919 initially resulted in slight increases in the soil exchangeable Ca^{2+} pool and base saturation (Figure 6a, 6b), but after 1922, the soil exchangeable Ca^{2+} pool and base saturation remained slightly below the corresponding values under the Ambient Scenario until the late 1970s. Although the disturbance to vegetation by the 1938 hurricane was much smaller compared to the forest cutting in 1919, this event also contributed to the pattern of slightly lower soil exchangeable Ca^{2+} pool and soil base saturation.

The stream concentrations of Ca^{2+} decreased to pre-disturbance levels 4 years after the cut (Figure 6c). The only significant difference between the predicted stream Ca^{2+} concentrations under the No Forest Disturbance Scenario and the Ambient Scenario was the high stream concentrations between 1920 to 1924 that occurred due to enhanced Ca^{2+} leaching from the soil following cutting of forest vegetation.

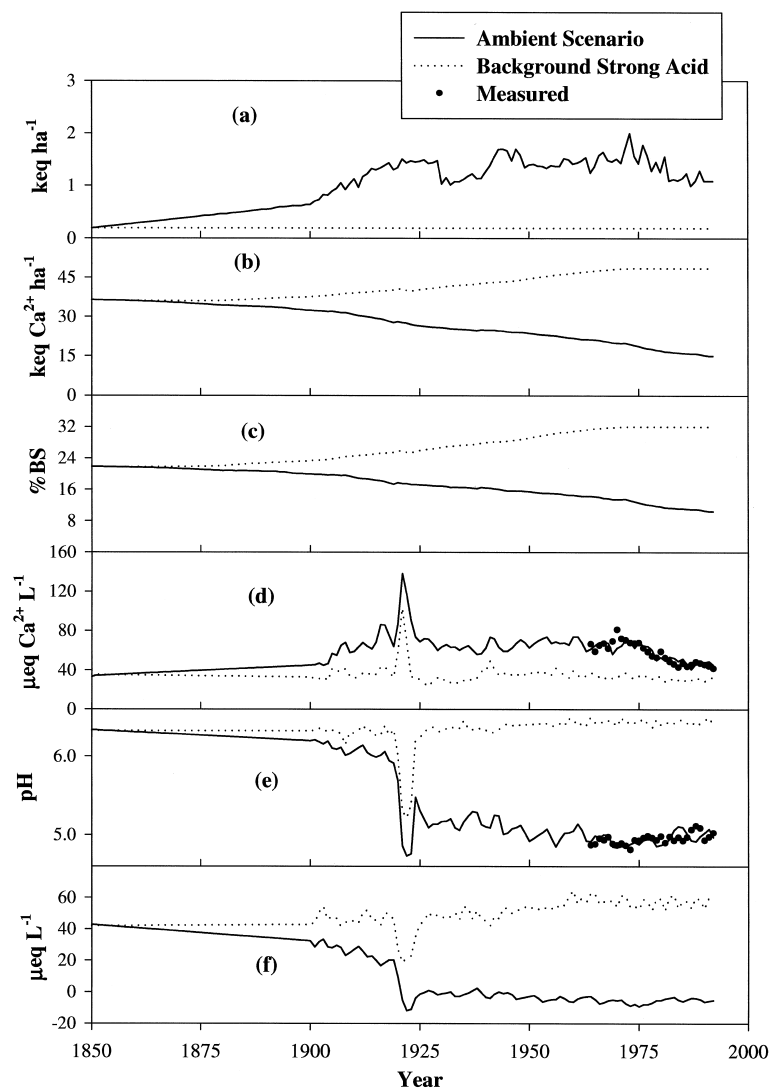


Figure 5. Total estimated deposition of strong acids (a), model simulated soil exchangeable Ca^{2+} (b), soil base saturation (c), stream Ca^{2+} concentration (d), stream pH (e) and ANC (f) for watershed 6 at the Hubbard Brook Experimental Forest, NH under two scenarios 1) estimated actual deposition (Ambient Scenario) and 2) background strong acid anion deposition scenario, for the period 1850 to 1995. Measured stream concentrations of Ca^{2+} and pH are included for comparisons.

Stream pH (Figure 6d) and ANC (Figure 6e) also decreased as a result of the forest cutting in 1919. This historical forest disturbance resulted in a decline of about $15 \mu\text{eq L}^{-1}$ and 0.6 pH units in stream ANC and pH, respectively, in 1922.

