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Effect of whole catchment liming on the episodic acidification of two adirondack streams

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Abstract. During the fall of 1989 7.7Mg/ha of calcium carbonate was applied on two tributary catchments (40 ha and 60 ha) to Woods Lake, a small (25 ha) acidic headwater lake in the western Adirondack region of New York. Stream-water chemistry in both catchment tributaries responded immediately. Acid-neutralizing capacity (ANC) increased by more than 200 μeq/L in one of the streams and more than 1000 μeq/L in the other, from pre-liming values which ranged from -25 to $+40$ μeq/L. The increase in ANC was primarily due to increases in dissolved Ca^{2+} concentrations. Most of the initial response of the streams was due to the dissolution of calcite that fell directly into the stream channels and adjacent wetlands. A small beaver impoundment and associated wetlands were probably responsible for the greater response observed in one of the streams.

After the liming of subcatchment IV (60 ha), Ca^{2+} concentrations increased with increasing stream discharge in the stream during fall rain events, suggesting a contribution from calcite dissolved within the soil and transported to the stream by surface runoff or shallow interflow. Concentrations of other ions not associated with the calcite (e.g. Na^+) decreased during fall rain events, presumably due to mixing of solute-rich base flow with more dilute shallow interflow. The strong relation between changes in Ca^{2+} and changes in NO_3^- concentrations during spring snowmelt, ($r^2 = 0.93$, slope = 0.96, on an equivalent basis) suggests that both solutes had a common source in the organic horizon of the soil. Increases in NO_3^- concentrations during snowmelt were balanced by increases in Ca^{2+} that was released either directly from the calcite or from exchange sites, mitigating episodic acidification of the stream. However, high ambient NO_3^- concentrations and relatively low ambient Ca^{2+} concentrations in the stream during the spring caused the stream to become acidic despite the $CaCO_3$ treatment.

In stream WO2 (40ha), Ca^{2+} concentrations were much higher than in stream WO4 because of the dissolution of calcite which fell directly into the upstream beaver pond and its associated wetlands. Calcium concentrations decreased as both NO_3^- concentrations and stream discharge increased, due to the dilution of Ca-enriched beaver pond water by shallow interflow. Despite this dilution, Ca^{2+} concentrations were high enough to more than balance strong acid anion (SO_4^{2-}, NO_3^-, Cl^-) concentrations, resulting in a positive ANC in this stream throughout the year. These data indicate that liming of wetlands and beaver ponds is more effective than whole catchment liming in neutralizing acidic surface waters.

Introduction

The Adirondack region in northern New York State is a large forested upland in which many lakes have been adversely affected by acidic atmospheric deposition (Asbury et al. 1989; Driscoll et al. 1991). About 25 percent of the lakes in the region have a pH <5 (Newton & Driscoll 1990). Woods Lake and its inlet streams are typical examples of an acidic lake/watershed system in the region. The Woods Lake watershed has been the site of research since 1978 on processes that affect the acid-base status of Adirondack lakes (Goldstein et al. 1983), and since 1985, on the effectiveness of lake liming as a strategy to mitigate acidification (Porcella 1989; Gubala & Driscoll 1991; Driscoll et al. 1995).

Terrestrial liming with crushed limestone has been used as a strategy to mitigate the effects of acidic deposition on surface waters (Howells & Brown 1986; Brown et al. 1988; Adams & Evans 1989; Westling & Hultberg 1990; Grieve 1990). It is potentially more effective than direct lake liming as it affects the upstream tributaries as well as the lake itself and the neutralization is predicted to last longer (Davis & Goldstein 1988; Blette & Newton 1996b). Howells & Dalziel (1992) found terrestrial liming to be a useful technique for neutralizing Loch Fleet in Scotland & Jenkins et al. (1991) found that applications of 10 to 16 Mg/ha in hydrologic source areas effectively eliminated episodic acidification of streams in upland Wales. However, this technique appears to work only where surface runoff and shallow interflow are dominant as Nisbet (1993) found that watershed liming in the same region of Wales was not effective at sites where vertical infiltration dominates.

Terrestrial liming with calcite results in the neutralization of acidic deposition in the upper soil horizons. Initially, the neutralization occurs as a by-product of direct dissolution of calcite.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (1)$$

With time, much of the Ca^{2+} released by this reaction is retained by the soil exchange complex (Blette & Newton 1996a).

$$Ca^{2+}\ 2R\text{—}H \rightarrow 2R\text{—}Ca + 2H^+ \qquad (2)$$

where R—H and R—Ca represent exchangeable hydrogen ion and calcium.

Theoretically, this process would continue until the soil-exchange sites become saturated with Ca^{2+} or all of the calcite dissolves. With subsequent inputs of acidic deposition, neutralization of H^+ occurs by the release of Ca^{2+} from exchange sites and retention of H^+ or Al^{3+} (the reverse of reaction 2). The effectiveness of these reactions is a function of the amount of calcite applied and the number of exchange sites in the shallow soil horizons not already occupied by base cations. The cation exchange capacity (CEC) of forest soil increases with increasing pH; therefore, one effect of liming will be to increase the CEC of the upper soil horizons (Blette & Newton 1996a). Only when enough Ca^{2+} is applied to increase the base saturation to a level that will allow Ca^{2+} to be the dominant cation in soil solution will long-term neutralization of surface water occur (Reuss & Johnson 1985).

In areas affected by acidic deposition, many upland streams and lakes with moderate to high acid-neutralizing capacity (ANC) experience episodes of acidification during peak flows (O'Brien et al. 1993; Wigington et al. 1992; Schaefer et al. 1990; DeWalle et al. 1988). Increasing the base flow ANC of streams via watershed liming does not necessarily prevent short-term declines in pH and ANC during peak flows. These short-term depressions of pH, accompanied by increases in inorganic monomeric Al concentrations, can have deleterious effects on fish populations (Carline et al. 1992). Wigington et al. (1992) have shown that, in general, the lower the base-flow ANC, the less the episodic chemical response. Prior to liming, the streams draining the Woods Lake watershed were chronically acidic and showed little chemical response to hydrologic events. This paper describes the chemical response of two tributaries during periods of high flow after the 1989 watershed liming and assesses the effectiveness of this technique in mitigating episodic acidification.

Experiment Design

Stream stage was recorded for discharge calculations at gages on WO2 and WO4 at 10-minute intervals in galvanized steel Parshall flumes with removable v-notch weirs for use during low-flow conditions. Each gage site was equipped with an automated water sampler for collecting high-flow samples. Ground-water stage was recorded every 10 minutes in 4-in (10.16 cm) ID PVC wells finished in till and located near both gages and near the lake in subcatchment II (Fig. 1). Additionally, four nonrecording 1.5 in (3.81 cm) ID wells were installed in the lower parts of the subcatchments (Fig. 1). All wells were closed at the bottom and contained 0.020 in (0.51 mm) slots in the lower 30 cm. Wells were installed only in areas of permanent groundwater.

