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Factors controlling soil water and stream water aluminum concentrations after a clearcut in a forested watershed with calcium-poor soils

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Abstract The 24 ha Dry Creek watershed in the Catskill Mountains of southeastern New York State USA was clearcut during the winter of 1996–1997. The interactions among acidity, nitrate (NO_3^-), aluminum (Al), and calcium (Ca^{2+}) in streamwater, soil water, and groundwater were evaluated to determine how they affected the speciation, solubility, and concentrations of Al after the harvest. Watershed soils were characterized by low base saturation, high exchangeable Al concentrations, and low exchangeable base cation concentrations prior to the harvest. Mean streamwater NO_3^- concentration was about 20 μmol l^{-1} for the 3 years before the harvest, increased sharply after the harvest, and peaked at 1,309 μmol l^{-1} about 5 months after the harvest. Nitrate and inorganic monomeric aluminum (Al_{im}) export increased by 4−fold during the first year after the harvest. Al_{im} mobilization is of concern because it is toxic to some fish species and can inhibit the uptake of Ca^{2+} by tree roots. Organic complexation appeared to control Al solubility in the O horizon while ion exchange and possibly equilibrium with imogolite appeared to control Al solubility in the B horizon. Al_{im} and NO_3^- concentrations were strongly correlated in B-horizon soil water after the clearcut ($r^2 = 0.96$), especially at NO_3^- concentrations greater than 100 μmol l^{-1}. Groundwater entering the stream from perennial springs contained high concentrations of base cations and low concentrations of NO_3^- which mixed with acidic, high Al_{im} soil water and decreased the concentration of Al_{im} in streamwater after the harvest. Five years after the harvest soil water NO_3^- concentrations had dropped below preharvest levels as the demand for nitrogen by regenerating vegetation increased, but groundwater NO_3^- concentrations remained elevated because groundwater has a longer residence time. As a result streamwater NO_3^- concentrations had not fallen below preharvest levels, even during the growing season, 5 years after the harvest because of the contribution of groundwater to the stream. Streamwater NO_3^- and Al_{im} concentrations increased more than reported in previous forest harvesting studies and the recovery was slower likely because the watershed has experienced several decades of acid deposition that has depleted initially base-poor soils of exchangeable base cations and caused long-term acidification of the soil.

Keywords Aluminum · Catskill Mountains · Forest harvesting · Nitrate · Soil water · Streamwater

Abbreviations

Al	Aluminum
Al^{3+}	Trivalent monomeric aluminum

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Al^{n+}	Sum of positively charged aluminum species
Al_{im}	Inorganic monomeric aluminum
Al_{mono}	Total monomeric aluminum
Al_{org}	Organic monomeric aluminum
Al_{tot}	Total aluminum
ANC	Acid-neutralizing capacity
Ca^{2+}	Calcium
C_B	Sum of base cations
$C_B - C_{AA}$	Sum of base cations minus sum of acid anions
Cl^-	Chloride
CEC	Cation exchange capacity
CO_2	Carbon dioxide
DOC	Dissolved organic carbon
F	Fluoride
H^+	Hydrogen
HBEF	Hubbard Brook Experimental Forest
HNO_3	Nitric acid
K^+	Potassium
Mg^{2+}	Magnesium
Na^+	Sodium
NO_3^-	Nitrate
$RCOO^-$	Organic acidity
SiO_2	Silicon dioxide
SO_4^{2-}	Sulfate
%BS	Percent base saturation
%C	Percent carbon
%N	Percent nitrogen

Introduction

Aluminum (Al) mobilization and transport has been a focus of research in forested watersheds during the past two decades because Al is toxic to aquatic biota. Inorganic monomeric Al (Al_{im}, also referred to as inorganic labile Al) can be toxic to some fish species (Schofield and Tronjar 1980; Baker and Schofield 1982; Baldigo and Murdoch 1997; Kaeser and Sharpe 2001; Baldigo et al. 2005); mortality has been reported at stream water Al concentrations greater than 7.5 μmol l^{-1} (Cronan and Schofield 1979; Baldigo and Murdoch 1997). Al_{im} can also inhibit the uptake of calcium by tree roots (Shortle and Smith 1988; Cronan and Grigal 1995) and thereby lower tree tolerance to stress.

Acid deposition is the main cause of increased Al mobilization and transport in the northeastern United States and Europe (Cronan and Schofield 1979; Johnson 1979; Reuss and Johnson 1985; Burns 1989; Matzner 1992; Dise et al. 2001). Mobilization of Al in soils results from an increase in sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations in water moving through the soil. Soil acidification is characterized by depletion of base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) through ion exchange with Al species [Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$] and hydrogen ion (H^+) (Reuss and Johnson 1986). In most regions large changes in soil acidity typically occur only after several decades of acid deposition because soils are initially well buffered. The most pronounced short-term effect of acid deposition on streams is episodic acidification, whereby rainstorms or snowmelt cause a sharp decrease in streamwater pH that is often accompanied by an increase in Al_{im} concentrations (Kahl et al. 1992; DeWalle and Swistock 1994; Wigington et al. 1996).

Besides soil water and streamwater pH, other controls on Al concentrations in soil and streamwater include organic complexation of Al, ion exchange reactions both in the soil and the stream, and mixing of acidic soil water with less acidic groundwater (Reuss and Johnson 1986; Lawrence et al. 1986; Baur and Feger 1992; Neal et al. 1992). These four factors are interrelated, but affect streamwater Al concentrations differently, and can change through time. The first factor, the pH of soil water and streamwater, has a direct effect on Al concentrations because it controls Al dissolution and speciation, which in turn determines the concentration of Al in streamwater (Reus and Johnson 1986). The second factor, organic complexation of Al, controls Al speciation and is also pH dependent (Tipping 1994); the more Al that is complexed with organic matter the less Al is present as Al_{im}. This distinction is important since organic Al (Al_{org}) is non-toxic and therefore does not represent a threat to the aquatic system (Gjessing et al. 1989). The third factor, ion exchange reactions, controls the precipitation and dissolution of Al and is also closely linked to pH. Lastly, mixing of soil water and streamwater high in Al with other low Al water sources can reduce Al concentrations through dilution, can affect Al speciation, and can cause Al precipitation in soil and within the stream (Neal and Christophersen 1989).

Several mineral phases can control the solubility of Al in mineral soils such as aluminum hydroxide (gibbsite) (Dahlgren et al. 1989), Al–SO_4 minerals such as jurbanite (Fernández-Sanjurjo et al. 1998), and Al–Si minerals such as allophone, imogolite, and kaolinite (Gustafsson et al. 1995, 1998; Simonsson and Berggren 1998). Some researchers have suggested that proto-imogolite or imogolite + proto-imogolite (or imogolite-type materials) may control Al solubility in simultaneous equilibrium with gibbsite (Farmer 1987; Dahlgren and Ugolini 1989; Zysset et al. 1999). Organic soils are often undersaturated with respect to mineral phases of Al (Bloom et al. 1979; Cronan et al. 1986; Walker et al. 1990; Berggren and Mulder 1995; Wesselink et al. 1996), and instead Al solubility is typically controlled by complexation reactions with soil organic matter (Walker et al. 1990; Berggren and Mulder 1995; Wesselink et al. 1996). Al solubility is still strongly pH dependent when controlled by organic complexation (Tipping 1994; Rustad and Cronan 1995; de Wit et al. 1999), however the slope of the pH-pAl relation is usually closer to two rather than the cubic relation defined by mineral phase solubility (Tipping et al. 1995; Berggren and Mulder 1995; Gustafsson et al. 2001). Few of these studies have linked the controls of soil Al solubility to stream Al concentrations and speciation and their importance relative to mixing of soil and groundwater (Neal and Christophersen 1989).

Forest harvesting can cause large changes in the rates of chemical cycling and in the export of nutrients and base cations from watersheds (Likens et al. 1969; Vitousek et al. 1979; Hornbeck and Kropelin 1982; Lawrence et al. 1987; Bormann and Likens, 1994; Reynolds et al. 1995; Rosén et al. 1996). First, harvesting decreases the uptake of nitrogen by trees and can increase the rates of N mineralization and nitrification (Likens et al. 1969; Vitousek and Melillo 1979; Vitousek 1981; Matson and Vitousek 1981; Hornbeck and Kropelin 1982; Burns and Murdoch 2005). The resulting excess nitrogen then passes through the soil as a strong acid (HNO_3), which leaches base cations and Al from the soil and causes a large export of base cations and Al from the watershed after the harvest (Lawrence et al. 1987; Neal et al. 1992; Reynolds et al. 1992; Dahlgren and Driscoll 1994; Reuss et al. 1997). Base-cation depletion and soil acidification after a harvest also can cause soil nutrient imbalances that lead to changes in tree species dominance and distribution in a forest, and to long-term forest decline and losses in productivity (Lundborg 1997; Adams et al. 2000). Dise and Gundersen (2004) concluded that the severity of the ecosystem response to environmental stress, such as an increase in soil water acidity, depends on the status of the ecosystem at the time of the stress and the long-term trends that have preceded the stress.

Previous studies have documented the effects that harvesting can have on soil water and streamwater Al concentrations. A whole-tree harvest in a 22.5 ha watershed at the Hubbard Brook Experimental Forest (HBEF), New Hampshire, resulted in streamwater acidification downstream of the harvest that affected an area five times larger than the area that was actually harvested (Lawrence and Driscoll 1988). Although there was a sharp increase in stream and soil water Al_{im} after the harvest there was no clear change in Al_{org} concentrations (Dahlgren and Driscoll 1994). After harvesting in three watersheds located throughout the United Kingdom Al concentrations increased sharply and were closely associated with total inorganic anion concentrations (Reynolds et al. 1992). In mid-Wales Great Britain there were large temporal variations in streamwater Al concentrations after a forest harvest that were attributed to changing contributions of acidic soil water and less acidic groundwater to the stream (Neal et al. 1992). The mixing of acidic soil water with nonacidic groundwater can cause in-stream changes in Al concentration and speciation (Burns 1989; Neal and Christophersen 1989). Although there is a consensus that soil acidification is responsible for the release of Al from soils after forest harvesting, the relative importance of pH, organic complexation, and mixing of acidic soil water with less acidic groundwater on streamwater Al concentrations is poorly quantified. In 1993, the US Geological Survey, in cooperation with the Frost Valley YMCA and the New York City Department of Environmental Protection, began a study of the effects of clearcutting in the Neversink River basin in the Catskill Mountains of New York State. The intent of this part of the study was to (1) evaluate the relative importance of ion exchange, mineral phase Al solubility, organic complexation, and mixing of acidic soil water and less acidic groundwater on streamwater Al concentrations after a clearcut and (2) determine how the influence of these factors on streamwater Al concentrations changed during the 9 year study.

