

HYDROLOGIC PATHWAYS AND CHEMICAL COMPOSITION OF RUNOFF DURING SNOWMELT IN LOCH VALE WATERSHED, ROCKY MOUNTAIN NATIONAL PARK, COLORADO, USA.

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Abstract. Intensive sampling of a stream draining an alpine-subalpine basin revealed that depressions in pH and acid neutralizing capacity (ANC) of surface water at the beginning of the spring snowmelt in 1987 and 1988 were not accompanied by increases in strong acid anions, and that surface waters did not become acidic (ANC < 0). Samples of meltwater collected at the base of the snowpack in 1987 were acidic and exhibited distinct 'pulses' of nitrate and sulfate. Solutions collected with lysimeters in forest soils adjacent to the stream revealed high levels of dissolved organic carbon (DOC) and total Al. Peaks in concentration of DOC, Al, and nutrient species in the stream samples indicate a flush of soil solution into the surface water at the beginning of the melt. Infiltration of meltwater into soils and spatial heterogeneity in the timing of melting across the basin prevented stream and lake waters from becoming acidic.

1. Introduction

Episodic acidification of surface waters during intense storm and snowmelt events is well documented in the northeastern United States, Canada, and Europe (Haines, 1981; Schofield *et al.*, 1985; Jeffries *et al.*, 1979). Chronic lake acidification in these areas has often been preceded by acidic episodes associated with spring snowmelt. Alpine and subalpine watersheds in the mountainous regions of the Western United States have been identified as some of the most sensitive areas in the world to the effects of acidic atmospheric deposition, but show little or no evidence of chronic acidification (Landers *et al.*, 1987; Turk and Spahr, 1991). Regional scale surveys however, cannot address the possibility of episodic acidification during storm or snowmelt events. Most of these watersheds receive the bulk of their annual precipitation in the form of snow, which accumulates the products of many months of deposition and then flushes through the system in a relatively short period in the spring and early summer.

Watershed contributions are expected to have little influence on snowmelt episodes in the high mountain basins of the western United States since soil cover is usually thin to non-existent and the residence time of meltwater is short due to steep topographic gradients. An assessment of the effects of snowmelt episodes requires

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frequent sampling, which is often impractical in remote, high elevation areas. As a result, relatively few studies have focused on the chemical changes in alpine and subalpine aquatic systems during snowmelt. Baron and Bricker (1987) documented depressions in pH and titratable alkalinity (acid neutralizing capacity; ANC) during three successive snowmelt seasons in Loch Vale Watershed in Rocky Mountain National Park, Colorado, but in none of these years did surface waters become acidic ($\text{ANC} < 0$). Vertucci (1990) reported that depressions in the ANC of West Glacier Lake, Wyoming were greater in magnitude than dilution of base cation concentrations, and were accompanied by increases in the concentrations of acid anions. He suggested that anthropogenic acidity in the snowpack could be responsible. Harte and Hoffman (1989) attributed a decline in the population of the Tiger Salamander in a western Colorado pond to episodic acidification during snowmelt. On the other hand, watershed interaction with snowmelt water may reduce the impact of acidic snowmelt events. Stoddard (1987) showed that groundwater inputs to Gem Lake in the Sierra Nevada prevented acidification during spring runoff.

We used the temporal patterns of chemical variations in water from soil solution, snowmelt, and stream runoff to investigate watershed processes which influence surface water chemistry during early snowmelt in the Colorado Rocky Mountains. We found that pH and ANC in surface waters were much higher than observed in meltwater collected from the base of the snowpack. Differences in composition between soil solutions and meltwater allowed us to use dissolved organic carbon (DOC) and total dissolved Al as geochemical indicators of soil-derived water. Our analysis indicated that a flush of water from forest soils moderated the inputs of strong acidity from the snowpack, preventing surface water acidification.

2. Methods

2.1. STUDY AREA

Loch Vale Watershed (LVWS) is a 660 ha northeast-facing basin located in Rocky Mountain National Park about 80 km NW of Denver, Colorado (Figure 1). Since 1981, it has been the site of a long-term ecological monitoring and research program. The watershed ranges in elevation from 3110 m at the outlet of the lowest lake, The Loch, to 4010 m at the Continental Divide. More than 80% of the basin surface consists of bedrock outcrop and active talus slopes. Bedrock consists primarily of Precambrian-aged granitic gneiss and schist (Cole, 1977; Mast, 1989). Several permanent snowfields and an active rock glacier, remnants of neoglacial activity, occupy about 1% of the watershed. In areas of relatively gentle slope, the valley floor is covered with glacial till of Pinedale age (Mast, 1989).