Grab samples of stream water and groundwater were collected for analysis of pH, ANC, major solutes, and aluminum fractions at 3-week intervals from January 1989 through March 1991, according to analytical methods discussed in Driscoll et al. (1996). A data logger connected to the automated samplers was programmed to collect high-flow stream samples every 30 minutes on the rising limb of the hydrograph and every 6 hours on the falling limb. Event

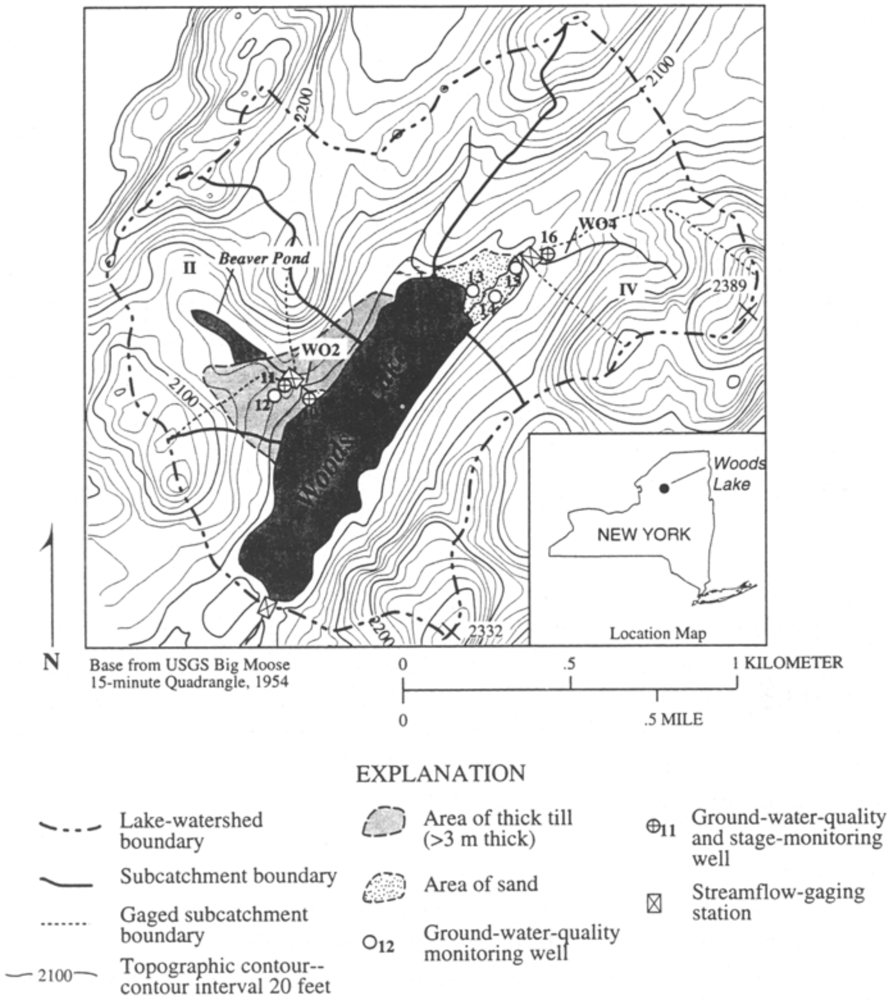


Fig. 1. Surficial geologic map of Woods Lake watershed showing subcatchment boundaries and the location of streamflow-gaging stations and groundwater wells.

samples were analyzed for dissolved organic carbon (DOC), and Al fractions at Syracuse University in Syracuse, NY; for Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} at Smith College in Northampton, MA; and for pH, ANC, H_4SiO_4, SO_4^{2-}, NO_3^{-}, and Cl^{-} at the U.S. Geological Survey (USGS) in Albany, NY by the same methods as the routine samples.

Pelletized calcium carbonate (1–4 mm) was applied by helicopter to subcatchments II and IV of the watershed in October of 1989 at a rate of 7.7 Mg/ha. The amount that actually reached the ground varied considerably across the subcatchments with more falling in subcatchment II (7.85 Mg/ha) than in subcatchment IV (5.91 Mg/ha) (Driscoll et al. 1995).

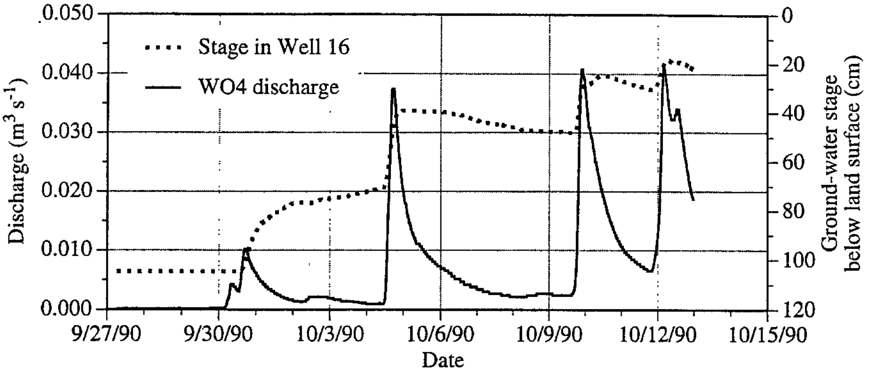
Results

Most of the calcite applied to the subcatchments in 1989 remained in the soils at the end of 1992. Blette & Newton (1996a) estimated that 47 percent of the calcite had dissolved but of this, only 9 percent was exported to surface water, while the remaining 91 percent was sequestered on soil exchange sites. Only 4 percent of the total calcium applied to the watershed was observed to have left the outlet of Woods Lake by the end of 1992. Despite the retention of calcium within the soils, the liming dramatically increased Ca^{2+} concentrations in the tributary streams. The chemistry of the groundwater system was studied in order to help determine the path by which this Ca^{2+} traveled to the stream.

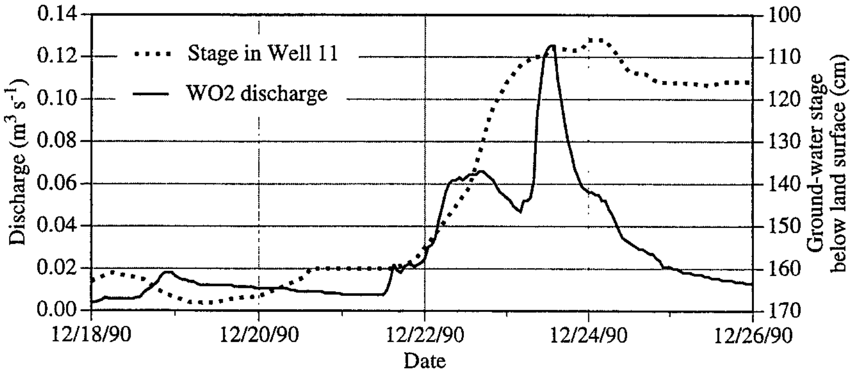
Ground-water

Ground-water reservoirs are perennial only in the lower elevations of the subcatchments where the slopes are gentler and surficial sediments thicker than at higher elevations. The sediments include till, peat, and alluvial sands (Newton & April 1982). The sands are primarily Holocene deposits formed by a combination of shoreline-wave transport and delta formation at the mouths of the inlet streams. Two sampling wells (10 and 13) were installed in sand, two (14 and 15) were installed in sand overlain by thin (<1 m thick) peat, and three (11, 12, and 16) were installed in till.

Ground-water levels in the till areas responded quickly to precipitation. For example, the response of the shallow water table in well 16 (subcatchment IV) in the early fall of 1990 was almost simultaneous with changes in stream discharge (Fig. 2). During this period, the increase in storm frequency, together with the decreasing rate of evapotranspiration, caused the water table to rise until it nearly reached the Oi horizon. The response of the deeper water table in the thick till at well 11 (subcatchment II) took only slightly longer to respond to rainfall than in the thin till at well 16. The stage in well 11 (10 m from the stream) generally rose during rain events in the fall and spring allowing groundwater to enter the stream. During dry periods in the summer, however, the stage in this well was generally lower than stream stage, indicating a loss of streamwater to the till near the gage. A series of flow measurements taken along this reach of WO2 in the summer of 1990 showed a downstream decline in streamflow (C.P. Cirmo, Syracuse University, personal communication), providing additional support that the stream reach in



a. Subcatchment IV



b. Subcatchment II

Fig. 2. Stream discharge and groundwater stage at stream WO4, September 27 through October 17 1990, and at stream WO2 December 18 through December 26, 1990.

WO2 below the beaver pond loses flow to groundwater under summer base flow conditions.