Site description

The study was conducted in the 24-ha Dry Creek watershed in the headwaters of the Neversink River basin in the Catskill Mountains of southeastern New York (41° 58′N, 74° 30′W) (Fig. 1). Additional streamwater samples and streamflow data were collected at the outlet of the adjacent Shelter Creek watershed (SC40, 104 ha) and at lower Shelter Creek (SC20) downstream from the confluence of DC57 and SC40, which drains 161 ha (Fig. 1). The Catskill Mountains are subject to some of the most acidic deposition in eastern North America, mean annual nitrate deposition was 4.3 kg N ha^{-1} year^{-1} and sulfate deposition was 8.4 kg S ha^{-1} year^{-1} from 1984 to 2001 (NADP 2006) and the poorly buffered soils have become more acidic through base cation depletion during the last several decades (Lawrence et al. 1999). The climate is humid continental, mean annual precipitation was 1,539 mm and mean annual temperature was 4.7°C from 1962 to 2001 at Slide Mountain about 5 km northeast of the study watershed (NCDC 2005). Precipitation was generally evenly distributed throughout the year and 20–25% occurred as snow. Runoff within the Neversink River basin averaged 980 mm from 1938 to 2001, about 1/3 of which occurred as snowmelt during March and April (Butch et al. 2002).

The Catskill Mountains are an uplifted plateau of Devonian age that has been eroded and dissected by streams (Buttner 1977). A thin layer of till was deposited by the most recent glaciation (Rich 1934). The bedrock within the Dry Creek watershed is sandstone and conglomerate interbedded with siltstone and shale (Way 1972). Differential weathering has created stair-step topography across most of the watershed, although till deposits on the west side obscure the stair-step topography; till thickness ranges from 0 m to 1.5 m. Elevation ranges from 706 m at the watershed outlet to 890 m at the upper divide. Soils are medium-textured excessively to moderately well-drained Inceptisols of the Arnot-Oquaga-Lackawanna association (Tornes 1979) but Spodosols occur in some areas. The forest floor is comprised of litter (Oi horizon) over an Oe horizon that is approximately 3 cm thick, and an Oa horizon that is also approximately 3 cm thick. A distinct separation between the forest floor and the mineral soil is usually present, but in some areas the Oa horizon is replaced by an organic-rich A horizon that

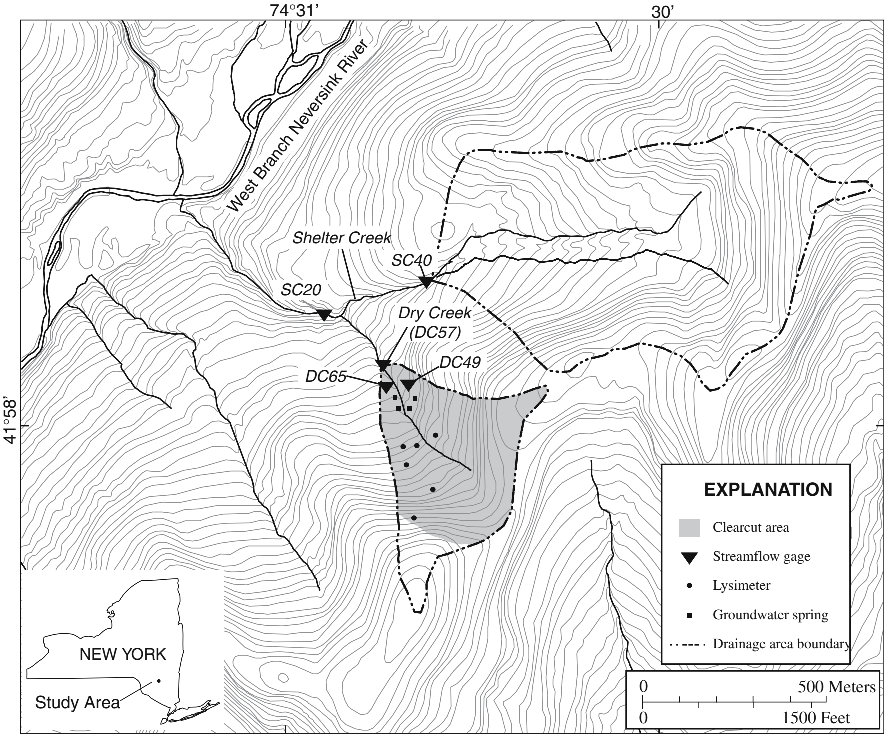

Fig. 1 Locations of clearcut area, streams, soil lysimeters, groundwater springs, and stream sampling sites in the Neversink River basin in southeastern New York

is approximately 5 cm thick. Where E horizons exist, they range from 2 cm to 10 cm thick and may overlie a Bh horizon up to 4 cm thick. In some areas Bs horizons can extend down to the 50 cm depth, but in most areas the majority of the profile is comprised of a Bw horizon over a Bc horizon that begins approximately 75–120 cm below the forest floor. Before clearcutting the overstory vegetation consisted of northern hardwoods including *Acer saccharum* Marsh. (sugar maple), *Fagus grandifolia* Ehrh. (American beech), and *Betula alleghaniensis* Britt. (yellow birch).

Seventy-five percent of the Dry Creek watershed was clearcut from December 1996 to March 1997. The forest had been selectively cut during the 1940s, but many trees 100+ years of age were present at the time of the clearcut. Slash (branches and tree tops) was left on the ground and arranged along temporary skid trails to create a ‘‘corduroy’’ surface to minimize soil disturbance and conserve nutrients in the watershed. Soil disturbance was minimized during the harvest so study results would provide an indication of the watershed response to other types of forest disturbance in this region that could decrease the uptake of N such as wind damage or insect infestation. A 6-ha area in the southwest corner of the watershed was not harvested because the area is protected as New York State ‘‘Forever Wild’’ land. The clearcut decreased the basal area of the harvested area of the watershed by 97% and by 80% for the entire watershed (Yorks 2001). The harvested area of the watershed was fenced to prevent deer-browsing and therefore to promote forest regrowth following the harvest**.** The Shelter Creek watershed (SC40) was selectively harvested in two phases in the winter of 1995–1996 and the fall of 1997 which resulted in about a 8% removal of the basal area, there was no discernable streamwater chemical response to the harvest and those results are not discussed further. The Neversink River basin and the Dry Creek watershed have been areas of extensive research on nitrogen cycling and the effects of acid rain since 1990. The pH of acid rain increased during the 1990s as a result of the Clean Air Act of 1990 (Murdoch and Stoddard 1993) but the acidity of streamwater within the Neversink River basin changed little because initially poorly buffered watershed soils were further depleted of base cations by decades of acid rain (Lawrence et al. 1999). In addition, NO_3^- has been gradually replacing SO_4^{2-} as the dominant acid anion in Catskill streams as the rate of SO_4^{2-} deposition has declined. Mean annual air temperature was a reasonable predictor of streamwater NO_3^- concentration in the Biscuit Brook watershed, a headwater catchment of the Neversink River basin, which suggests that from 1984 to 1997 N mineralization and nitrification had a greater control on streamwater mean annual NO_3^- concentration than annual N deposition or uptake of N by vegetation (Murdoch et al. 1998). In the Dry Creek watershed, groundwater springs were a significant source of NO_3^- in streamwater during baseflow by delivering NO_3^- that was recharged primarily during the biologically inactive season (Burns et al. 1998).

Methods

The study was divided into three periods: preharvest (water years 1993–1996 prior to the clearcut), harvest (water years 1997–1999, the clearcut year and 2 years after the clearcut) and postharvest (water years 2000–2001, 4 and 5 years after the clearcut). The water year is defined as October 1 through September 30. For some of the analyses the study period was grouped into a nonharvest period, which combined the pre- and postharvest periods and a harvest period (water years 1997–1999).

Field methods

Soil samples were collected from 43 soil pits within the Dry Creek watershed before the harvest; 12 of these were sampled at 0.1 m depth intervals from each soil horizon and the other 31 were sampled by horizon—one sample from each horizon. An additional 16 soil pits were sampled at 0.1 m depth intervals 2 years after the harvest.

There were two types of water sampling conducted during the study (1) soil lysimeters and groundwater springs were sampled biweekly or monthly to characterize the chemistry of streamwater sources during the study and (2) three gaging stations were established within the watershed where discharge was monitored and grab sampling and automated storm sampling were conducted to estimate solute export and quantify the contribution of soil water and groundwater sources to the stream. A description of both types of sampling follows.

Soil water was collected from six sets of zero-tension soil lysimeters. Each set consisted of three lysimeters at each of three depths 5–10 cm in the O horizon, 25–30 cm in the B horizon, and at the bottom of the B horizon, referred to hereafter as the lower B horizon, whose depth ranged from 40 cm to 90 cm depending on location. The three lysimeters at each depth drained to one receptacle that was vented to the atmosphere to prevent vapor-lock. The receptacles were sampled approximately monthly throughout the study. Four small groundwater springs that emerged from the foot of hillslopes in the watershed were sampled biweekly to characterize the chemistry of groundwater that contributed to streamflow throughout the study.