Forest soils have developed on the moraine veneer below 3300 m elevation, covering about 5% of the area of the catchment. Complete profile descriptions and chemical analyses can be found in Walthall (1985). Soil pH (1:1 paste) ranges between 3.7 and 4.8. Cation exchange capacity of these soils ranges from 50 to 100 ceq kg^{-1} ,

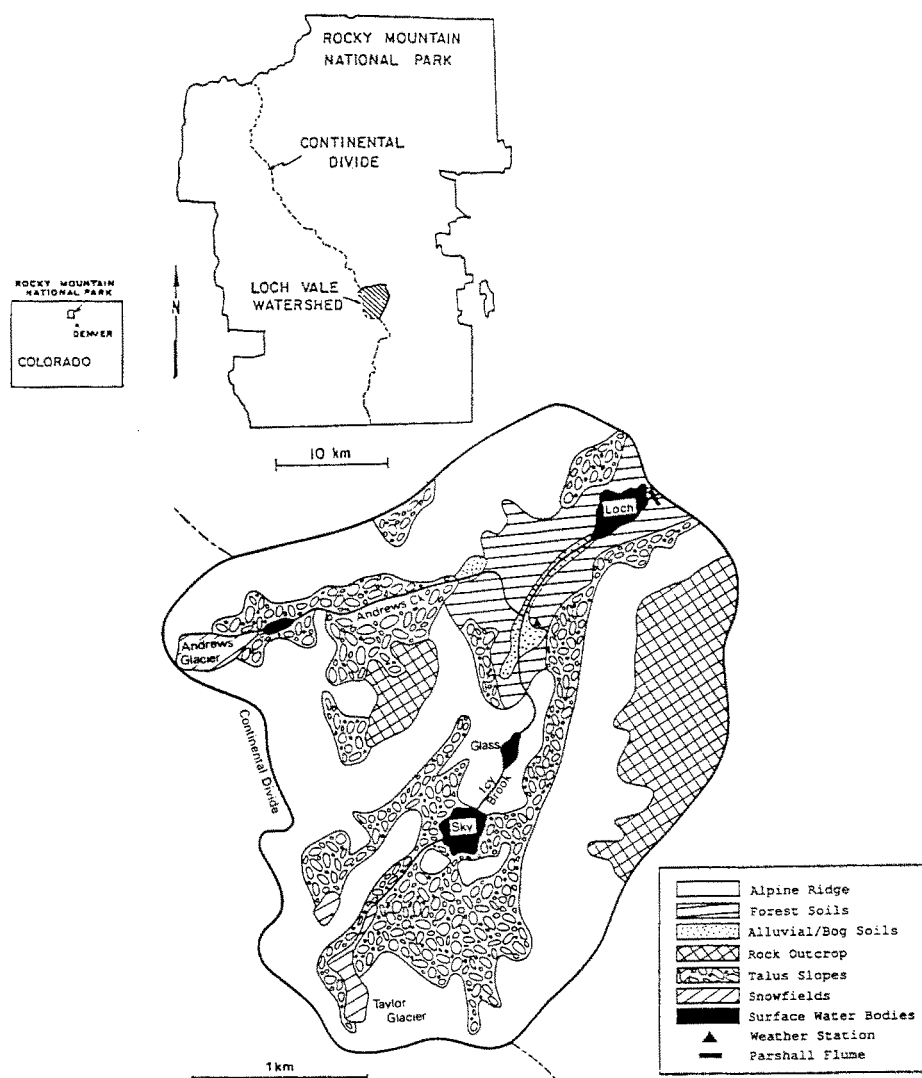


Fig. 1. Map showing location and major landforms of study area.

but base saturations are quite low, with a mean of 23% in the organic surface layers and decreasing to below 10% in the deeper horizons. The exchange complex is dominated by Ca (Walthall, 1985; Baron and Walthall, 1985). Soil development is very heterogeneous, varying in depth from 1 to 50 cm. These soils support a mature forest of Engelmann spruce (*Picea engelmannii*) and subalpine fir (*Abies lasiocarpa*), which covers about 6% of the total land area (Arthur, 1990). Alluvial and bog soils occupy only about 1% of the watershed, but have a disproportionate influence on surface water chemistry due to their position adjacent to stream channels.