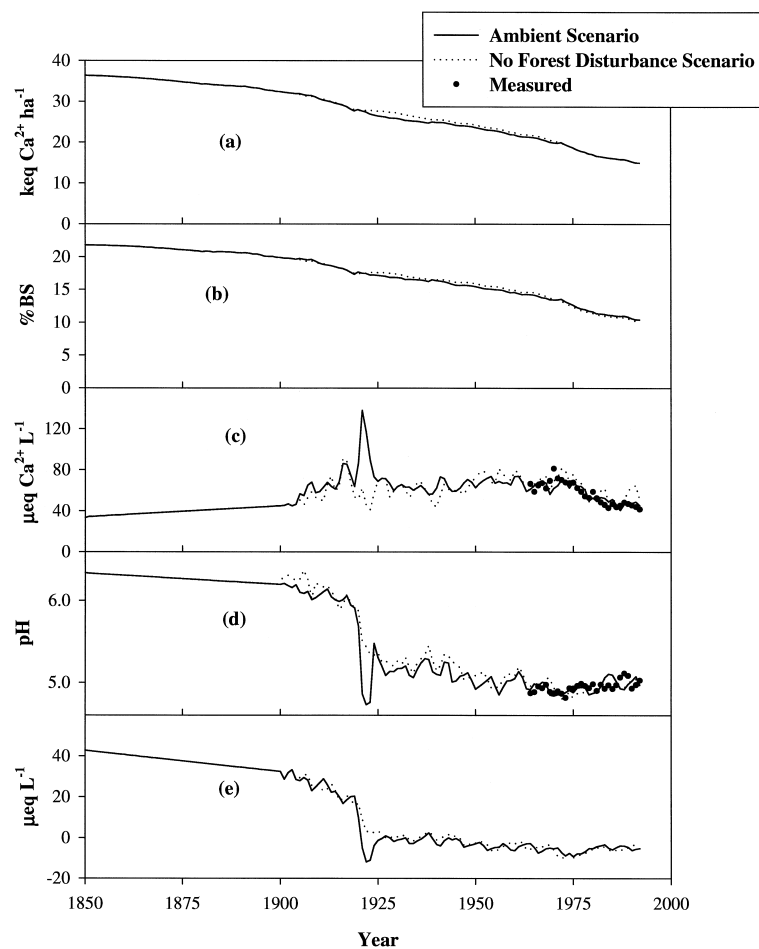


Figure 6. Model simulated soil exchangeable Ca^{2+} (a), soil base saturation (b), stream Ca^{2+} concentrations (c), stream pH (d) and ANC (e) for watershed 6 at the Hubbard Brook Experimental Forest, NH under two scenarios 1) estimated actual deposition (Ambient Scenario) and 2) no historical forest disturbance scenario, for the period 1850 to 1995. Measured stream concentrations of Ca^{2+} and pH are included for comparisons.

Uncertainty analysis

Variability of the background deposition of chemical constituents between 5% to 20% of the long-term measured bulk deposition at the HBEF was expressed as average sensitivity index for the periods 1850–1900, 1900–1950 and > 1950 (Table 1). The estimated average sensitivity indices were generally very low, with values decreasing over the simulation period after 1850.

Table 1. Summary of the average sensitivity indexes of modeled soil exchangeable Ca^{2+} (ExCa), soil base saturation (%BS), stream Ca^{2+} , stream pH and stream ANC for the simulation periods 1850–1900, 1900–1950 and > 1950 to the assumption of background bulk deposition of chemical constituents.

Simulation Period	Sensitivity indexes				
	Soil		Stream		
	ExCa	%BS	Ca^{2+}	pH	ANC
1850–1900	–0.10	–0.08	0.16	–0.02	–0.16
1900–1950	–0.05	–0.03	0.01	–0.01	–0.08
> 1950	–0.02	–0.01	0.01	–0.01	–0.05

Discussion

Our model simulations indicate that the soil pools of exchangeable basic cations as well as stream water concentrations of Ca^{2+} , stream pH and ANC have been influenced by a combination of atmospheric deposition of strong acid anions, atmospheric deposition of basic cations and past forest cutting/disturbance.