Stream discharge was recorded every 15 min by electronic dataloggers at the outlet and at two sub-basins within the Dry Creek watershed (Fig. 1). The watershed outlet (DC57) was gaged at an H-flume. One perennial groundwater spring (DC49; 7.3 ha) was gaged using a trapezoidal flume where the spring emerged from the bottom of a hillslope about 100 m from Dry Creek (Fig. 1). One intermittent stream that drains 3.3 ha (DC65) was gaged with a V-notch weir about 30 m upstream from where it joins Dry Creek. DC65 flowed during snowmelt and in response to storms; water chemistry at the site was similar to that of B-horizon soil lysimeters. Therefore, soil water solute export was estimated from DC65 streamwater. Water samples were collected weekly or biweekly from October 1, 1993 to September 30, 2001 at all gaging stations and storm samples were collected by stage-activated automatic samplers. Grab samples were transported on ice to the laboratory immediately after collection; stormflow samples were retrieved soon after storms (maximum of 1 week after collection) and transported to the laboratory for analysis.

Laboratory methods

Soil samples were air dried and sieved (4 mm for forest floor and 2 mm for mineral soil) before analyses for total N, exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+ in 1 M NH_4Cl), pH (0.01 M $CaCl_2$ and water), and for loss-on-ignition in accordance with EPA standard methods (Blume et al. 1990), and for exchangeable acidity (Al, H^+ in 1 M KCl) by the method of Thomas (1982).

Soil water and streamwater samples were kept chilled at 4°C until analysis by ion chromatography for Cl^-, SO_4^{2-}, and NO_3^- and atomic absorption spectrophotometry for Na^+, K^+, Ca^{2+}, Mg^{2+}, and total Al (Al_{tot}) (Lawrence et al. 1995). A flow-injection spectrophotometric system was used to analyze dissolved silica (SiO_2), an ion selective electrode was used to analyze total fluoride, a Dohrmann carbon analyzer for dissolved organic carbon (DOC), a pH electrode for pH, and an auto-titrator for ANC (acid neutralizing capacity) (Lawrence et al. 1995). Speciated Al was determined by complexation with pyrocatechol violet according to a two-channel flow injection method (Henshaw et al. 1988). The first channel yields total monomeric Al (Al_{mono}) on an untreated aliquot, and the second channel yields organic monomeric Al (Al_{org}) after the sample passes through a cation exchange resin. Inorganic monomeric Al was estimated as the difference between Al_{mono} and Al_{org}. DOC samples were filtered through nominal 0.7 μ glass fiber filters prior to analysis. In December 1998 the analytical method for Ca^{2+}, Mg^{2+}, SiO_2, and Al_{tot} was changed to inductively coupled plasma—optical emission spectrometry; the old and new methods were used concurrently for 3 months to ensure comparability of results.

Data analyses

Soil chemical data were used to calculate the cation exchange capacity (CEC), the percent base saturation (%BS), and the calcium/aluminum ratio (Ca:Al) of each soil sample. Data from the incrementally sampled soil pits were identified as belonging to Oi, Oa/As, B and lower B horizons. Results from soil chemical analyses were separated into preharvest and postharvest periods to identify changes in soil chemistry that occurred as a result of the clearcut.

Soil water chemistry was averaged for the six lysimeter sites in the watershed for each sample date at each soil horizon. The result was an average soil water chemistry for the O, B, and lower B soil horizons for each sample date. Annual means were calculated for O-horizon, B-horizon, and lower B-horizon soil water, although correlation analyses were applied only to O-horizon and B-horizon soil water because lower B-horizon soil water was similar to B-horizon water (Table 1). The chemical-equilibrium model ALCHEMI (Schecher and Driscoll 1988) was used to calculate Al speciation and mineral saturation indices for O-horizon and B-horizon soil water. Model variables included stream-water temperature and ionic concentrations (Al_{im} for aluminum). The partial pressure of CO_2 in the soil water was assumed to be in equilibrium with atmospheric CO_2; this assumption was considered acceptable because the equilibrium of carbon species has little effect on Al speciation at low pH values. The model uses pH, SO_4^{2-}, SiO_2 and total F to calculate the distribution of Al species. Total F was measured for 564 of the 745 samples used in ALCHEMI (Total F is measured for samples with pH < 5.2 and Al_{im} concentrations above 1 μmol l^{-1}, where appreciable total F concentrations are expected). Total F was calculated for the remaining 181 samples based on linear regression equations developed for Ca^{2+} and total F with the samples for which both solutes were measured. Different equations were calculated for soil water from each horizon all with r^2 values >0.8. Modeled Al species concentrations were used in annual watershed charge balances and to investigate the solid phase controls on Al solubility in the Dry Creek soils.

Total annual solute loads for the outlet (DC57), the groundwater spring (DC49), and the intermittent stream (DC65) were estimated using the non-linear regression equation of Johnson et al. (1969) that

Table 1 Mean soil water, groundwater springs, and watershed gaging station water chemistry in Dry Creek watershed before, during, and after the clearcut (December 1996 to March 1997)

Water Source[a]	n	pH	ANC	Ca	Mg	K	Na	Cl	NO_3^-	SO_4^{2-}	DOC	SiO_2	Al_{tot}	Al_{mono}	Al_{org}	Al_{im}
Preharvest water years 1994–1996																
O horizon	151	4.5	−50.1	36.1	15.1	18.0	8.8	15.6	73.1	48.9	823.2	28.9	24.7	17.7	7.0	10.7
B horizon	134	4.7	−28.5	30.5	14.8	5.6	12.6	16.4	40.9	54.4	177.3	28.6	16.6	13.3	1.4	12.0
Lower B horizon	187	4.7	−19.5	23.3	13.8	4.9	10.8	16.6	34.9	54.5	144.7	33.4	27.2	16.3	1.2	15.1
Groundwater springs	166	6.2	87.9	76.1	36.4	7.3	22.6	16.4	22.1	63.3	57.6	48.0	21.8	0.9	0.3	0.5
DC65 (soil water)	74	4.5	−35.4	20.5	11.4	12.6	9.4	16.2	27.5	49.1	287.4	25.8	17.3	10.0	2.0	8.0
DC49 (gw spring)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DC57 (outlet)	223	6.0	30.6	54.9	26.3	7.6	17.0	15.4	20.4	57.0	165.2	37.4	10.5	2.0	0.9	1.1
Harvest water years 1997–1999																
O horizon	141	4.3	−81.8	55.7	24.9	28.3	8.0	16.1	260.4	39.8	699.4	27.8	39.8	31.1	6.4	24.7
B horizon	181	4.4	−57.0	67.1	33.5	21.9	11.5	17.7	345.3	39.1	175.7	34.2	58.6	46.5	1.7	44.8
Lower B horizon	197	4.5	−42.1	60.9	31.6	18.7	11.1	17.7	331.0	36.8	163.0	35.1	70.4	51.5	1.6	49.9
Groundwater springs	110	6.4	104.3	105.8	48.8	10.2	28.0	15.3	122.6	50.7	76.0	43.2	7.3	1.3	0	1.3
DC65 (soil water)	202	4.3	−53.9	44.8	24.2	25.3	9.0	15.6	259.4	36.1	262.7	31.8	49.6	37.7	2.3	35.4
DC49 (gw spring)	302	6.3	122.3	107.3	49.3	10.2	30.7	14.9	105.8	52.6	76.8	44.0	1.4	0.7	0.2	0.5
DC57 (outlet)	299	5.6	6.3	85.5	53.2	17.4	17.2	16.1	206.9	41.7	162.8	35.3	17.6	7.8	0.7	7.1
Postharvest water years 2000–2001																
O horizon	61	4.6	−30.8	26.4	12.0	21.8	7.1	10.6	25.1	45.9	559.4	32.0	13.3	6.7	3.2	3.5
B horizon	82	4.6	−24.6	25.2	12.1	9.7	7.9	9.4	22.2	51.6	224.4	32.7	13.1	7.6	1.0	6.6
Lower B horizon	86	4.7	−15.7	21.8	11.3	11.2	7.3	9.0	20.2	53.7	184.3	36.7	18.2	9.8	0.7	9.0
Groundwater springs	72	6.6	124.0	86.8	41.3	10.2	25.2	13.2	38.1	57.1	72.2	44.4	2.5	0.2	0	0.5
DC65 (soil water)	92	4.7	−17.2	24.1	13.1	14.3	7.5	10.0	28.4	47.9	242.2	35.7	13.7	6.2	1.1	5.1
DC49 (gw spring)	105	6.7	143.0	91.3	43.1	9.8	28.0	13.3	32.3	57.5	71.9	45.6	1.6	0.2	0	0.2
DC57 (outlet)	213	6.1	39.0	56.4	26.4	15.0	15.2	11.9	33.0	50.9	208.9	36.3	4.1	1.1	0.3	0.8

Site locations are shown in Fig. 1

[a] Soil water is averaged from six sets of zero tension lysimeters. Groundwater spring chemistry is averaged from four springs within the watershed. DC49 is a gaged groundwater spring, DC65 is a small gaged intermittent stream used as a surrogate for soil water, and DC57 is the watershed outlet. Values are nonvolume weighted means in μmol l^{-1}

predicts concentration as a function of discharge. Nonlinear regression equations were developed for NO_3^- and Ca^{2+} for harvest and nonharvest periods. Separate equations for harvest and nonharvest periods were needed because the relation between discharge and concentration changed after the clearcut. Nitrate required four separate periods to reflect the changes that occurred in the discharge-concentration relation; Ca^{2+} required two periods. The fit was too poor to be used for load estimation for some periods at DC57, and DC65; concentrations during those periods were estimated using linear interpolation between sample concentrations. The load estimates provided by the linearly interpolated data were considered reasonable because of the frequent sample collection (weekly or bi-weekly and storm sampling).

Results

Soil chemistry and soil–water chemistry response to the harvest

Soil chemistry data generally indicate acidification at the shallowest depths (Oi and Oa/As) as a result of the harvest and little or no acidification in the B and lower B horizon (Table 2). This pattern is exemplified by post-harvest decreases in exchangeable cations and pH in the Oi and increases in exchangeable Al and H^+ in the Oa/As, whereas little change was evident in these parameters in the B or lower B horizon. The calculated parameters, %B.S. and Ca:Al also show this pattern of post-harvest change with depth; decreased %B.S. and Ca:Al in the Oi, and little change in the B or lower B.