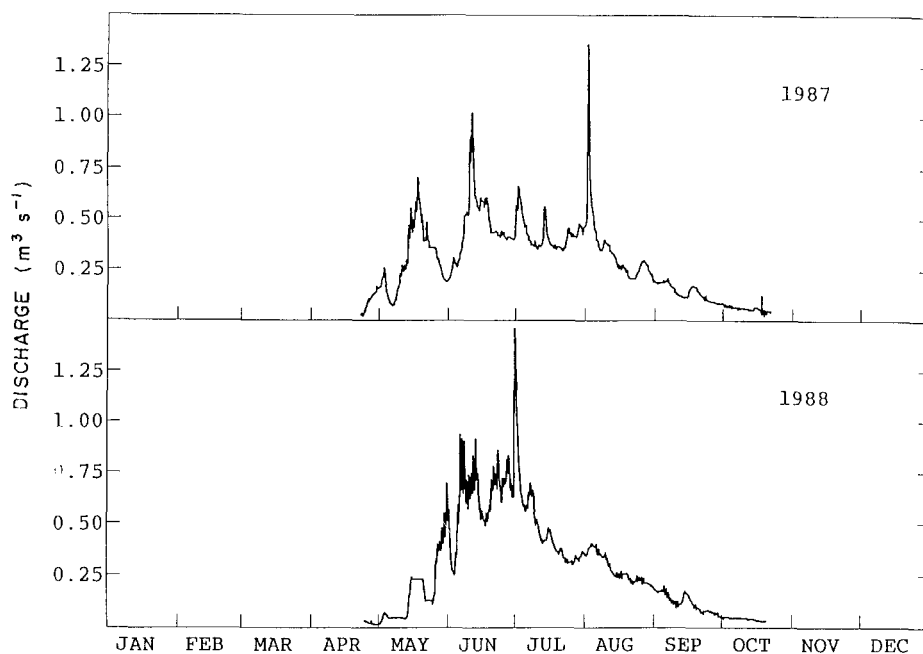


Fig. 2. Hydrographs for the Loch Outlet, 1987 and 1988.

These highly organic soils are characterized by base saturations of less than 13% (Walthall, 1985).

Accumulation of snowpack in LVWS begins in November of each year, and the melt begins in mid- to late-April. More than 75% of the annual water input to the basin is in the form of snow. Midwinter melting events are extremely rare, and snowpack temperatures remain below 0 °C above the 'depth hoar' zone from about November through late March. Peak runoff occurs late May to early June, with 40 to 50% of annual runoff occurring by July 1 (Figure 2). Meltwater from the permanent snowfields contributes to stream discharge through August, and baseflow is maintained by groundwater seepage until early winter. From December through February there is no baseflow.

The volume of The Loch is about 60 000 m³, but during winter more than half of the total water volume of the lake freezes. The remaining water is confined to a narrow channel between the inlet and outlet, so at the beginning of snowmelt the lake is more appropriately treated as part of Icy Brook. Baron and Bricker (1987) documented major increases in solute concentrations under winter ice cover; these were attributed to the exclusion of dissolved ions from lake ice.

2.2. SAMPLE COLLECTION AND ANALYSIS

Snowmelt water was collected at the base of the snowpack at three sampling sites using 3.7 × 3.7 m plastic lysimeters with 15 cm sides. The lysimeters were installed

in the fall of 1986, and grab samples were collected daily to semi-weekly in the spring of 1987. Snowmelt water was not collected in 1988.

Wet deposition was collected and analyzed as part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Sampling protocols and analytical methods are detailed in Peden (1986).

Twenty zero-tension, fritted glass plate lysimeters (8.5 cm diameter; Corning Glass Works, Inc.) were placed randomly at 10 sites in two 0.4 ha plots. These lysimeters were placed in pairs at two depths in the soils; just below the organic layer in the O_{ie} horizon, and in the mineral soil (B horizon). The actual depths of these horizons varied, but averaged 10 cm for the forest floor lysimeters and 20 cm for those placed in the mineral soil. Care was taken to avoid disturbance of the soil column.

Sixteen porous-cup tension lysimeters (Soil Moisture Equipment, SP 39045 653X1-B2M2) were placed as deeply as possible into the mineral soil (Bs horizon). All lysimeters were leached with HCl and copiously rinsed with deionized water prior to placement in the field, where they were allowed to equilibrate with the soil for more than a year before data were collected.

Snowmelt and soil solutions were collected in acid-washed polyethylene bottles, then filtered through a pre-rinsed $0.45\ \mu\text{m}$ membrane (Nuclepore) filter within 6 hr of collection. Aliquots for DOC determination from the soil solution samples were stored in precombusted glass vials, and aliquots for cation and Al analysis were acidified with HCl. These samples were analyzed at the University of Wyoming by methods detailed in Arthur (1990).