Pre-industrial chemistry

Model estimates of the pre-industrial stream water concentration of Ca^{2+} and stream ANC of $32 \mu\text{eq L}^{-1}$ and $40 \mu\text{eq L}^{-1}$, respectively, are somewhat greater than empirical estimates of $20 \mu\text{eq L}^{-1}$ and $20 \mu\text{eq L}^{-1}$ for stream Ca^{2+} and ANC reported by Likens et al. (1998). One major difference in these estimates might be due to the assumed weathering supply of Ca^{2+} to the watershed. The estimated weathering supply used in these simulations was $78 \text{ mol ha}^{-1} \text{ yr}^{-1}$. This value is $\sim 25 \text{ mol ha}^{-1} \text{ yr}^{-1}$ higher than the estimate used by Likens et al. (1998). While our estimate of the annual average bulk deposition of Ca^{2+} during the period 1940–1955 was about 4 times higher than the period 1976–1992 under the Ambient Scenario, the estimate of Likens et al. (1998) was about 7 times greater. In addition, simulated leaching loss of Ca^{2+} during the 1955–1975 period was 1.2 times greater than that during the 1976–1993 period. This flux is lower than estimates given by Likens et al. (1998), which specified that the leaching loss during 1955–1975 was 1.9 times greater than during the 1976–1993 period. Although there are differences in these values, both studies indicate that historical atmospheric Ca^{2+} deposition and stream losses of Ca^{2+} were higher during the 1940 and 1950s compared to observations after 1975. Model calculation of stream pH indicates that the estimated pre-industrial stream pH was more than 1 pH unit higher than current observed values.

Modeled effects of acidic deposition

Low inputs of strong acid anions resulted in the net accumulation of Ca^{2+} on soil cation exchange sites, lower stream Ca^{2+} concentrations and higher values of stream pH and ANC. On the other hand, under elevated inputs of strong acid anions and lower inputs of basic cation from atmospheric deposition, a significant depletion of Ca^{2+} from soil exchange sites was required to account for the increased leaching losses of Ca^{2+} associated with the enhanced leaching of strong acid anions from the watershed, and the resulting lower stream pH and ANC values, as reported in several other studies (Kirchner 1992; Driscoll et al. 1995; Kirchner and Lydersen 1995; Bailey et al. 1996). The HBEF, like many watersheds in the northeastern US, is sensitive to strong acid deposition because they are generally characterized by shallow depositions of surficial materials, with slow rates of chemical weathering and low concentrations of exchangeable basic cations in the soil (April and Newton 1985; Driscoll 1991). The effect of the pool of exchangeable basic cations was observed in long-term model simulations conducted on the effects of strong acid reductions to a mixed deciduous forest at Coweta, North Carolina (Johnson et al. (1993, 1995)) and a red spruce forest in the southern Appalachians (Johnson et al. (1996, 1995)). At Coweeta, leaching associated with SO_4^{2-} was governed by the high SO_4^{2-} adsorption capacity of the soil. Varying S deposition strongly affected simulated leaching of basic cations, but limited effects were evident to total soil pool of exchangeable Ca^{2+} because of its large size. At the acid-sensitive red spruce forest of the southern Appalachians, large reductions in simulation of strong acid anions greatly decreased predicted leaching of basic cations, and resulted in large changes in exchangeable base cation pools over a 30 -yr period.

While elevated inputs of strong acid anions led to the depletion of nutrient cations from the soil exchangeable pools, the elevated atmospheric deposition of basic cations from atmospheric deposition offset this leaching by strong acids anions from soil to a lesser extent. The importance of basic cation deposition was modeled by Wesselink et al. (1995) in beech and spruce forests at Solling Germany, in which elevated strong acid input caused marked acidification before the 1970s. Following the decline in atmospheric deposition of strong acids (after 1976), acidification of soils and waters continued because of decline in basic cation deposition. From 1900 to 1990, our simulated net loss of Ca^{2+} from soil cation exchange sites under background deposition of basic cation at the HBEF was as 5.7 keq ha^{-1} , which is about half the net gain of soil exchangeable Ca^{2+} under background deposition of strong acid anions of 11 keq ha^{-1} , compared to the Ambient Scenario. These values suggest that although historical deposition of strong acid anions had a more significant contribution regulating the acid-base status of soils and waters at the HBEF, anthropogenic deposition of basic cations was also important. In addition, comparison of stream output under background basic cation deposition and background strong acid deposition indicates that deposition of strong acid anions had a much stronger control on stream Ca^{2+} concentrations than the atmospheric deposition of basic cations. Johnson et al. (1999) also conducted model simulations to investigate the relative contribution of basic cation deposition in the southern Appala-