The greatest changes in soil water and groundwater chemistry observed as a result of harvesting were NO_3^- concentrations, which increased 4- to 10-fold during the harvest period relative to the preharvest period (Table 1, Fig. 2). Before the harvest O-horizon soil water had the highest mean NO_3^- concentrations of any water sampled in the watershed, during the harvest period B-horizon soil water had the highest NO_3^- concentrations, and during the post-harvest period groundwater springs had the highest mean concentrations (Table 1). The concentrations of the aluminum species Al_{tot}, Al_{mono}, and Al_{im} also increased sharply by as much as 4-fold as a result of the harvest. Little or no change was evident in Al_{org} concentrations after the harvest indicating that the increases in Al_{tot} and Al_{mono} concentrations in these waters resulted only from increased Al_{im} concentrations after harvesting. Nitrate and Al_{im} concentrations decreased during the postharvest

Table 2 Soil properties in Dry Creek watershed before and after forest harvesting (1996–1997)

Horizon	*n*	pH-w	pH-Ca	%LOI	%C	%N	C:N	Exchangeable cations, $Cmol_c\ kg^{-1}$								
								Ca	Mg	K	Na	Al	H^+	CEC	%B.S.	Ca:Al
Preharvest																
Oi	11	4.50	3.88	88	47.8	2.69	18.6	23.55	4.70	3.83	0.09					
Oa/As	16	3.83	3.21	34	17.7	1.03	16.4	3.53	0.87	0.63	0.03	4.73	4.09	13.87	35.8	0.75
B	79	3.90	3.38	5	2.5	0.18	11.8	0.38	0.12	0.11	0.02	5.34	1.74	7.72	8.0	0.07
Lower B	47	4.40	3.78	2	0.9	0.14	7.3	0.15	0.04	0.06	0.01	3.53	0.48	4.27	6.1	0.04
Postharvest																
Oi	27	4.06	3.38	78	41.9	2.23	18.7	13.88	2.69	1.63	0.05					
Oa/As	26	3.77	3.13	43	24.2	1.38	17.4	3.96	0.82	0.71	0.04	7.82	4.80	18.15	29.7	0.51
B	98	4.13	3.46	4	3.7	0.25	13.5	0.26	0.08	0.12	0.01	5.48	1.54	7.49	6.7	0.05
Lower B	34	4.40	3.71	2	0.9	0.07	12.9	0.11	0.03	0.07	0.01	3.65	0.42	4.29	5.2	0.03

Means are from 12 soil pits that were sampled at 10 cm intervals and 31 soil pits that were sampled by horizon before the clearcut (preharvest) and 16 soil pits that were sampled at 10 cm intervals 2 years after the clearcut (postharvest). The difference in sample numbers between horizons reflects sampling at 10 cm intervals through each horizon

pH-w = pH measured in water, pH-Ca = pH measured in calcium chloride, % LOI = percent loss on ignition, %C = percent carbon, %N = percent nitrogen, CEC = cation exchange capacity, %BS = percent base saturation, Ca:Al = the calcium/aluminum ratio of the soil

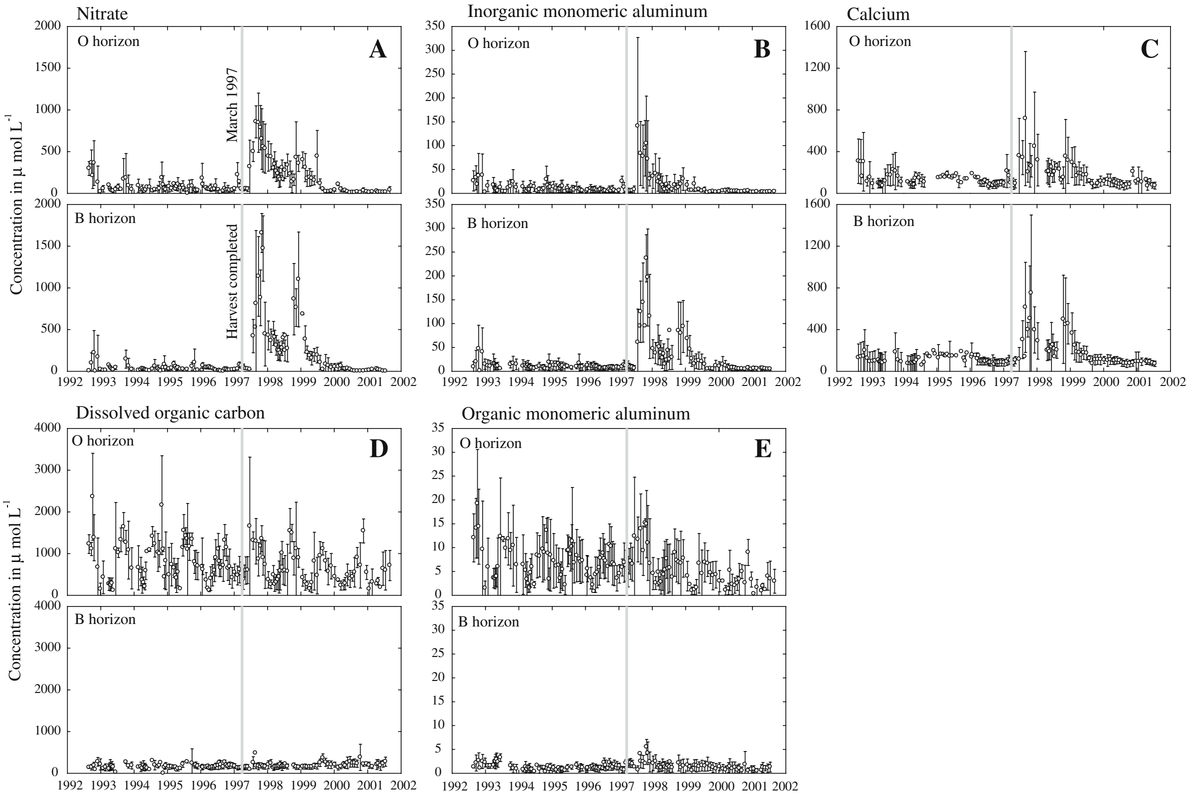

Fig. 2 Concentrations of (**A**) Nitrate, (**B**) Inorganic monomeric Aluminum, (**C**) Calcium, (**D**) Dissolved organic carbon, and (**E**) Organic monomeric Aluminum in soil water from 6 sets of zero tension lysimeters in the Dry Creek watershed in the Catskill Mountains of southeastern, NY (site locations are shown in Fig. 1, values are means for all lysimeters sampled on a given date error bars indicate 1 std. dev. from the mean)

period in O- and B-horizon soil water to values less than those of the preharvest period.

The base cations Ca^{2+}, Mg^{2+}, and K^+ also showed large increases in concentrations of up to 3-fold in soil water and springs as a result of the harvest (Table 1, Fig. 2). There were decreases in pH and ANC. Similarly to NO_3^- and Al_{im}, Ca^{2+}, Mg^{2+}, and K^+ concentrations decreased during the postharvest period to values less than those of the preharvest period. These changes were paralleled by postharvest increases in pH and ANC to values greater than those of the preharvest period.

Sulfate concentrations also decreased in soil water and groundwater springs during the harvest period. These decreased SO_4^{2-} concentrations combined with increased NO_3^- concentrations resulted in a shift of the most dominant acidic anion from SO_4^{2-} to NO_3^- during the harvest period (Fig. 3). Dissolved organic carbon and SiO_2 showed little or no change as a result of the harvest.

The B-horizon soil water generally showed greater and more persistent changes than O-horizon soil water in some of the key chemical constituents that responded to harvesting. First, Ca^{2+} and NO_3^- concentrations were greater in O-horizon soil water than in B-horizon soil water before the harvest, but increased to a greater extent in the B than in the O horizon during the harvest period (Table 1). These changes were sufficient to cause a shift to values that were greater in the B than in the O horizon during the harvest period. Al_{im} concentrations also increased to a greater extent in the B than in the O horizon from the preharvest to harvest periods, though these concentrations were greater in the B than in the O horizon prior to the harvest. Second, elevated Ca^{2+}, NO_3^-, and Al_{im} concentrations

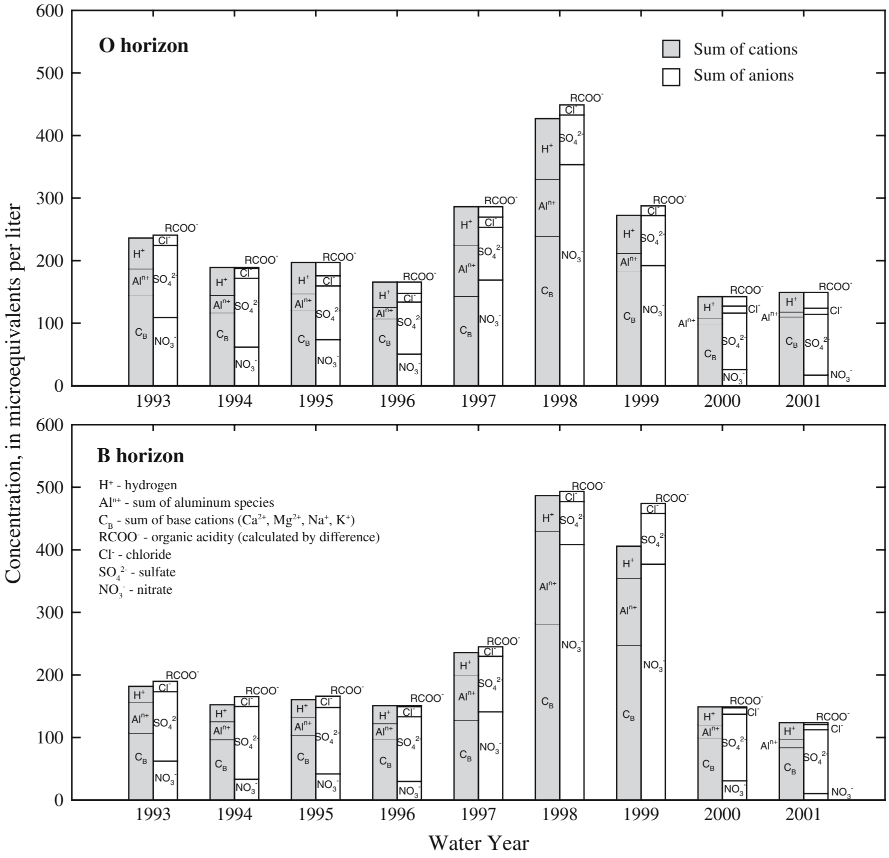

Fig. 3 Distribution of ionic species in soil water within the Dry Creek watershed in the Catskill Mountains of southeastern, NY 1993–2001. The harvest was completed in March, 1997. Locations of watershed and sampling sites are shown in Fig. 1

persisted longer in B-horizon soil water than in the O horizon (Fig. 2).