The ANC of the groundwater varied across the two subcatchments with groundwater samples generally falling into one of three groups:

(1) High ANC. The highest ANC (358 μeq/L; Table 1) was found in well 13, screened in the sand deposit at the north end of the lake in subcatchment IV. This well was driven to a depth of 257 cm, and, because the water table was virtually at the land surface, this is the maximum depth below the water table from which groundwater was collected. The high ANC was associated with relatively high concentrations of base cations and relatively low concentrations of SO_4^{2-} and NO_3^-. This well had the highest mean concentrations of Ca^{2+}, Mg^{2+}, Na^+ and H_4SiO_4 of all wells sampled. The high H_4SiO_4 concentration suggests that primary mineral weathering may be important in supplying high concentrations of base cations in deep groundwater.

Table 1. Average chemistry of groundwater from wells at Woods Lake, N.Y., 1990.

	Well 10	Well 11	Well 12	Well 13	Well 14	Well 15	Well 16
Well data							
Well depth (cm)	140	230	73	264	236	147	142
Depth to water (cm)	20	208	20	0	5	26	68
Material	Sand	Till	Till	Sand	Peat & Sand	Peat & Sand	Till
No. of samples	11	9	14	11	15	16	16
Constituent or property							
pH	4.81	4.83	5.95	6.64	5.87	6.24	4.92
ANC	8	5	103	358	121	118	6
DOC	157	397	75	57	100	267	171
SO_4	84.6	59.5	53.3	28.9	39.6	10.0	66.1
NO_3	16.3	128.7	104.9	35.8	7.3	0.5	39.1
Cl	10.3	8.3	7.4	7.2	7.3	7.5	7.6
Ca	24.1	68.4	95.8	119.3	48	32.8	31.0
Mg	9.3	17.1	26.7	46.4	16.0	11.4	6.8
Na	45.9	54.1	78.6	153.0	71.1	38.1	30.9
K	6.7	75.6	19.6	20.8	7.9	16.0	6.1
Al, monomeric	33.6	35.5	2.1	2.0	2.0	4.0	31.1
H_4SiO_4	180.3	147.0	218.4	292.7	198.0	184.4	114.1

[Concentrations are in μmol/L except ANC which is in μeq/L.
Well locations are shown in Fig. 1.]

(2) Intermediate ANC. The ANC at three wells ranged from about 100 to 120 μeq/L. Wells 14 and 15 are finished in sand deposits beneath thin peat in subcatchment IV, and well 12 is finished in a shallow groundwater seep area within the thick till deposit in subcatchment II. Although the samples from these wells had similar ANC values, the processes that regulate their acid-base chemistry differ markedly. Groundwater derived from till had relatively high SO_4^{2-} and NO_3^- concentrations accompanied by high base-cation concentrations (mainly Ca^{2+} and Na^+), whereas groundwater from the sand overlain by peat had relatively low base-cation concentrations and extremely low SO_4^{2-} and NO_3^- concentrations (Table 1). This pattern indicates that primary mineral weathering accounts for the moderate ANC in the groundwater from the till, whereas denitrification and sulfate reduction within the peat and sand produce the moderate ANC values in waters draining these deposits.

(3) Low ANC. Water samples from the remaining three wells had low ANC values (5 to 10 μeq/L), high monomeric Al concentrations, and low pH

(Table 1). These samples represent groundwater from just below the water table in areas of till and were similar in composition to stream water prior to liming. Samples from well 10 in subcatchment II were not representative of the surrounding material because the well is only a few meters from the lake where the groundwater is affected by exchange with lake water. Samples from well 16, screened in thin till within subcatchment IV, had relatively low base-cation concentrations and high SO_4^{2-} and NO_3^- concentrations. Samples from well 11, finished in thick till in subcatchment II, had higher base-cation concentrations than those from well 16 because the water table at the well location is deeper ensuring that recharge water must travel further through the base-cation-rich till. Well 11 had a lower ANC than nearby well 12, which was also located in the thick till area, because well 12 is at the end of a groundwater flowline, whereas well 11 is at the beginning of one (as indicated by O^{18} data, Douglas A. Burns, personal communication).

Ground-water samples showed little temporal variation in chemistry, except for those from the intermediate ANC wells (12, 14, 15) which varied by about 50 μeq/L annually. The ANC of these waters was lowest in late spring and early summer and highest from late September to early October. Ground-water chemistry at these wells did not appear to change significantly after the lime treatment, therefore it is unlikely that any chemical response observed in the streams could be due to dissolved calcite moving along deep flow paths through the groundwater reservoir.

Surface Water

Hydrographs and flow duration curves (Fig. 3) for the two streams in the limed subcatchments show that WO4 is "flashier" than WO2. The gaged part of subcatchment IV has steeper slopes than subcatchment II; it is covered with thin till and has abundant bedrock outcrops, whereas subcatchment II has a large area of gentle slopes and contains the beaver pond and an area of thick till. Although thick till underlies about 20 percent of subcatchment II, only 5 percent occurs within the gaged portion (Fig. 1). Thus, the higher baseflow measured at WO2 than at WO4 is most likely caused by the release of water from the pond during low-flow periods rather than from storage within the groundwater system.

Evapotranspiration was estimated as the difference between total precipitation and total runoff for 1990 and 1991, corrected for changes in hydrologic storage. The evapotranspiration estimates (Table 2) are generally lower than the estimate of 38 percent for the whole watershed in water years 1980 and 1981 by Peters & Murdoch (1985). The larger average value for subcatchment II (35 percent) than for subcatchment IV (25 percent) reflects evaporation from the beaver pond and associated wetlands in subcatchment II. Meteoric

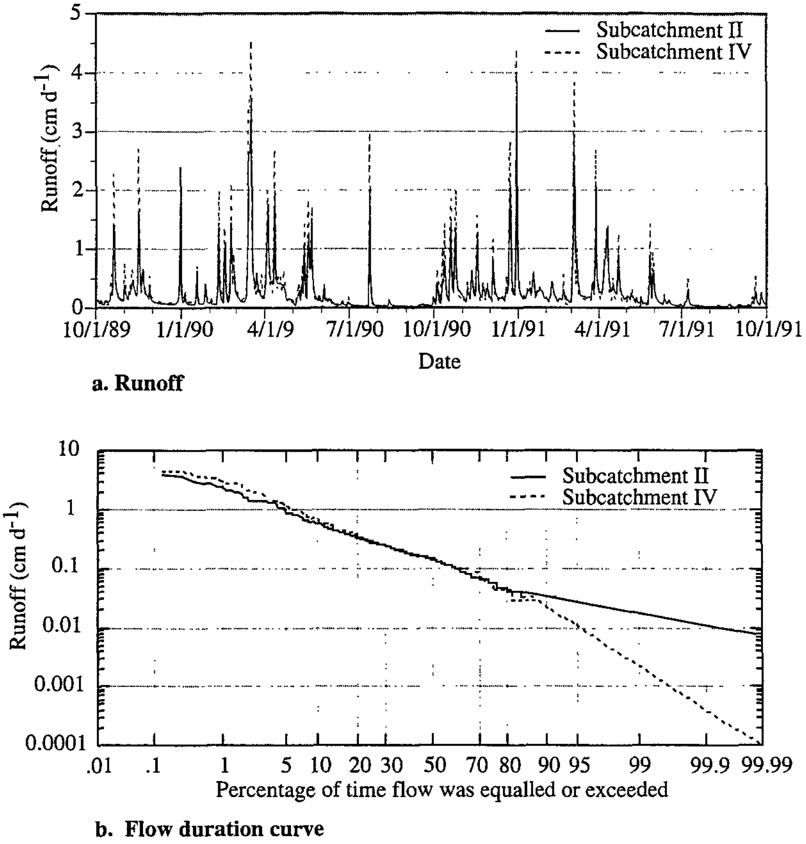
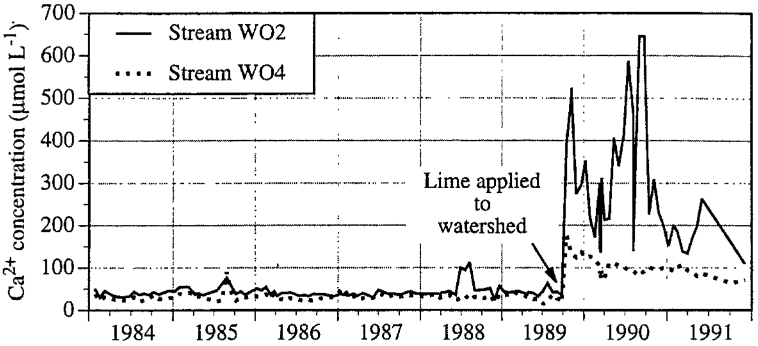


Fig. 3. Mean daily discharge and flow duration curves of streams WO2 and WO4, water years 1990–91.