chians and at Coweeta reporting mixed results. At the acid-sensitive site in the southern Appalachians, a 50% reduction in basic cation deposition reduced leaching of basic cation by 40% compared to 17% by a 50% reduction of in S and N deposition over a 24-yr simulation period, and the effects of basic cation deposition occurred largely through changes in the exchangeable basic cation pool. On the other hand at Coweeta, a 50% reduction in basic cation deposition caused very slight reduction ($< 4\%$) in basic cation leaching while a 50% reduction in N and S deposition decreased basic cation leaching by 16% over a 24-yr period.

The general observations from these modeling studies suggest that the relative contribution of basic cation inputs is controlled by the status of the forest ecosystem with respect to N and S, and the size of the soil cation exchange pool. When the forest is accumulating S and N, basic cation deposition plays a minor role in leaching of basic cations. In contrast, under conditions of net release of S or N, the additional supply of SO_4^{2-} or NO_3^- from the soil becomes important in the depletion of soil cation pools allowing the inputs of basic cations to mitigate acidification. The relative contribution of SO_4^{2-} versus NO_3^- on the acid-base status at the HBEF was modeled by Gbondo-Tugbawa and Driscoll (2002a). Their results suggests that the recovery of soil base saturation and stream ANC were enhanced by decreases in SO_4^{2-} about 1.6 times and 1.3 times, respectively, compared to equivalent decreases in NO_3^- deposition.

Effect of historical forest disturbance

Forest cutting enhances leaching of Ca^{2+} from the soil to the stream water, and decreases stream pH and ANC. Model calculations, however, indicate that historical disturbance to the forest biomass (i.e. the cutting in 1919, and the hurricane in 1938) had little impact on the exchangeable cation soil pools at the HBEF. This observation is consistent with experimental results of a whole-tree harvest which showed that although there was marked redistribution of exchangeable cations within the soil solum, exchangeable pools of basic cations were unchanged following the disturbance (Johnson et al. (1991, 1997)).

Forest cutting results in the reduction of vegetation uptake, which is a large sink of Ca^{2+} , causing a net adsorption of Ca^{2+} to soil exchange sites immediately after the disturbance. This explains why the net release of Ca^{2+} from the soil exchange pool in W6 became negative (i.e. net accumulation) in during the first two years following the cut in 1919 (1920 and 1921; Figure 7). This exchangeable Ca^{2+} was subsequently depleted as the forest biomass aggraded and deposition of strong acid anions continued. Studies conducted on the impact of clear-cutting on exchangeable pools have yielded mixed results. While no depletion of exchangeable basic cation were reported for northern hardwood sites in New Hampshire (Snyder and Harter 1985; Johnson et al. 1991) as well as a mixed oak forest in Tennessee (Johnson and Todd 1998), large decreases in exchangeable base cation pools were observed following whole-tree harvesting of northern hardwood stands in northern Michigan (Mroz et al. 1985). Previous modeling studies on the other hand support the depletion of exchangeable base cations during vegetation regrowth following

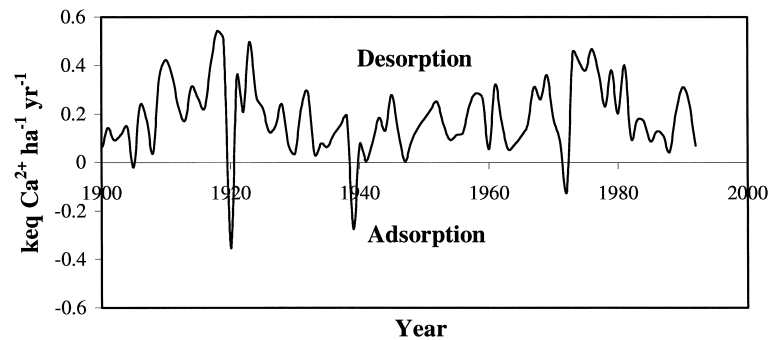


Figure 7. Rates of change of model simulated soil exchangeable Ca^{2+} for watershed 6 at the Hubbard Brook Experimental Forest, NH for the period 1960 to 1995 under the Ambient Scenario. Positive values denote net release from cation exchange sites, while negative values indicate net adsorption.

cutting disturbances (Ferrier et al. 1995; Johnson et al. 1995). Federer et al. (1989) using an input-output budget approach, suggested that forest harvest combined with leaching losses associated with acidic deposition could reduce the total Ca^{2+} in soil by 20–60% in 120 years.