Although base cation (Ca^{2+}, Mg^{2+}, and K^{+}), H^{+}, and Al_{im} concentrations increased as a result of the harvest, they did not increase in equal proportions relative to the total positive charge in soil solution. Base cations made up the largest percentage of the cation charge balance throughout the study and showed the largest absolute increase as a result of the harvest (Fig. 3). The sum of positively charged Al species (Al^{n+}) in B-horizon soil water represented about 20% of the cation charge balance during the preharvest period but increased to 30% during the harvest period a 6-fold increase in response to the large increase in NO_3^- concentrations (Fig. 3). The response of O-horizon soil water was similar—Al^{n+} increased 5-fold from 14% of the cation charge balance during the preharvest period to 25% during the harvest period.

According to ALCHEMI model results Al^{3+} accounted for most of the increase in Al_{mono} concentrations in O- and B-horizon soil water after the harvest (Fig. 4). Al_{mono} consisted of nearly equal amounts of trivalent monomeric aluminum (Al^{3+}) and Al_{org} (Al^{3+} 46%, Al_{org} 42%) in O-horizon soil water during the preharvest period. During the harvest period, Al^{3+} increased and accounted for 71% of Al_{mono}, whereas Al_{org} concentrations remained essentially constant which decreased the proportion of Al_{org} to 20%. During the postharvest period, Al^{3+} accounted for 38% and Al_{org} 43% of Al_{mono} in O-horizon soil water similar to the preharvest period. Al^{3+} was an even more dominant form of Al_{mono} in B-horizon soil water than in O-horizon soil water, accounting for 70% before the harvest, 83% during the harvest period, and 68% during the postharvest period.

Surface water response to the harvest

Changes in streamwater chemistry at the Dry Creek watershed outlet (DC57) as a result of the harvest

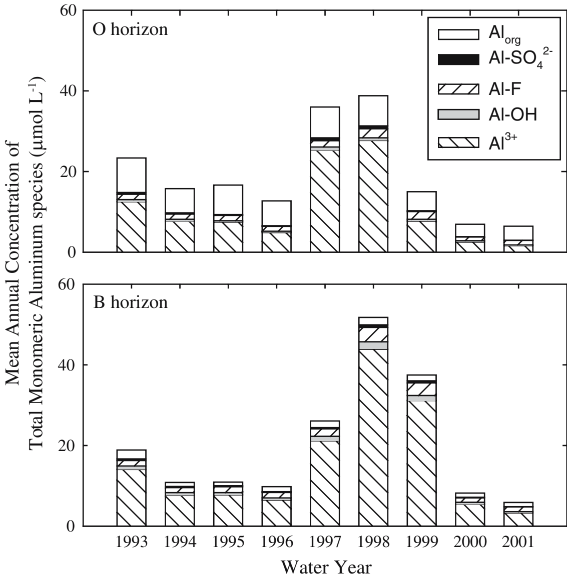

Fig. 4 Mean annual distribution of five monomeric aluminum species in soil water within the Dry Creek watershed, 1993–2001. The harvest was completed in March, 1997

were similar to those observed in soil water and groundwater springs (Table 1). The increases in soil water NO_3^- and Al_{im} concentrations were greater than those in Dry Creek, but the increases in Dry Creek represented a greater percent increase than those in soil water. Other changes in streamwater chemistry at Dry Creek such as increases in base cation concentrations and decreases in pH and ANC values were similar in direction to those of soil water and were comparable in magnitude or even greater than those of soil water, particularly compared to the response of Ca^{2+} and Mg^{2+} in O-horizon soil water.

Nitrate concentrations returned close to preharvest concentrations during 2000 (Fig. 5), but the mean value during the 2000–2001 postharvest period was 33 µmol l^{-1}, elevated relative to the preharvest mean value of 20.4 µmol l^{-1} (Table 1). In contrast, Al_{im}, Ca^{2+}, and Mg^{2+} concentrations and pH had all returned to preharvest values during the postharvest period (Table 1). Only K^+ concentrations like those of NO_3^- remained slightly elevated during 2000–2001.

Nitrate export at DC57 increased by about 4-fold to about 30 kg ha^{-1} year^{-1} during 1998 the first water year after the harvest (Fig. 6). Stream NO_3^- concentrations increased more than any other measured chemical constituent. The increased NO_3^- export measured in 1998 occurred despite stream runoff that was slightly less than that of the previous year (Fig. 6).

Export of Ca^{2+} also increased during 1998, but not as much relative to preharvest years as NO_3^- export (Fig. 6). Soil water Ca^{2+} export (as represented by DC65) increased about 2-fold from 1997 to 1998, but unlike that of NO_3^-, Ca^{2+} export at DC65 remained less than that at the watershed outlet. Groundwater (DC49 and other springs) contributed a greater proportion of Ca^{2+} export at the outlet than soil water because groundwater Ca^{2+} concentrations were about twice those of soil water and remained higher than soil water throughout the study period.

Additional streamwater samples and streamflow data were collected at (1) Shelter Creek (SC40), adjacent to Dry Creek and (2) Lower Shelter Creek (SC20) downstream from the confluence of Dry Creek (DC57) and Shelter Creek (SC40) (Fig. 1). Shelter Creek (SC40) contributed an average of 60%, and DC57 contributed an average of 8% of the total discharge measured downstream at Lower Shelter Creek (SC20) during the 6 years when all three gages were in operation (1994–2000). Shelter Creek (SC40) provided a nearly 8-fold dilution of the discharge of DC57, and dilution was about 12-fold at Lower Shelter Creek (SC20). There was a short period of increased Al_{im} concentrations at the Lower Shelter Creek gaging station (SC20) after the Dry Creek harvest from November 1997 to January 1998 (Data not shown). Nitrate concentrations at the SC20 gaging station were elevated for about 2 years after the Dry Creek harvest and peaked at 120 µmol l^{-1} (Data not shown). The small response of stream water concentrations at SC20 was presumably caused by dilution of stream water from the Dry Creek watershed with stream water from the Shelter Creek watershed; Shelter Creek had a pH of about 6.0 and Al_{im} concentrations of <2 µmol l^{-1} at baseflow. Dilution by inflowing groundwater accompanied by in-stream precipitation of Al minerals also likely occurred downstream of the gage on Dry Creek upstream of where it enters Shelter Creek. Additional precipitation of Al minerals may have occurred downstream of the confluence of Dry Creek and Shelter Creek as Dry Creek with more acidic water and higher Al_{im} concentrations mixed with the less

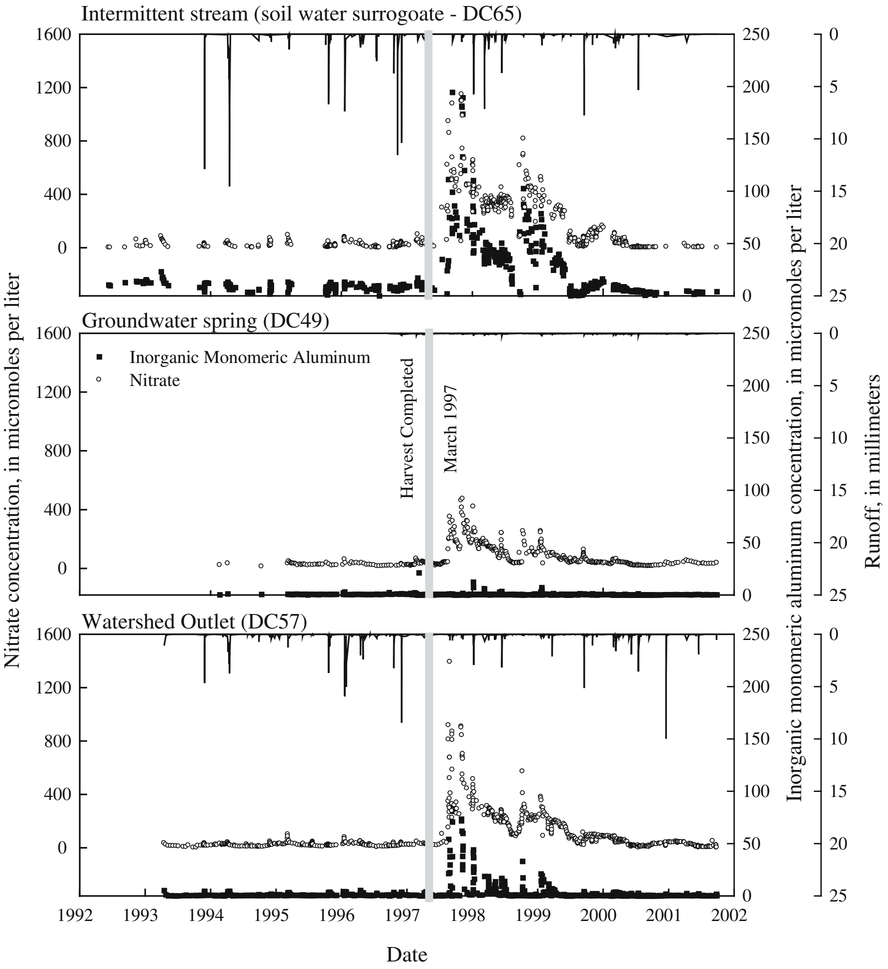

Fig. 5 Runoff and concentration of nitrate and inorganic monomeric aluminum (Al_{im}) at the intermittent stream used as a soil water surrogate (DC65), a groundwater spring (DC49), and the watershed outlet (DC57) from 1993 to 2001 (location of each site is shown in Fig. 1)

acidic Shelter Creek, but Al precipitation was not measured in this study.