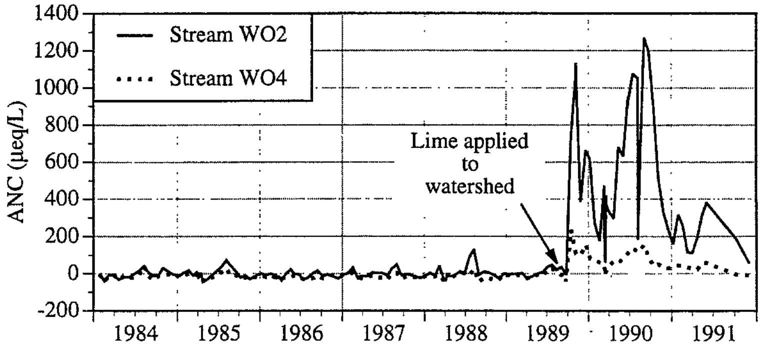
Table 2. Runoff, precipitation, and evapotranspiration (as calculated from the difference between precipitation and runoff, corrected for changes in storage) from subcatchments II and IV of Woods Lake for 1990 and 91 water years.

Water year	Runoff (cm) WO2	Runoff (cm) WO4	Precipitation (cm)	Storage change (cm)	Evapotranspiration (percent) Subcatchment II	Evapotranspiration (percent) Subcatchment IV
1990	93.3	109.8	133.4	−10	38	25
1991	96.7	107.1	143.3	0	33	25

water lines constructed with O^{18} and deuterium data from the streams also reveal greater rates of evaporation in subcatchment II (Burns & Aulenbach 1995).



a. Calcium



b. Acid-Neutralizing Capacity

Fig. 4. Calcium concentrations and acid nuetralizing capacity in streams WO2 and WO4, 1984–91.

Prior to liming, the ANC of both streams was near zero. Immediately after liming, the ANC and Ca^{2+} concentrations of both streams sharply increased (Fig. 4). Most of this increase was the result of rapid dissolution of calcium carbonate that fell directly into the stream channels and the beaver pond. Because the beaver pond in subcatchment II was larger (1.3 ha) than the area of stream channel in subcatchment IV (estimated to be <0.1 ha), the greater immediate response to liming in subcatchment II is not surprising (Cirmo & Driscoll 1996 provide a full discussion of the effects of liming on the beaver pond).

Episodic Acidification

If watershed liming is to be considered an effective method of mitigating the effects of acidic deposition, the treatment must not only effect an increase in the base-flow ANC of the inlet streams, but it must also eliminate short-

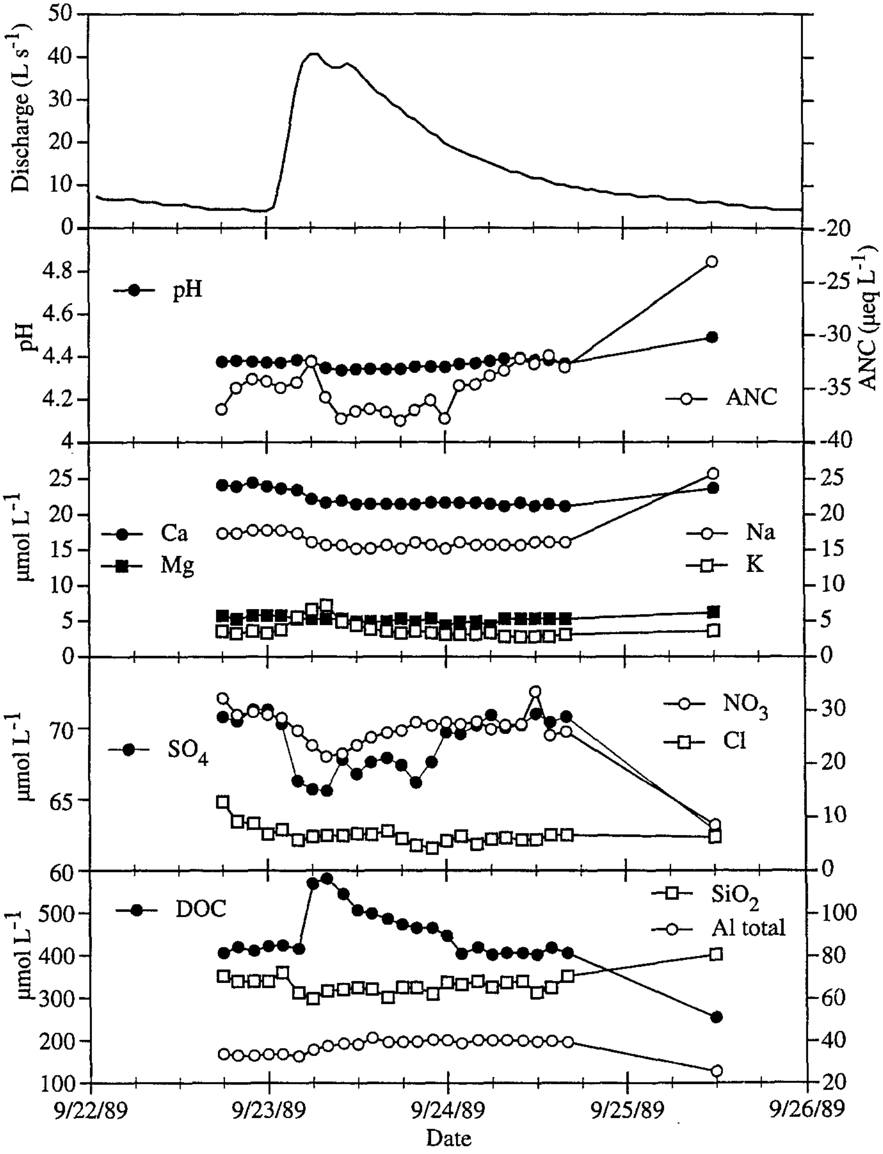


Fig. 5. Hydrologic and chemical response of stream WO4 to the 30 mm of precipitation associated with remnants of hurricane Hugo, September 23–26, 1989.

term acidification (ANC<0 μeq/L). The sampling program was designed to evaluate how episodic changes in water chemistry were altered by base treatment.

Subcatchment IV (Stream WO4)

Prior to liming, the inlet streams, were acidic with ANC values generally below zero (Cirmo & Driscoll 1996). During the one high flow period that was sampled prior to liming, approximately 30 mm of precipitation fell during passage of the remnants of Hurricane Hugo (September 23–26, 1989) causing stream discharge in WO4 to increase from 5 L/s to 40 L/s (WO2 was not sampled during this storm) (Fig. 5). Stream pH and ANC were 4.4 and −36 μeq/L, respectively, before the event and showed little change through the peak-flow period. Nitrate and SO_4^{2-} concentrations decreased during the event and DOC concentrations increased, but concentrations of the other measured constituents changed little (Fig. 5). These data confirm observations from earlier studies at the Woods Lake outlet, in which pH and ANC changed little from low- to high-flow conditions (Schofield et al. 1985).