Uncertainty in background deposition

Our sensitivity analysis indicates that model simulations of soil basic cation exchange pool, stream Ca^{2+} , pH and ANC were not sensitive to changes in the assumed background deposition of chemical constituents. Before 1900, soil pool of exchangeable basic cations were relatively very large and the acidity in precipitation was probably controlled by carbon dioxide and organic acids, since elevated inputs of strong acid occurred after 1900s.

Comparison of modeled dynamics of basic cations with other estimates at the HBEF

At the HBEF, the rate of release of Ca^{2+} from soil cation exchange sites from 1850 to 1992 (Figure 7) under the Ambient Scenario was highest around 1918 a period corresponding to the first peak in SO_2 emissions and forest cutting, and also in the mid 1970s, coinciding with marked decline in atmospheric deposition of S and basic cations and the net release of SO_4^{2-} from soil S pools (Gbondo-Tugbawa et al. 2002b). This result disagrees with the analysis of Likens et al. (1998), which suggested that the highest rate of soil depletion of Ca^{2+} occurred after the mid 1950s. The decline in soil exchange pool of basic cation occurs following a marked decline in atmospheric deposition of strong acids because of the net release of strong acid anions from soil organic and adsorbed pools. This phenomenon, referred to as progressive acidification, was estimated to account for 15–20% of the basic cations leached from the soil at the HBEF (Kirchner 1992). This form of acidification can cause significant delay in watershed recovery. Gbondo-Tugbawa et al. (2002b) es-

timated a response time of about 15 years to reduce stream SO_4^{2-} concentrations by 50% following a significant reduction in SO_4^{2-} deposition.

Likens et al. (1998) also specified that reduction in atmospheric deposition of Ca^{2+} associated with particulate emissions control contributed some 20% of the apparent depletion of soil labile pool of Ca^{2+} at the HBEF. Using a mass balance approach Driscoll et al. (1989) suggested that as much as 77–85% of the decline in stream concentrations of basic cations could be explained by decreases in the atmospheric deposition of basic cations. By comparing a hypothetical simulation (High PM Scenario; Figure 8) in which the total deposition of basic cation was assumed to remain at its peak value of $0.66 \text{ keq ha}^{-1} \text{ yr}^{-1}$ after 1950, and results of the Ambient Scenario (Figure 8a), we observed that a response time of about 8 to 10 years was required to detect a significant difference in the soil exchangeable Ca^{2+} pool and stream concentrations of basic cations in response to decreases in atmospheric deposition of basic cations (Figure 8b, 8c). This delay is probably due to that fact the deposition input is relatively small compared to the size of the exchangeable soil Ca^{2+} pool. A reduction in deposition of Ca^{2+} associated with particulate matter controls, contributed about 27% of the depletion of the soil Ca^{2+} exchange pool at the HBEF, which compares to the estimate of 20% by Likens et al. (1998). Finally, the sum of basic cations in stream water declined after 1950 under this hypothetical scenario as it did under the Ambient Scenario. The difference in stream concentrations of the sum of basic cations between the hypothetical High PM and the Ambient Scenarios ranged between 5% and 25% (Figure 8c), values which are significantly lower than the estimates of 77–85% given by Driscoll et al. (1989). Our results therefore suggest that leaching associated with atmospheric deposition of strong acid anions has more control on stream output of basic cations than atmospheric deposition of basic cations, and that basic cations (particularly Ca^{2+} and Mg^{2+}) have a strong affinity for the cation exchange sites.