Interactions among chemical species

High concentrations of Al_{im} in soil water and streamwater are of concern because this form of Al is toxic to aquatic biota. The relation between solutes, as expressed in bivariate plots, can provide an indication of the effect exerted by one solute on another and thereby provide an understanding of the mechanisms responsible for Al_{im} release after the harvest. Al_{org} is not toxic to aquatic biota, accounted for 20–43% of the Al_{mono} in O-horizon soil water, and was the largest component of Al_{mono} during the postharvest period (Fig. 4). Al_{org} concentrations in O-horizon soil water were well correlated to DOC (Fig. 7) where concentrations of the two constituents were high relative to B-horizon soil water. Al_{im} was not significantly correlated with DOC and concentrations of NO_3^- and Al_{im} were not well correlated with Al_{org} concentrations in O- or B-horizon soil water (Data not shown).

Hydrogen ion concentration was significantly correlated with NO_3^- and Ca^{2+} concentration in O- and B-horizon soil water (Fig. 8), but the correlations were strongest for the B horizon (Fig. 8A, B). NO_3^- was correlated with Al_{im} and Ca^{2+} concentrations in O- and B-horizon soil water (Fig. 8C, D), again correlations were strongest for the B horizon.

The negative logarithm of hydrogen ion activity (pH) and the negative logarithm of Al^{3+} activity plus ½ the negative logarithm of imogolite (H_4SiO_4) activity (pAl + ½ pH_4SiO_4) and pH versus pAl for soil solutions, perennial springs, and streamwater at the watershed outlet (DC57) were plotted to inves-

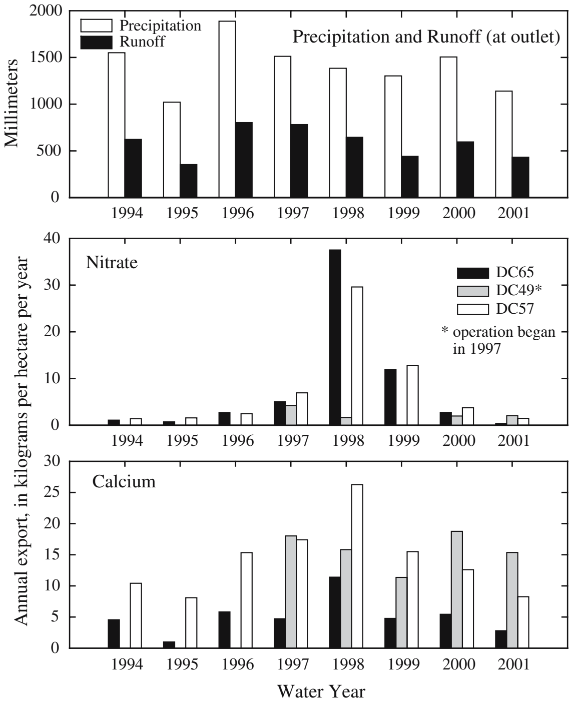

Fig. 6 Runoff, precipitation, and estimated nitrate (as N) and calcium export at sites DC65 (soil water surrogate), DC49 (groundwater spring), and DC57 (watershed outlet) water years 1994–2001. (Precipitation data are from the Biscuit Brook National Atmospheric Deposition Program deposition collection station)

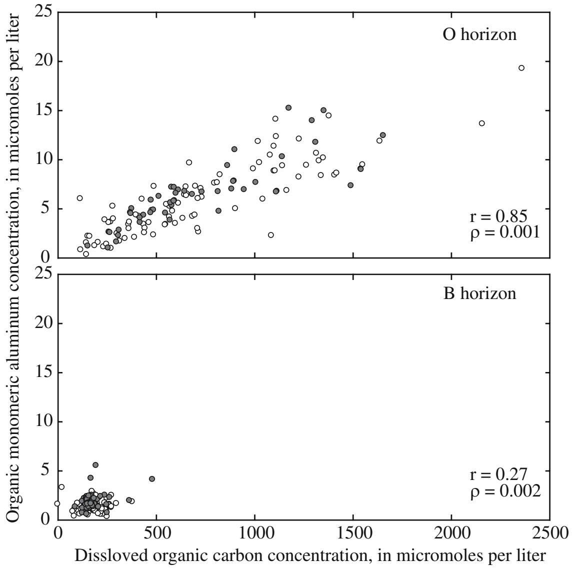

Fig. 7 Dissolved organic carbon and organic monomeric aluminum concentrations in soil water in the Dry Creek watershed in the Catskill Mountains of southeastern, NY

tigate the solid phase controls on Al solubility in soil solutions and determine the relative contributions of soil water and shallow groundwater to streamflow at the watershed outlet (Fig. 9). Imogolite (log $*K_s$ = 6.00; Farmer and Fraser 1982) and proto-imogolite (or imogolite-type materials) ($*K_s$ = 7.02; Lumsdon and Farmer 1995) were considered the most likely mineral phases that would control Al solubility given recent studies that have failed to find gibbsite in acidic forest soils (Gustafsson et al. 1995, 1998; Zysset et al. 1999) and that B-horizon soil water from this study was undersaturated with respect to gibbsite (Fig. 9). Although pH and pAl + ½ pH_4SiO_4 were strongly correlated in the O horizon, O-horizon soil water was undersaturated with respect to imogolite solubility (Fig. 9). The majority of B-horizon soil water samples plotted on or close to the imogolite equilibrium line, although the slope of the relation between pH and pAl + ½ pSi was less than 3 (2.4 for B-horizon soil water samples). Water from perennial springs had a pH and pAl + ½ pSi slope of 1.9 (Fig. 9). Streamwater at the outlet (DC57) had a slope of 1.6 and pH and pAl + ½ pH_4SiO_4 values spanned a large range of the activities calculated for soil water and groundwater. The chemical composition of streamwater at the outlet appeared to be influenced more by the perennial springs than soil water.

The sum of base cations (C_B) minus the sum of acid anions (C_{AA}) was used in place of pH to further investigate Al mobilization because C_B represents the ability of the watershed to buffer acidity through release of base cations and C_{AA} largely represents the input of inorganic acidity from nitrification and acidic deposition. The concentration of Al_{im} was strongly related to C_B-C_{AA} at C_B-C_{AA} values less than 0 μeq l^{-1} in DC65 streamwater, which was used as a surrogate for soil water (Fig. 10). In groundwater represented by DC49, C_B-C_{AA} rarely dropped below 0 μeq l^{-1} and Al_{im} concentrations were consistently low even after the harvest. In outlet streamwater (DC57) the majority of C_B-C_{AA} values were greater than 0 μeq l^{-1} and the most acidic samples were collected during the harvest period.

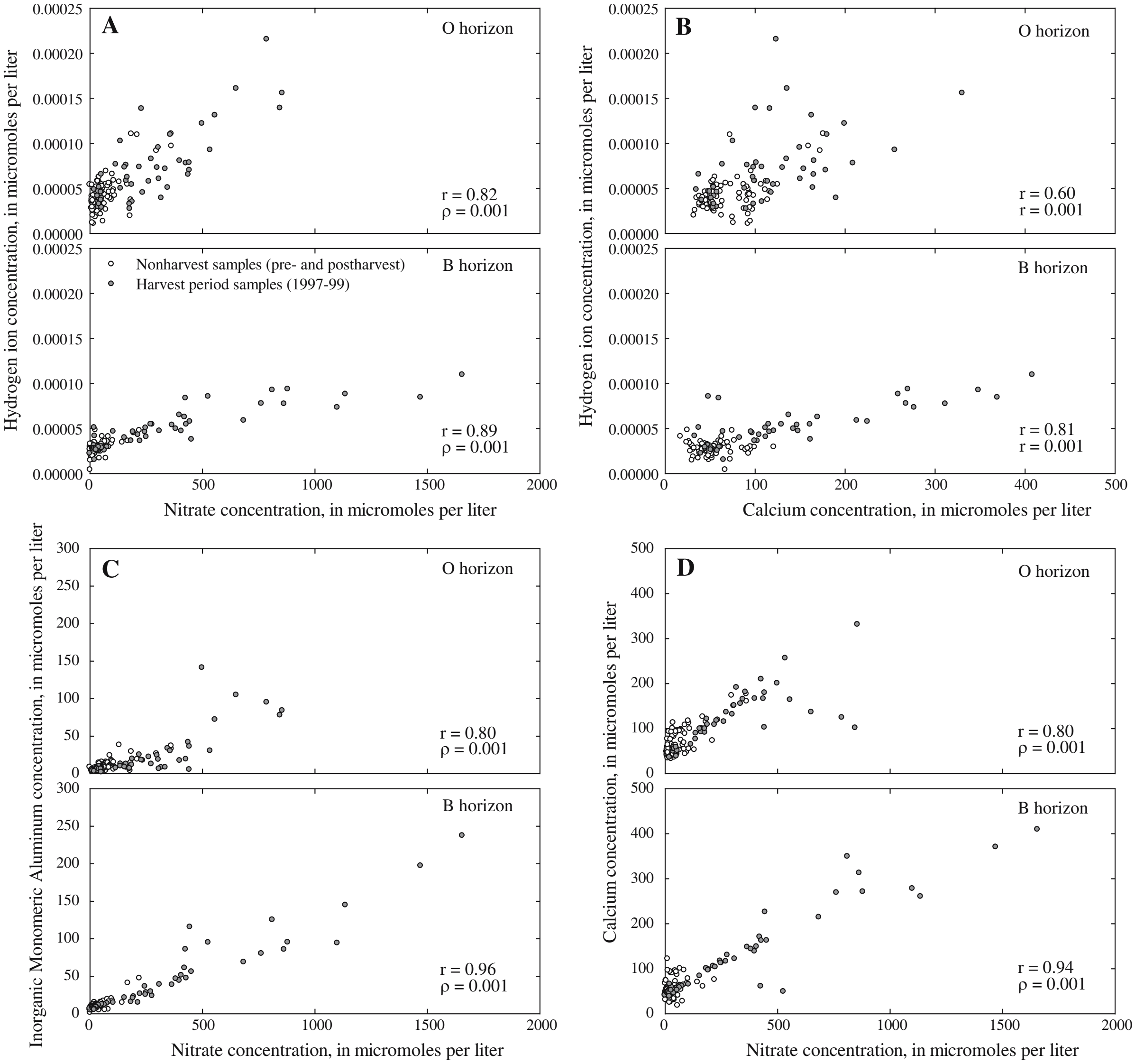

Fig. 8 Bivariate plots of selected solutes in soil water in the Dry Creek watershed in the Catskill Mountains of southeastern, NY