Hydrologic events were again sampled during both the fall and spring beginning 1 year after treatment to determine whether episodic acidification was mitigated by liming. The most dramatic change in stream ANC occurred during the early fall of 1990 (September–October) when stream ANC decreased by 80 μeq/L, from $\approx$100 μeq/L to $\approx$20 μeq/L. The relatively high summer ANC was associated with relatively low concentrations of SO_4^{2-} and NO_3^-, which were likely caused by vegetative uptake and/or reduction processes in riparian wetlands. As stream discharge increased at the end of the growing season, SO_4^{2-} and NO_3^- concentrations increased. Most of the initial 80 μeq/L decrease in ANC can be explained by a corresponding increase in SO_4^{2-}; a linear regression analysis of changes in SO_4^{2-} concentrations and ANC during this period showed a slope of −1.07 ($r^2 = 0.92$). Nitrate concentrations generally increased during the late fall, with the largest increase occurring between mid-November and mid-December. The total change in NO_3^- concentration ($\approx$100 μeq/L) was slightly greater than the total change in SO_4^{2-} concentration ($\approx$80 μeq/L) from September through December 1990.

Two rain events in October 1990 were representative of short-term chemical changes in WO4 after lime treatment (Fig. 6). The stream ANC was about 20 μeq/L before the events, decreased 10 μeq/L during the first event, recovered, and then decreased by nearly 30 μeq/L to near 0 μeq/L during the second event. The pH decreased from 5.7 to 5.2 in the first storm and from 5.5 to 4.9 in the second. A charge-balance analysis revealed that ANC in WO4 during these events was most strongly affected by increases in Ca^{2+}, NO_3^-, and SO_4^{2-} concentrations, with minor contributions from decreases in Na^+ and K^+ concentrations. The increases in strong-acid anion concentrations caused decreases in ANC, but these acidifying processes were largely offset by increases in Ca^{2+} concentrations, which diminished the degree of

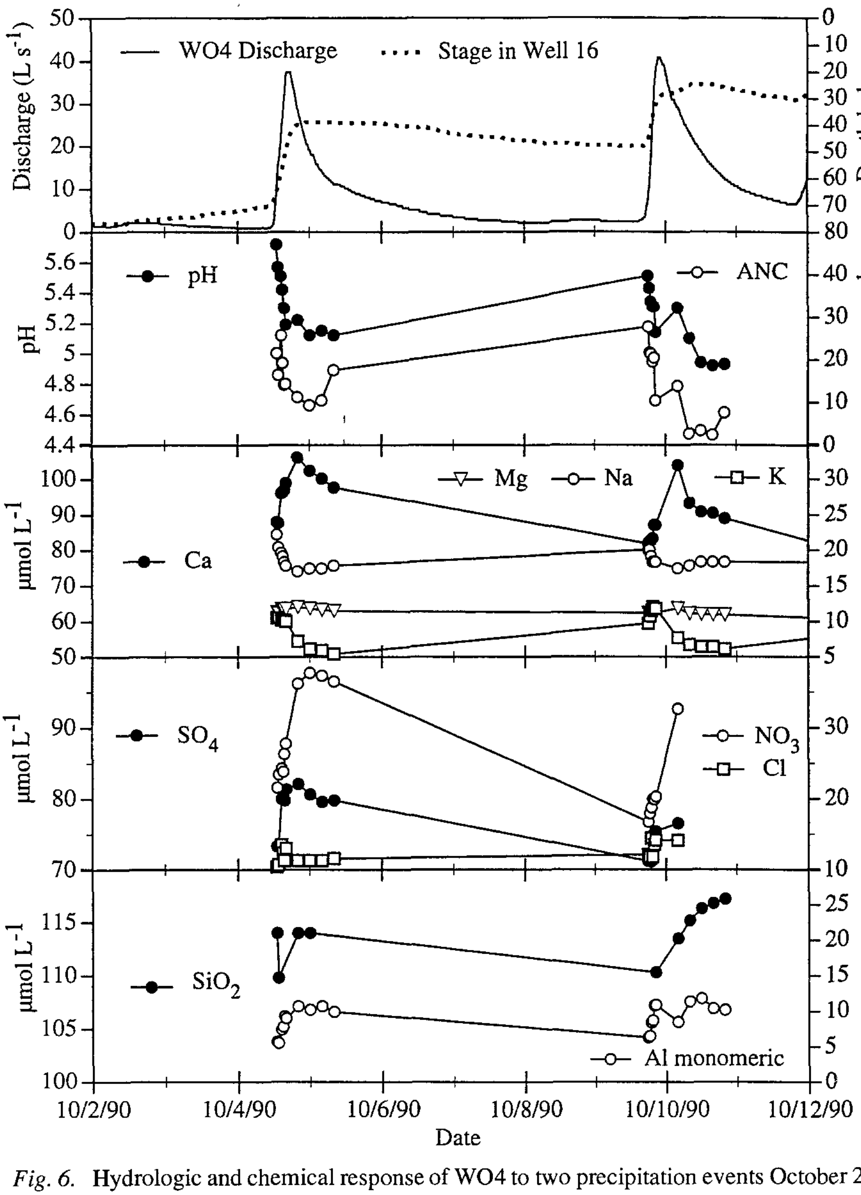


Fig. 6. Hydrologic and chemical response of WO4 to two precipitation events October 2–12, 1990.

episodic acidification. The ability of the watershed to supply Ca^{2+} prevented ANC from reaching negative values during this period.

During spring snow melt in early March 1991, the ANC was generally <0 and pH ranged from 4.8 to 4.7 (Fig. 7). Nitrate concentrations were high

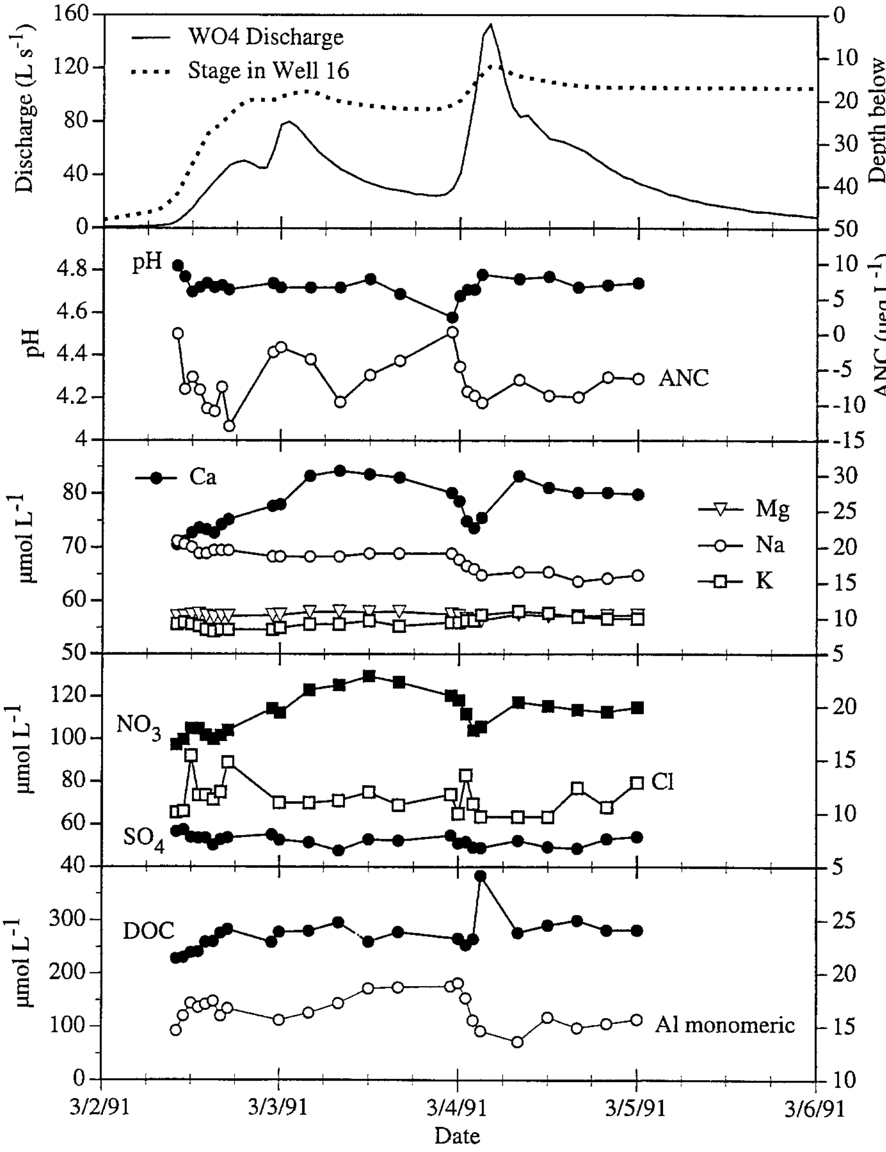


Fig. 7. Hydrologic and chemical response of stream WO4 to an early snowmelt event, March 2–6, 1991.