The depletion of Ca^{2+} from soil exchange sites indicates that cation exchange processes are important in controlling the acid-base chemistry of surface waters. Johnson et al. (1996) suggested that changes in base cation pools and base saturation, capacity effects (Reuss and Johnson 1986), resulted in changes in soil solution chemistry over a short period at the southern Appalachians. Several investigators have reported that accumulation of cations in aggrading biomass can also cause significant depletion of exchangeable nutrient cations from forest soils (Johnson et al. 1988; Johnson and Todd 1990; Knoepp and Swank 1994; Richter et al. 1994; Huntington et al. 2000). In forest soils in the southeastern US, the annual rate of Ca^{2+} uptake into merchantable wood exceeds soil leaching losses by a factor of more than five (Huntington et al. 2000). The depletion of soil pools of exchangeable cations associated with the three disturbances simulated in this study is complicated by the potential for accumulation in aggrading biomass. However, our Reference Scenario in which the atmospheric deposition of all chemical constituents were maintained at their background values throughout the simulation period (1850–1992) did not indicate any significant depletion in the exchangeable soil Ca^{2+} pool and the soil base saturation in 1992 decreased from its initial value of 22% to 20% in the 1990s. This result corroborates observations from previous wa-

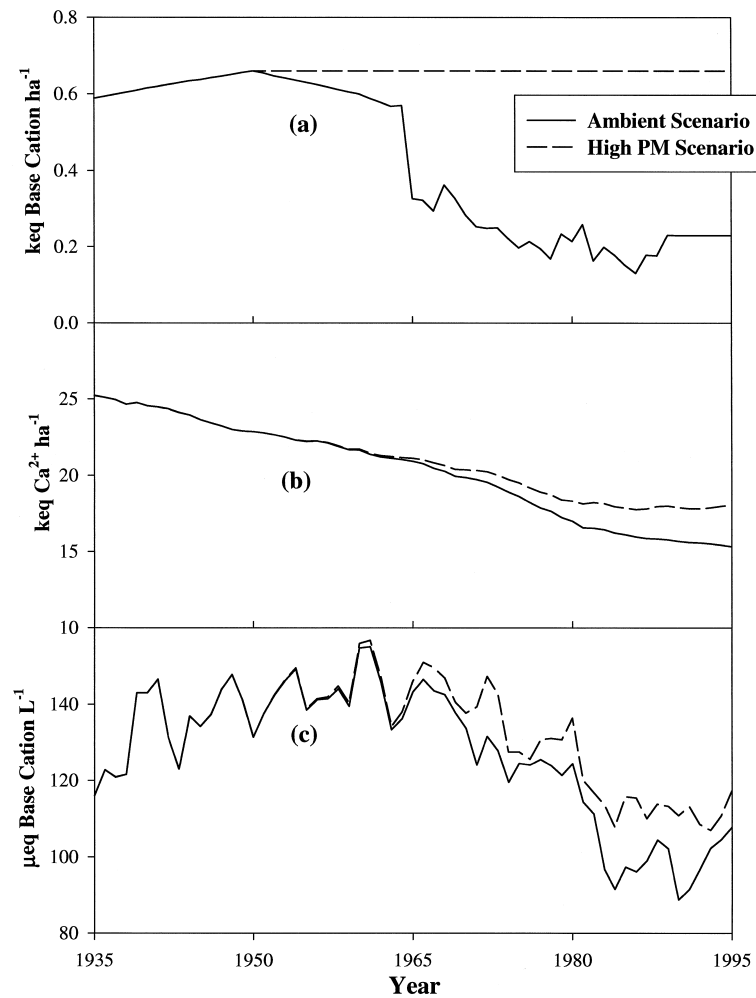


Figure 8. Total deposition of basic cations (a), model simulated soil exchangeable Ca^{2+} pool (b) and stream concentrations of basic cations (c) for watershed 6 at the Hubbard Brook Experimental Forest, NH for the period 1935 to 1995. Model simulations were made under two scenarios 1) estimates of actual deposition (Ambient Scenario), and 2) continued elevated emissions of particulate matter after 1950 and associated deposition of basic cations (High PM scenario).

tershed studies in New Hampshire (Bailey et al. 1996; Likens et al. (1996, 1998); Yanai et al. 1999) that soil Ca^{2+} depletion cannot be explained by biomass accumulation.