Discussion

Soil aluminum solubility

O-horizon soil water was undersaturated with respect to gibbsite, imogolite, and proto-imogolite solubility (Fig. 9A and E). Many earlier studies have reported aluminum undersaturation in organic soils (Bloom et al. 1979; Cronan et al. 1986; Walker et al. 1990; Berggren and Mulder 1995; Wesselink et al. 1996; Simonsson and Berggren 1998), which has been attributed to complexation reactions with soil organic matter. The slope of the pH-pAl relation for O-horizon soil water was 2.0, which is consistent with an Al solubility control by organic complexation (Tipping et al. 1995; Berggren and Mulder 1995; Gustafsson et al. 2001). The strong correlation between DOC and Al_{org} (Fig. 7) in Dry Creek O-horizon soil water suggests that Al_{org} concentration is closely related to the amount of organic matter in solution (Fig. 7). Nevertheless, Al^{3+} was the dominant form of Al measured in O-horizon soil water (Fig. 4) and there was a strong correlation between pAl + ½ pH_4SiO_4 and pH indicating that, as has been

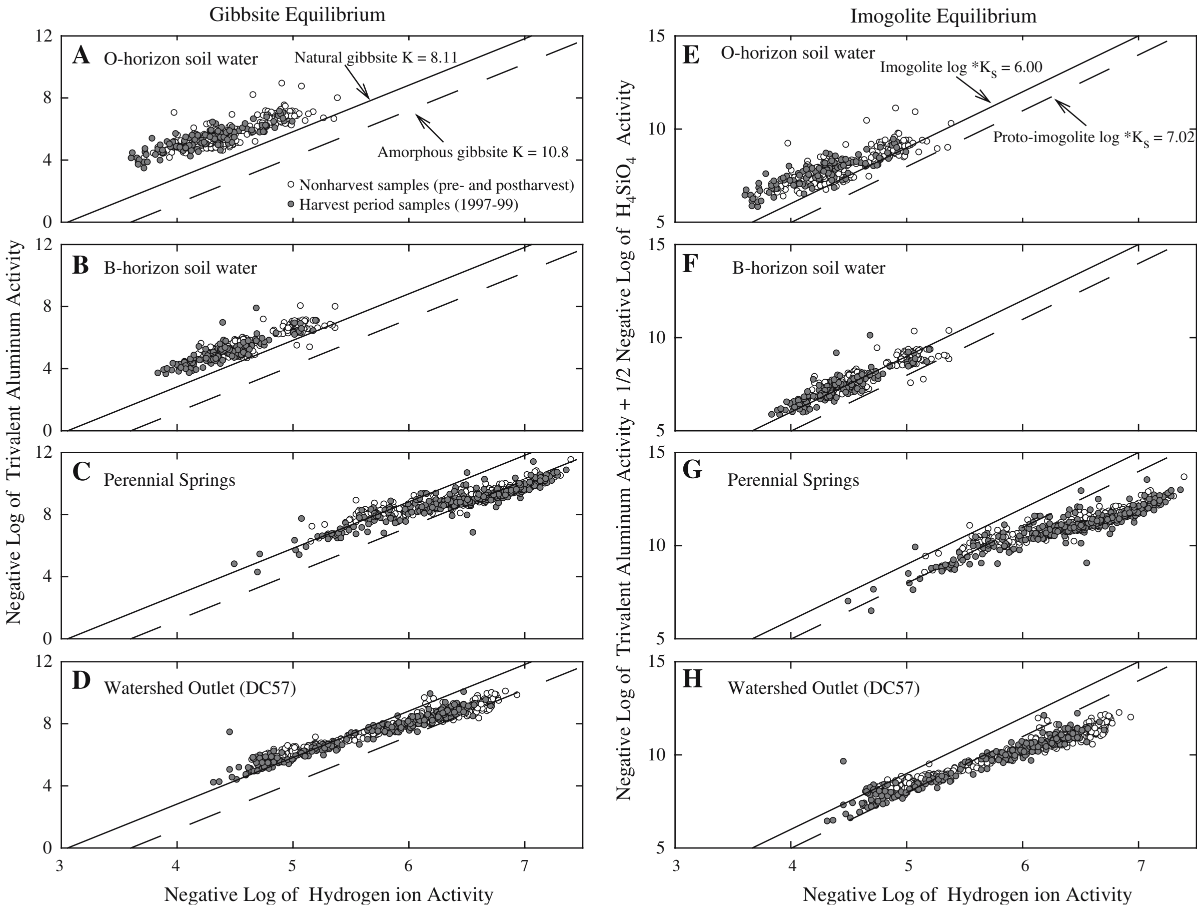

Fig. 9 Negative log of trivalent aluminum activity (pAl) and negative log of hydrogen ion activity (pH) (panels **A–D**) and negative log of trivalent aluminum activity plus ½ negative log of H_4SiO_4 (imogolite) activity (pAl + ½ pH_4SiO_4) and negative log of hydrogen ion activity (pH) (panels **E–H**) in soil water samples from O and B horizons, groundwater from 4 perennial springs, and outlet streamwater (DC57) in Dry Creek watershed in the Catskill Mountains of southeastern, NY

reported previously (Tipping 1994; Rustad and Cronan 1995; Berggren and Mulder 1995; de Wit et al. 1999), Al solubility controlled by complexation with organic matter is still strongly pH dependent. Cronan et al. (1986) and Walker et al. (1990) found that the degree of Al saturation of organic exchange sites, or the bound Al ratio, and solution pH controlled Al solubility in organic soils. Previous studies of Al mobility in organic forest soils have indicated that soil pH, the amounts of bound and free Al, and the form of soil water DOC all affect Al concentration and form in soil water (Ares and Ziechman 1988; Reuss et al. 1990; Walker et al. 1990). Some of these factors changed dramatically after the harvest, pH decreased rapidly which caused a large increase in free Al (Al^{3+}). The amount of bound Al in soil solution (Al_{org}) remained constant throughout the study as did soil water DOC concentration (Fig. 4). It is unclear whether organically bound Al in the soil was depleted since organically extracted soil Al was not measured.

B-horizon soil water appeared to follow the theoretical pH-pAl + ½ H_4SiO_4 equilibrium relation for imogolite (Fig. 9F), little carbon was available within this horizon for organic complexation of Al (Fig. 7). B-horizon soil water was undersaturated with respect to gibbsite ($Al(OH)_3$) (Fig. 9B). Previous studies have suggested equilibrium with $Al(OH)_3$ as a control on Al solubility (Dahlgren et al. 1989) or a simultaneous equilibrium between $Al(OH)_3$ and an imogolite-type material (proto-imogolite, allophone, or imogolite) (Farmer 1987; Dahlgren and Ugolini 1989). The removal of trees from the watershed decreased the uptake of N, which resulted in excess N

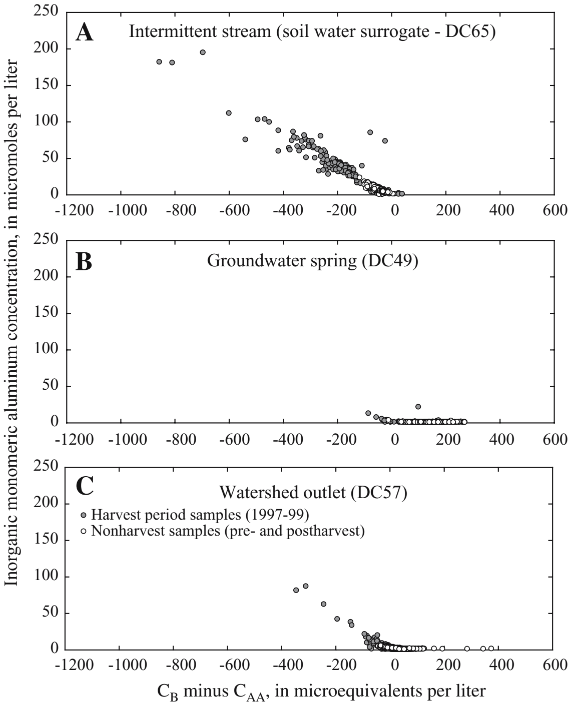

Fig. 10 Inorganic monomeric aluminum as a function of sum of base cations (C_B) minus sum of acid anions C_{AA} in streamwater for an intermittent stream that is used as a surrogate for soil water (DC65), groundwater from spring DC49, and streamwater at the watershed outlet (DC57) in Dry Creek watershed in the Catskill Mountains of southeastern, NY

within the soil. This excess N was nitrified (Burns and Murdoch 2005) and transported through the soil as a strong acid (HNO_3) that decreased soil water pH and mobilized Al_{im} most likely through ion exchange and dissolution of imogolite or imogolite-type materials. Much of the acidity created by the harvest was buffered through cation exchange reactions as evidenced by the large increase in base cation concentrations (Fig. 3), but when $C_B - C_{AA}$ concentrations dropped below zero the additional acidity was buffered by Al mobilization. These results follow the stages of soil acidification described by Ulrich (1983) where initial acidity is buffered by the carbonate system then by cation exchange and eventually by Al mobilization.

Sources of streamwater aluminum

B-horizon soils were likely the principal source of Al_{im} to streamwater in that the highest concentrations of Al_{im} measured throughout the study period were in B-horizon soil water (Table 1). Mean Al_{im} concentration during the harvest period increased by 14.0 μmol l^{-1} in O-horizon soil water, by 32.8 μmol l^{-1} in B-horizon soil water, and by 6.0 μmol l^{-1} at the watershed outlet (DC57). While the increase in B-horizon soil water Al_{im} concentration was the highest, the increase in stream water Al_{im} concentration represented a higher relative increase and at a mean concentration of 7.1 μmol l^{-1} was toxic to brook trout (*Salvelinus fontinalis*) (Baldigo et al. 2005). The increase in soil water Al_{im} concentrations was triggered by a decrease in soil water pH that resulted from the large pulse of NO_3^- that passed through the soil after the harvest as discussed previously. Streamwater NO_3^- concentrations before the harvest never exceeded 100 μmol l^{-1} the threshold below which NO_3^- and Al_{im} were not strongly correlated. As soil water NO_3^- concentrations increased above 100 μmol l^{-1} Al_{im} was leached from the soil (Fig. 8) and transported to the stream (Fig. 5).