and increased to 130 μeq/L after the initial peak flow, then decreased during the rising limb of the main peak and increased again immediately thereafter. Calcium and monomeric Al concentrations showed a similar pattern. The declines at peak flow were likely caused by dilution of stream water by direct precipitation and surface runoff. Sulfate concentrations changed little throughout this period. Dissolved organic carbon (DOC) concentrations increased during the initial part of the snowmelt and remained high throughout the sampling period; the maximum DOC concentration corresponded to the time of peak stream discharge.

Subcatchment II (Stream WO2)

Although WO2 stream chemistry was largely controlled by processes in the beaver pond about 100 m upstream of the gage (Cirmo & Driscoll 1996), chemical changes were evident during precipitation and snowmelt events. Samples were collected during a rain storm from October 18 to 20, 1990, when stream discharge increased from 50 to 250 L/s and groundwater levels rose from 240 cm to 70 cm below the land surface at adjacent well 11 (Fig. 8). During the event, ANC increased with discharge from 725 μeq/L to 775 μeq/L at peak flow, then decreased during stream recession. Calcium concentrations increased in a similar manner while the other base-cation concentrations varied by less than 5 μeq/L during the event. Sulfate concentrations increased throughout the event with the greatest increase occurring during the rising limb. This pattern likely reflects the mixing of storm runoff containing relatively high SO_4^{2-} concentrations with beaver pond water containing relatively low SO_4^{2-} concentrations. During low-flow periods much of the incoming SO_4^{2-} is retained in the pond by reduction processes (Cirmo & Driscoll 1996), but the decreased retention time of the pond during events diminished the effectiveness of these processes. Nitrate concentrations decreased as streamflow increased, probably due to dilution, then slowly increased during streamflow recession. A charge-balance analysis indicated that increases in Ca^{2+} concentration were largely responsible for increased ANC during the event. The increase in SO_4^{2-} concentration was off-set by a decrease in NO_3^- concentration so that there axes resulted in no net change in ANC during the event.

The response of stream chemistry to rainfall near the end of the spring snowmelt was quite different from that of fall rain events (Fig. 9). During the period March 27 to 31, 1991 stream discharge increased from about 10 L/s to 100 L/s, and groundwater levels at adjacent well 11 increased 40 cm, to a depth of about 1 m below land surface in the thick-till area near the stream gage. Stream Ca^{2+} concentrations, ANC, and pH all increased during the initial discharge rise on March 27, but decreased through the peak-flow period until the latter part of the recession. Sodium, Mg^{2+}, and H_4SiO_4 concentrations decreased slightly during the event and NO_3^- concentrations increased 30 μeq/L just after the peak; concentrations of other constituents varied little. Sulfate concentrations did not change as they had during the

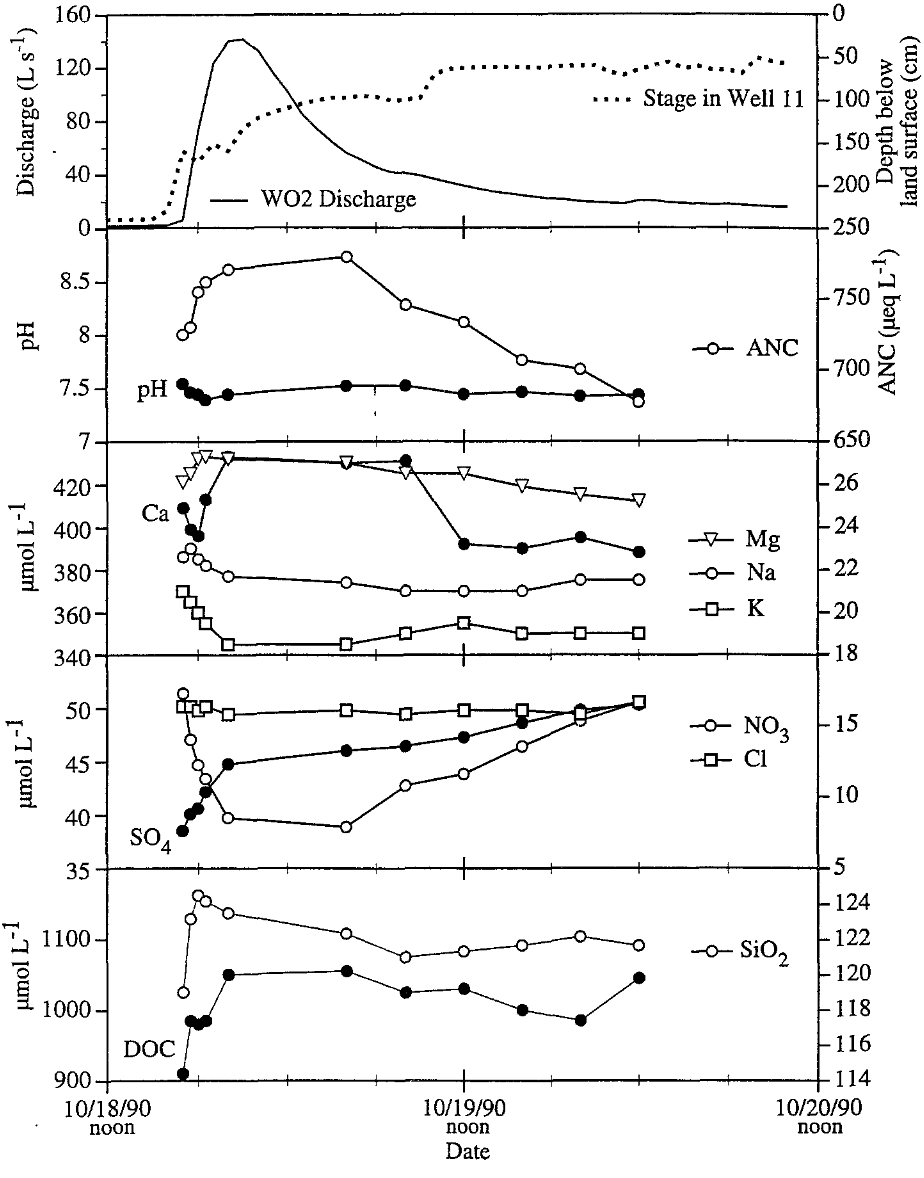


Fig. 8. Hydrologic and chemical response of stream WO2 to a typical fall storm, October 18–20, 1990.

fall storm because significant SO_4^{2-} reduction does not occur in the winter (Cirmo & Driscoll 1993, 1995). As in the fall storm, however, changes in Ca^{2+} concentrations were coincident with changes in ANC during the snowmelt.