Comparison of modeled results with field studies at other sites

We also compared the model results with long-term field studies of basic cation dynamics at other forest ecosystems. Using PnET-BGC, we estimate that between

1900 and 1992 a 50% reduction occurred in the soil pool of exchangeable basic cations, recent studies have reported much higher reductions in pools exchangeable basic cations over relatively short durations. Acidic deposition was reported to have caused a 53–76% reduction in soil pools of exchangeable basic cations in a 35-year period in China (Dai et al. 1998). A 10% reduction in base saturation was reported for a Danish spruce forest, from 1985 to 1996 (Hovmand and Bille-Hansen 1999). In the Adirondack region of New York, studies on long-term changes in basic cation pools in the forest floor showed that historic depletion of Ca^{2+} of $0.06 \text{ keq ha}^{-1} \text{ yr}^{-1}$ from 1931 to 1984, was several times lower than the rate of depletion of $0.43 \text{ keq ha}^{-1} \text{ yr}^{-1}$ from 1986 to 1990 (Johnson et al. 1994). This result is significantly different from our PnET-BGC calculations, which showed that the rate of depletion of soil exchangeable Ca^{2+} at the HBEF from 1931 to 1984 was $0.18 \text{ keq ha}^{-1} \text{ yr}^{-1}$, while the corresponding depletion rate during the period 1986 to 1990 was estimated as $0.06 \text{ keq ha}^{-1} \text{ yr}^{-1}$. Differences in rates of soil Ca^{2+} depletion calculated for the HBEF using PnET-BGC reflect the high loading of strong acid anions that occurred through early portion of the last 70 years coupled with marked declines in strong acid inputs in recent years. These differences suggest that reconstructing historical patterns of soil pools and the acid-base status of surface waters will depend on the assumptions made on historical inputs of chemical weathering and atmospheric deposition of strong acid anions and basic cations.

Conclusions

Historical controls on soil pools of exchangeable basic cations and the acid-base status of streams at the HBEF have been influenced by the long-term atmospheric deposition of strong acid anions, particularly SO_4^{2-} , and the atmospheric deposition of basic cations associated with particulate matter emissions. Model simulations suggest that the historical deposition of strong acid anions had the most influence in controlling soil pools and stream water chemistry. In addition, the calculations also suggest that vegetation accumulation of Ca^{2+} following the 1919 clear-cut had little effect on soil exchangeable base cation pools.

Over a period of 150 years, soil base saturation, and stream pH and ANC have changed from $\sim 22\%$, ~ 6.3 and $\sim 45 \mu\text{eq L}^{-1}$ to current values of $\sim 10\%$, ~ 5.0 and $\sim -5 \mu\text{eq L}^{-1}$, respectively. The current values lie within the critical threshold values that coincide with deleterious effects to biotic resources. Although elevated loading of strong acids anions clearly have had the most effect on soil and stream chemistry, atmospheric deposition of basic cations also appears to be important in regulating the acid-base status of soils and aquatic ecosystems. Model simulations suggest that stream concentrations of Ca^{2+} can decline under both high and low inputs of basic cation or under conditions of high or lower soil base saturation. Thus changes in the atmospheric deposition of basic cations will also impact the future response of forest nutrients cycles and stream chemistry to changes in atmospheric deposition and human disturbance. Predicting future trends of acidification requires

input of projected or anticipated atmospheric deposition input to ecosystem models. Most analysis involving acidification models have focused on atmospheric deposition of strong acids, especially SO_4^{2-} , and their role in soil and surface water acidification. This assumption is valid only if the atmospheric deposition of basic cations remains constant. In fact it appears that reductions in atmospheric deposition of basic cations have partially offset reductions of strong acid anions, reducing the recovery of soil and surface water in response to controls of SO_2 emissions.

While the results indicate that historical forest cutting and harvesting has little long-term effect on soil of exchangeable nutrient cations pools, this by no means suggests that repeated forest harvesting would not threaten the sustainability of the forest ecosystem. In our simulation, the release of Ca^{2+} from litter resulting from logging residue was important, as well as weathering inputs. Repeated biomass harvest removal will reduce Ca^{2+} mineralization due to decreases in the supply of litter to the soil organic pool. Because the active soil organic Ca^{2+} pool in PnET-BGC turns over rapidly, a reduction in pool size will reduce the flux of Ca^{2+} produced by mineralization. If mineralization becomes less important, then vegetation will depend more on exchangeable Ca^{2+} pools following forest cutting.

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