Results from the ALCHEMI model and soil water lysimeters both indicate that the increases in Al_{mono} concentrations after the harvest were caused by the large increases in Al_{im}, primarily in the form of Al^{3+} (Table 1 and Fig. 4). The decrease in the percent of Al_{mono} that consisted of Al_{org} in O-horizon soil water as a result of the harvest was caused by the large increase in Al_{im} mostly in the form of Al^{3+}. During the postharvest, concentrations of Al^{3+}, Al_{im}, and accordingly Al_{mono} decreased as uptake of N increased in a regenerating forest accompanied by decreased NO_3^- leaching and increased soil water pH. Throughout this cycle of disturbance and recovery, Al_{org} concentrations remained about the same.

Factors that determined stream-water Al concentrations

Mean streamwater Al_{im} concentrations during the harvest period were 7.1 μmol l^{-1} and peak concentrations were as high as 86 μmol l^{-1}. These high concentrations caused 100% mortality of caged brook trout during April of the first year after the harvest (Baldigo et al. 2005). The Al solubility controls in the soil affected the Al concentrations in streamwater to the extent that soil water contributed to streamflow, and it is possible that the contribution from soils increased after harvesting as a result of decreased transpiration. However, groundwater was also a major component of streamflow in this watershed (Fig. 9), indeed groundwater discharge from springs is the principal source of streamflow during low flow periods in the Catskill Mountain region (Burns et al. 1998). Groundwater in this watershed was less acidic and had higher base cation concentrations and lower NO_3^- concentrations than soil water during the preharvest period (Table 1). Although NO_3^- concentration increased after the harvest, the pH of groundwater (at DC49) remained >5.5 and Al_{im} concentration remained low. As a result, groundwater C_B-C_{AA} rarely dropped below zero during the harvest period though when it did there was a corresponding increase in Al_{im} concentration (Fig. 10). Neither groundwater from the springs nor outlet streamwater (DC57) followed the theoretical solubility relationship for imogolite (Fig. 9). The relationship shown in Fig. 9, however, is affected by analytical uncertainty. Al_{im} is calculated by subtracting Al_{org} from Al_{mono} and the reporting limits for those constituents are both 1.5 µmol l^{-1}; only 11% of the data from the perennial springs and 42% of the data from the watershed outlet (DC57) had Al_{mono} concentrations greater than 1.5 µmol l^{-1} and much more of the data were close to the reporting limit. As a result Al_{im} concentrations were too low to allow much confidence in calculations of Al solubility controls in these waters.

The relation between C_B-C_{AA} and Al_{im} shown in Fig. 10 demonstrates the threshold level of acidity that must be reached before Al_{im} is mobilized. The threshold value for C_B-C_{AA} of approximately zero is consistent with results from a stream in an unharvested watershed in the Neversink River watershed where DOC concentrations are similarly low (Lawrence et al. 2007). Prior to the cut, mixing acidic soil water with well-buffered groundwater resulted in values of C_B-C_{AA} that were above zero in most streamwater samples, and Al_{im} concentrations that were correspondingly low. Acidification following the harvest decreased concentrations of C_B-C_{AA} in streamwater, which resulted in substantial increases in Al_{im} concentrations (Fig. 10).

Measurements made at Lower Shelter Creek (SC20, 161 ha), 0.25 km downstream from the outlet of the harvested watershed, showed only a small and short-lived increase in streamwater Al_{im} concentrations as a result of the harvest likely because there was about a 12-fold dilution of streamwater from the Dry Creek watershed (24 ha). The mixing of waters from the harvested (DC57) and lightly harvested (SC40) watersheds also increased the streamwater pH, which could have caused precipitation of Al minerals and a change in Al speciation (Neal and Christophersen 1989). Although many factors influenced streamwater Al_{im} concentrations at the outlet of the harvested watershed, dilution with streamwater from a lightly harvested watershed (8% removal of basal area) downstream from the harvest, and possibly in-stream Al precipitation and speciation (not measured), reduced streamwater Al_{im} and NO_3^- concentrations to background levels.

Comparison of results to previous forest harvesting studies

The results from this study generally agree with those of previous forest harvesting studies (Likens et al. 1969; Lawrence et al. 1987; Neal et al. 1992; Reynolds et al. 1992; Reuss et al. 1997), there was a sharp increase in soil water and streamwater NO_3^- concentrations accompanied by increases in base cation and Al_{im} concentrations. The contributions from acidic soil water and less acidic groundwater controlled the variation in streamwater pH and Al_{im} after a clearcut in 1987 in the Hafren forest in mid-Wales, Great Britain (Neal et al. 1992) in a manner similar to that observed here. Nonetheless, streamwater NO_3^- and Al_{im} concentrations from this study were much higher (NO_3^- 1,390 µmol l^{-1}; Al_{im} 86.4 µmol l^{-1}) than those reported for previous forest harvest studies in Colorado and New Hampshire (Lawrence et al. 1987; Reuss et al. 1997; Herrmann et al. 2001). The soils in the Dry Creek watershed have undergone decades of acidification by high rates of acid deposition that have decreased soil base saturation (Lawrence et al. 1999). Removing the trees from the watershed increased this rate of acidification by HNO_3 leaching of these already base-poor soils and resulted in larger peak streamwater NO_3^- and Al_{im} concentrations than have been reported in similar studies. The higher peak concentrations measured during this study may have been evident because of the emphasis on storm-event sampling at Dry Creek. These results underscore the importance of frequent sampling, particularly during storms, after disturbances to capture the magnitude of the streamwater response. Another difference between this and previous studies is that stream water NO_3^- concentrations had not fallen below preharvest concentrations in the stream by the end of 2001, 5 years after the harvest (Fig. 5). Preharvest soil water and streamwater NO_3^- concentrations and N deposition rates in Dry Creek were much higher than those measured in other harvesting studies (Lawrence et al 1987; Reynolds et al. 1992; Reuss et al. 1997). As forest regeneration continues and the demand for N increases streamwater NO_3^- concentrations will probably fall below preharvest concentrations, but these results support the conclusions of Dise and Gundersen (2004) that the response of an ecosystem to environmental stress depends on its state at the time of the stress and the long-term trends that have brought the ecosystem to its current state.

Conclusions

The 24-ha Dry Creek watershed showed sharp and substantial increases in NO_3^-, Al_{im}, and base cation (Ca^{2+}, Mg^{2+}, K^+) concentrations in streamwater and soil water in response to a 1996–1997 clearcut. The response of NO_3^- and Al_{im} concentrations in streamwater were similar, though higher than that reported for other forest harvesting studies. Streamwater NO_3^- concentrations had not fallen below preharvest levels 5 years after the harvest. In contrast, streamwater NO_3^- concentrations were below detection during the growing season 3 years after a whole-tree harvest at the Hubbard Brook Experimental Forest (Dahlgren and Driscoll 1994). Deer fence surrounding the Dry Creek watershed facilitated regeneration of a new forest dominated by pin cherry (*Prunus pensylvanica*) during the first few years, and soil water NO_3^- had fallen below preharvest values within 3 years after the harvest. The slightly elevated NO_3^- concentrations in streamwater 5 years after the harvest were likely the result of little attenuation or denitrification during transport through the groundwater flow system, which has been shown to have a residence of time of 2 years or more in this region (Burns et al. 1998).

Before the harvest soils in the Dry Creek watershed were characterized by low base saturation and high exchangeable Al concentrations and outlet streamwater NO_3^- concentrations averaged about 20 μmol l^{-1}. Organic complexation appeared to control Al solubility in the O-horizon and ion exchange and perhaps equilibrium with imogolite appeared to control Al solubility in the B-horizon. Because all of these solubility controls are strongly pH-dependent, the sharp decrease in soil water pH caused by the harvest resulted in large increases in Al_{im} in O-horizon and B-horizon soil water. Al_{im} concentrations were strongly related to those of NO_3^- in B-horizon soil water at NO_3^- concentrations greater than about 100 μmol l^{-1} and $C_B{-}C_{AA}$ values below about 0 μeq l^{-1} indicative of high rates of HNO_3 leaching of soils after harvesting. Below these thresholds acidity was buffered by base cations and streamwater Al_{im} concentrations were unrelated to pH and NO_3^- concentrations; above the thresholds the additional acidity was buffered in large part by Al mobilization.

Much of the Al mobilized in the soil by the harvest was transported to the stream as Al_{im}, which caused 100% mortality of caged brook trout (*Salvelinus fontinalis*) at the watershed outlet during the first year after the harvest (Baldigo et al. 2005). Streamwater Al_{im} concentrations were controlled by soil Al solubility to the extent that soil water contributed to streamflow, however streamflow had a large groundwater component that was characterized by circumneutral pH-low Al_{im} concentrations, and only slightly elevated NO_3^- concentrations. Mixing of low pH-high Al_{im} soil water with neutral pH-low Al_{im} groundwater ameliorated the effects of the harvest on the stream to some extent, but there was still a large increase in NO_3^- and Al_{im} export after the harvest. In-stream precipitation and dissolution of Al may also have affected streamwater Al_{im} concentrations, but this factor was not quantified.

Downstream from the harvested watershed streamflow was diluted by streamflow from an adjacent lightly harvested watershed to the point that NO_3^- and Al_{im} concentrations were only slightly elevated above background concentrations even during the 3 years immediately after the harvest. The status of the ecosystem at the time of the disturbance, low soil base saturation and high acid deposition, affected the magnitude of the response to the harvest and the rate of recovery from the disturbance. Frequent sampling, especially during storms, was necessary to characterize the magnitude of the soil water and stream water response to the harvest.

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