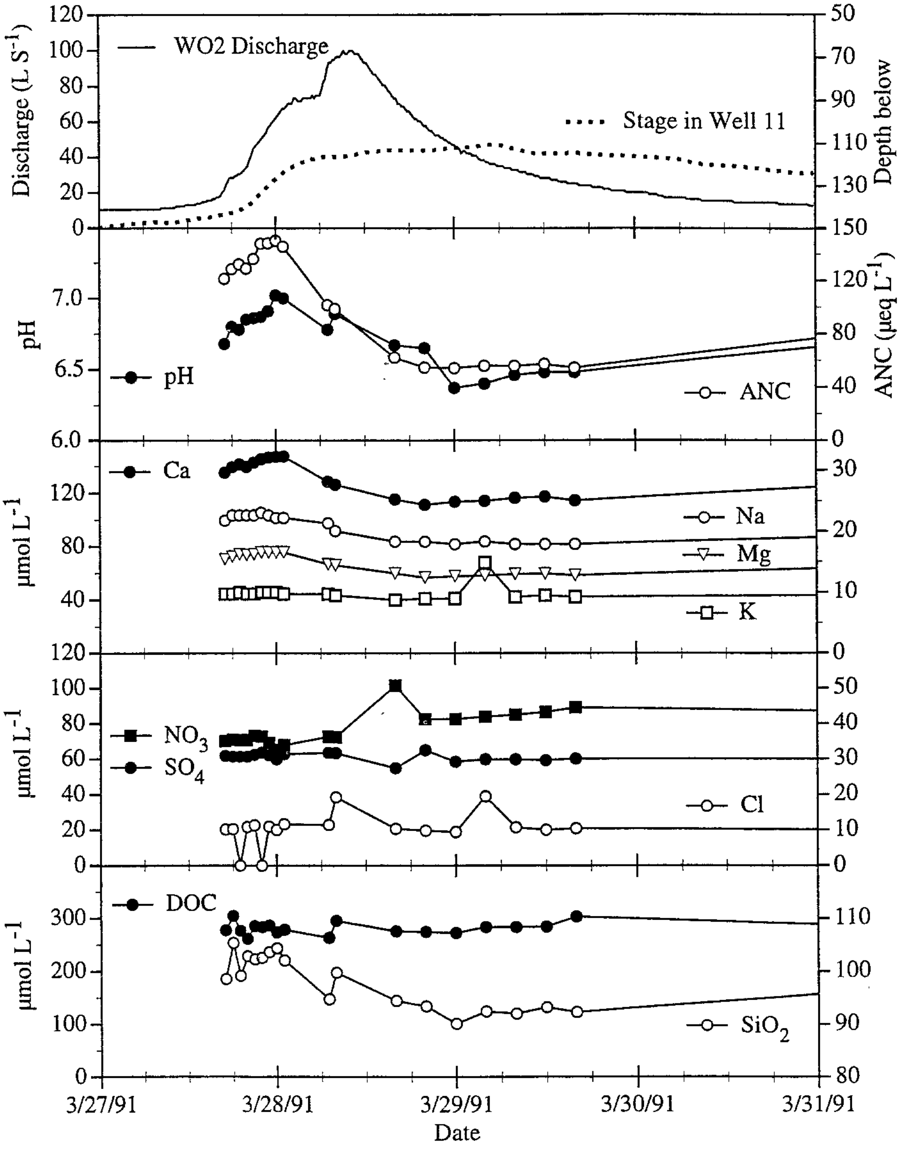


Fig. 9. Hydrologic and chemical response of stream WO2 to a late snowmelt event, March 27–31, 1991.

The increase in NO_3^- concentration after peak flow did not appear to result in a change in ANC through this period.

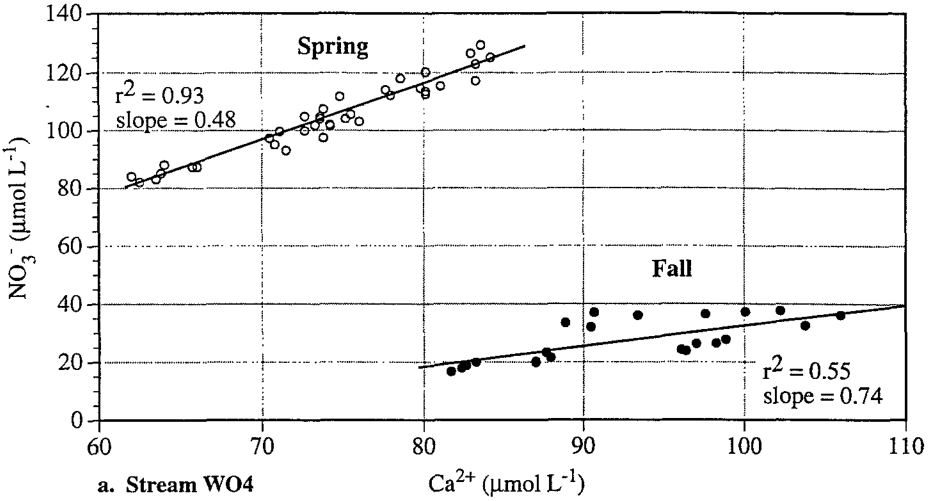
Discussion

The effects of watershed liming differed markedly between the two streams. At stream WO2, Ca^{2+} concentrations increased from a preliming average of 86 μeq/L to 490 μeq/L, whereas at WO4 the increase was from 60 μeq/L to 192 μeq/L. This difference was largely due to the beaver pond and associated wetlands in subcatchment II which provided an environment wherein most of the added calcite dissolved readily and entered the surface water system directly. The high ANC of the stream was clearly related to the release of Ca^{2+} derived from calcite dissolution as indicated by the high correlation between stream Ca^{2+} and ANC from linear regression analysis ($r^2 = 0.99$; slope = 1.16). In the summer and fall of 1990, SO_4^{2-} and NO_3^- concentrations were lower in stream WO2 than stream WO4 because of reduction and uptake processes which occurred in the pond (Cirmo & Driscoll 1995). During fall rain events, SO_4^{2-} concentrations gradually increased and then persisted at elevated concentrations as water with a low SO_4^{2-} concentration was gradually flushed from the pond. Why NO_3^- concentrations in stream WO2 decreased from a pre-event value of 10 μeq/L to 5 μeq/L during the event of October 18 and 19, is unknown; perhaps the wetted perimeter of the beaver pond expanded into surrounding wetland soils where biologic uptake and reduction processes had caused low NO_3^- concentrations. The increase in DOC concentrations in the stream during the event is consistent with this hypothesis.

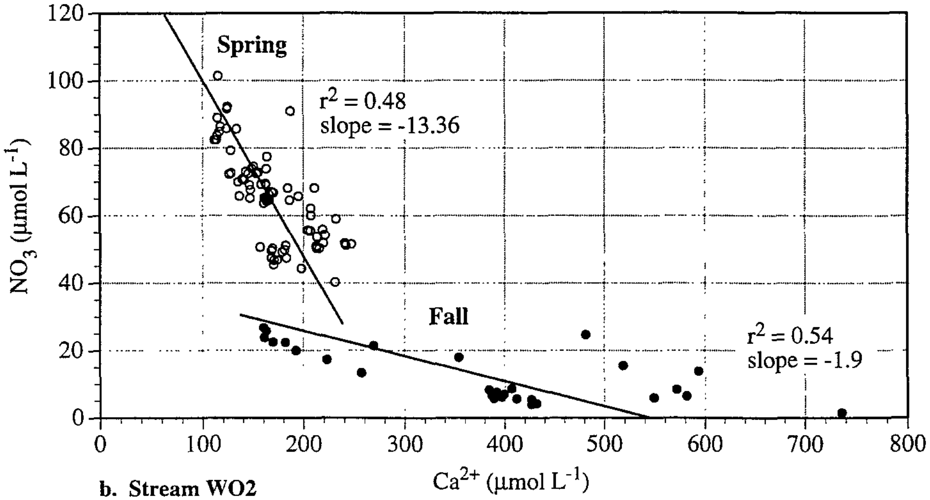
In contrast, the gaged part of catchment IV lacks significant wetlands; therefore, most of the lime that fell directly into the stream was probably used up by the fall of 1990. After that time, elevated concentrations of Ca^{2+} in streamwater likely reflected leaching of dissolved calcite and H^+—Ca^{2+} cation exchange from the soil. Since fall 1990, Ca^{2+} concentrations have steadily decreased at a rate of about 50 μeq/yr ($r^2 = 0.60$) suggesting that the supply of Ca^{2+} and associated ANC to drainage water was declining through the remainder of the study.