Grab samples were collected daily to weekly at the Loch Outlet during the spring of 1987 and 1988. The transition to less frequent sampling was determined on the basis of the stream pH: our objective was to document rapid chemical changes in the stream during the pH depression early in the snowmelt period. Samples were filtered at $0.4\ \mu\text{m}$ within 6 hr of collection. Aliquots for Ca, Mg, Na, K, Fe, Mn, and Al analysis were acidified to pH 1.0 with HNO_3 , and an aliquot for the analysis of NH_4 and PO_4 was preserved with HgCl_2 . DOC samples were collected in precombusted glass bottles and filtered using precombusted glass-fiber filters and flasks. ANC was measured by electrometric titration. All surface water samples were analyzed at the U.S. Geological Survey Central Laboratory in Arvada, CO by methods detailed in Fishman and Friedman (1985).

Stream discharge from the watershed was calculated from continuous measurements of stream stage in a Parshall flume at the outlet of The Loch. The flume used was calibrated for stream stages of 6 cm or more, so very early flow in both years was unmeasurable.

3. Results

3.1. SNOWMELT

Of the three snowmelt collectors installed, only one (#3) effectively sampled the

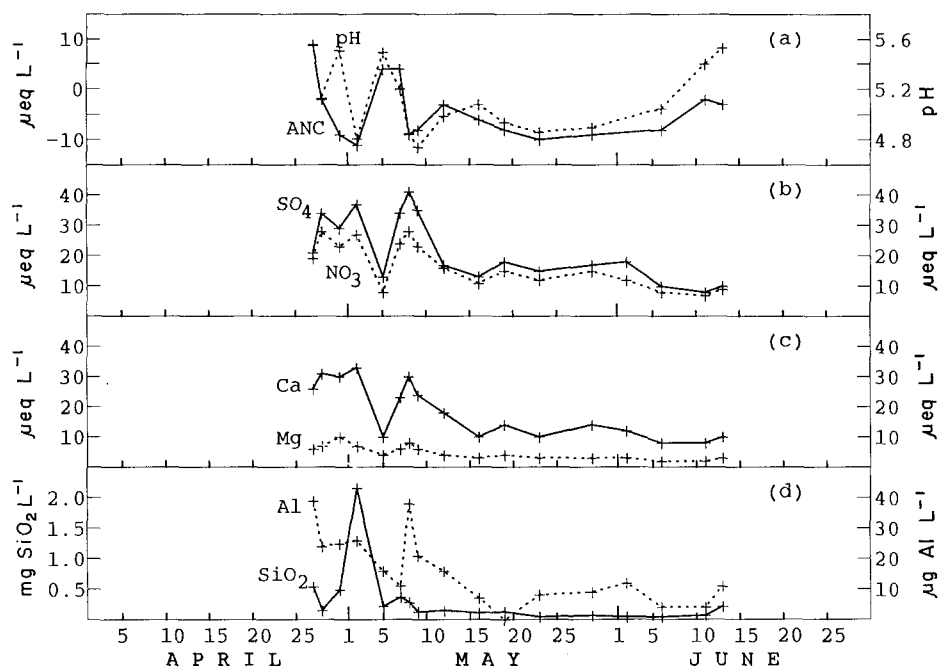


Fig. 3. Temporal plot of (a) pH, ANC; (b) SO_4 , NO_3 ; (c) Ca, Mg; and (d) Al, SiO_2 , in meltwater samples collected at snowmelt lysimeter #3 in 1987.

meltwater in 1987. A small stream of overland flow ran through one, and another was buried so deeply in a snowdrift that it was not found by field crews until the melt period was nearly over.

Concentrations of most ions in the meltwater were highest in the early samples, and declined during the snowmelt period (Figure 3). Peaks in concentration of SO_4 and NO_3 were 20 to 40 $\mu\text{eq L}^{-1}$, a two- to five-fold increase over the snow concentrations of 7 to 10 $\mu\text{eq L}^{-1}$ in wet-only NADP samples (NADP/NTN, 1989). Elevated levels of SiO_2 and Al in a few samples may have been the result of debris which accumulated in the collector before it was completely buried in the fall, or may have resulted from contamination by soil water. Most meltwater samples were acidic ($\text{ANC} < 0$), except during a cold period about May 5 when meltwater production in the snowpack nearly ceased. The snowmelt pH minimum was 4.7. By late May, pH of the meltwater was 5.5, and acid anion concentrations were lower, between 10 and 20 $\mu\text{eq L}^{-1}$.