Base cation concentrations in Adirondack lakes tend to decrease during periods of high flow, particularly in lakes of moderate to high ANC, (Driscoll & Van Dreason 1993; Schaefer et al. 1990). The evidence from Hurricane Hugo at stream WO4 indicates that dilution of Ca^{2+} concentrations during rain events prior to liming was slight, but that some dilution would be expected even when base flow concentrations are low (50 μeq/L at WO4). After liming, Ca^{2+} concentrations generally increased with increasing discharge, except during the periods of highest flow associated with the spring snowmelt, when some dilution occurred (Figs. 8 and 10).

Calcium concentrations in streamwater fluctuate during the year with changes in hydrologic flow paths (Chen et al. 1984). In an untreated catch-



a. Stream WO4



b. Stream WO2

Fig. 10. Nitrate concentration in relation to Ca^{2+} concentration in streams WO4 and WO2 during fall 1990 and spring 1991 highflow events.

ment, the deeper the flow path through the till, the higher the Ca^{2+} concentration. For example, the Ca^{2+} concentration of groundwater in shallow well 16, in the thin till of subcatchment IV was low (62 μeq/L); at well 11 in the recharge area of the thick till in subcatchment II it was higher (136 μeq/L); and at shallow well 12 in a groundwater seep in subcatchment II it was highest (238 μeq/L). These three wells, which represent three different positions along a hypothetical flow line, show the increase in Ca^{2+} concentration that occurs through increased subsurface residence time. The corresponding increase in H_4SiO_4 at these wells suggests that primary mineral weathering is an important mechanism for supplying this Ca^{2+}.

Flow path also affects groundwater NO_3^- concentrations. Nitrate concentrations were highest in the thick till area within subcatchment II, presumably, as a result of the timing of the major recharge during late-fall rain storms and spring snowmelt. At these times both surface waters and soil waters were characterized by high NO_3^- concentrations (Geary & Driscoll 1995; Cirmo & Driscoll 1995); therefore the recharge water would also be expected to have elevated NO_3^- concentrations. In contrast, NO_3^- concentrations were low in groundwaters from thin till areas that were primarily recharged early in the fall when NO_3^- concentrations are still low. Little recharge occurs later in the fall and winter because the groundwater reservoir is already filled to capacity and forces most stormwater to move rapidly to the stream as surface runoff or shallow interflow.

Despite the continued presence of calcite in its watershed, the ANC in stream WO4 decreased from the fall of 1990 to the spring of 1991, when the stream became acidic during snowmelt (<0 μeq/L). Stream acidification resulted largely from increases in strong acid associated with increased NO_3^- concentrations ($\Delta \approx 85$ μeq/L) and decreased Ca^{2+} concentrations ($\Delta \approx 35$ μeq/L). Calcium concentrations in WO4 decreased during this period through the progressive dissolution and removal of calcite that had previously fallen in the stream channel. The total decrease in ANC in WO4 was only about 20 μeq/L however, because some of the acidification was offset by a decrease in SO_4^{-2} concentrations ($\Delta \approx 45$ μeq/L) and a decrease in organic acidity indicated by a decrease in DOC concentrations ($\Delta \approx 250$ μmolC/L).

Although a general decrease in Ca^{2+} concentrations and an increase in NO_3^- concentrations occurred from fall to spring in stream WO4; during individual events there was a positive correlation between the two solutes (Fig. 10). This relation was weaker during the fall 1990 storms ($r^2 = 0.55$; slope = 0.74), when there was still some effect from the dissolution of calcite remaining in the stream channel. But by the spring snowmelt of 1991, little calcite remained in the channel, and Ca^{2+} concentrations in the stream were lower. The strong correlation ($r^2 = 0.93$; slope = 0.48) between Ca^{2+} and NO_3^- concentrations during snowmelt suggests they have a common source during this period. Soil-chemistry data indicate that the lime treatment added a large pool of exchangeable Ca^{2+} to the soil organic horizon (Blette & Newton 1996a). The organic horizon was the likely source of flow-induced increases in Ca^{2+} and NO_3^- concentrations during the spring snowmelt. The stoichiometric increase in Ca^{2+} and NO_3^- concentrations with flow during the snowmelt suggests that the H^+ that would have accompanied NO_3^- in the absence of lime treatment was replaced by Ca^{2+}. If Ca^{2+} had not accompanied NO_3^-, ANC would have declined by at least an additional 20 μeq/L during the peak runoff.

The strong correlation between Ca^{2+} and NO_3^- concentrations in stream WO4, also suggests the possibility of a direct relation between the processes that produce these two constituents. That soil nitrification rates increase as pH increases toward 7 is generally recognized (Dancer et al. 1973), and during the EWLS, the liming was found to increase soil-nitrification rates as much as threefold (Simmons et al. 1996). However, Simmons et al. (1996) also found that excess root uptake of nitrogen offset increased nitrification rates and resulted in no net change in NO_3^- leaching due to liming. Through the winter, however, when root uptake is minimal, the presence of lime in the soil could have increased the nitrification rate, and provided more available NO_3^- for leaching in the spring than would have been available in the absence of lime (Geary & Driscoll 1996; Cirmo & Driscoll 1996). Chemical data collected since 1984 at WO4 indicates that stream NO_3^- concentrations always increase through the winter and early spring, but because high-flow samples were not collected during snowmelt prior to liming, the pre- and post- liming stream NO_3^- concentrations cannot be compared to evaluate changes in soil NO_3^- leaching.

Conclusion

Watershed liming had little or no effect on the chemistry of groundwater in either of the treated subcatchments because most of the Ca^{2+} either was held in the upper part of the soil or was released to surface water during periods of shallow lateral flow. In contrast, the lime treatment had an immediate effect on stream chemistry because the calcite fell directly into the stream channels, beaver pond, and associated wetlands. The long-term effect of watershed liming on surface waters however, is a function of the flow path of water as it moves to the stream.

Flow path is also an important determinant of groundwater chemistry. Ground-water flow paths tend to be deeper with longer subsurface residence times in areas of thicker surficial sediments than in areas with thin cover. Deep flow paths lead to increased base-cation concentrations as mineral weathering reactions occur. Areas in which the water table is relatively deep receive winter and spring recharge with high NO_3^- concentrations whereas areas where the water table is close to land surface do not, because most of this NO_3^--enriched water moves as surface runoff or rapid interflow through the shallow horizons of the soil and thus, never reaches the groundwater reservoir.

The areas with high NO_3^- concentrations in groundwater are in locations least affected by watershed liming - those with thick till. The dominance of vertical flow paths in these regions increases the probability that the Ca^{2+} supply from calcite dissolution will be retained on an exchange site before it reaches the surface water. Areas where water moves as rapid interflow through the shallow soil are the most effective at adding Ca^{2+} from the lime to the stream. The strong correlation between NO_3^- and Ca^{2+} concentration during hydrologic events in subcatchment IV (thin till) is characteristic of water moving along shallow flow paths, although low ANC values suggest that not enough calcite was added to mitigate acidic drainage waters.

Watershed liming can be a successful technique for mitigating the effects of acidic atmospheric deposition on surface waters. Success depends on adequate liming in areas in which the dominant flow paths are through the uppermost soil layers. These are generally areas of saturated soils, such as swamps and wetlands. The higher evapotranspiration rates calculated for subcatchment II than for subcatchment IV reflect the larger area of saturated soil in subcatchment II. This, coupled with the presence of a beaver pond that also received calcite during the lime application, explains why the response in stream WO2 was so much greater than the response in stream WO4.

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