3.2. SURFACE WATERS

Flowing water was first observed in 1987 at the Loch Outlet on March 13, following a period of unseasonably warm temperatures. Stream water was sampled from a hole excavated through the snowpack during March and part of April, but stream discharge remained too low to measure until April 22 (Figure 4a). Beginning on

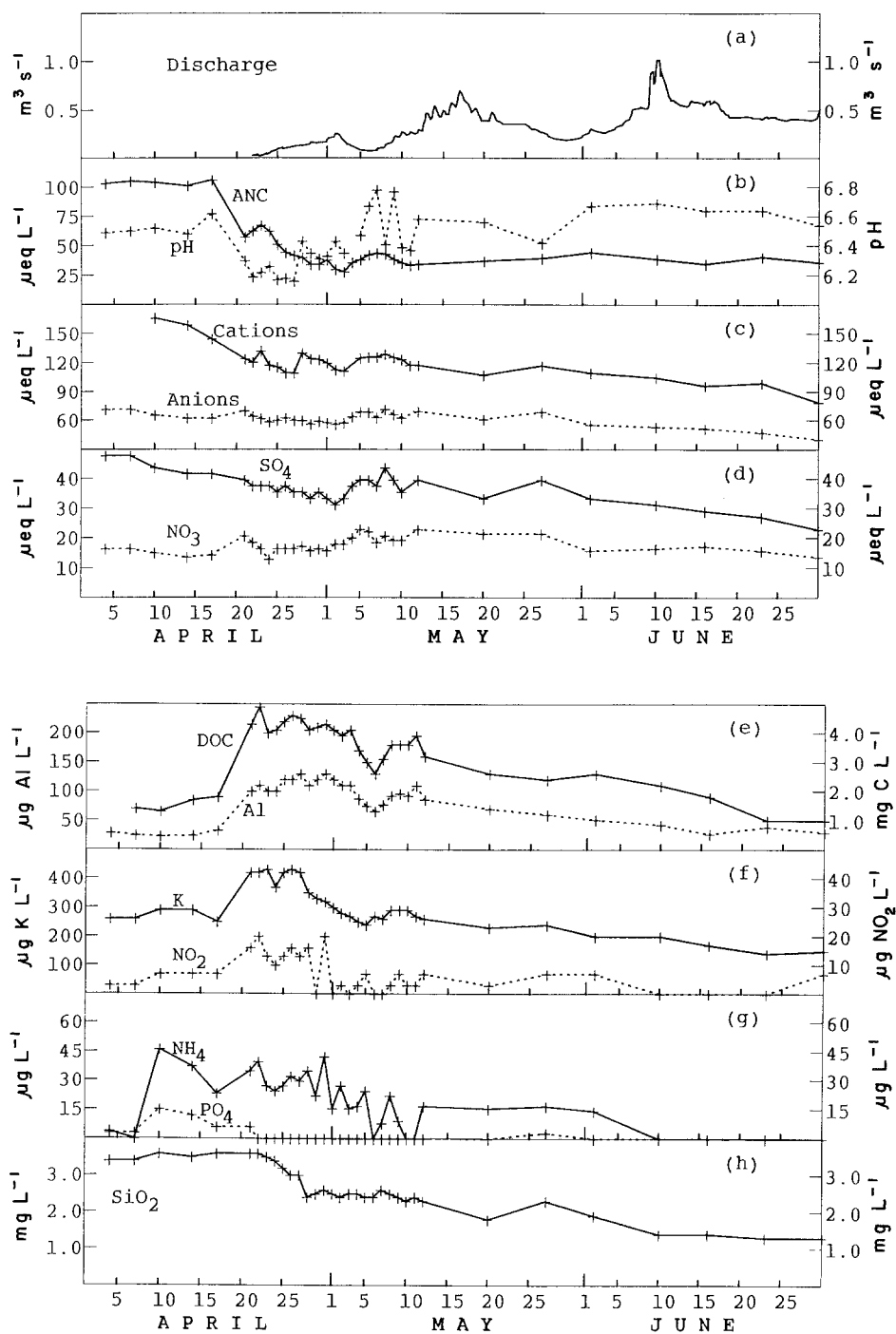


Fig. 4. Stream discharge and chemical parameters at the Loch Outlet, April through June of 1987.

April 17, pH and ANC showed steep declines (Figure 4b), with pH reaching a minimum of 6.16 on April 27 and minimum ANC of $28 \mu\text{eq L}^{-1}$ on May 3. ANC remained between 35 and $45 \mu\text{eq L}^{-1}$ for the rest of the period, and pH stabilized at about 6.5 after a peak of 6.78 in early May. The sum of the cations (Ca, Mg, Na, K, and NH_4) declined during the period, while the sum of the acid anions (NO_3 , SO_4 , and Cl) remained nearly constant (Figure 4c).

Sulfate concentrations in early samples were higher than those measured in the meltwater, and generally declined throughout the period, with the exception of a small peak associated with lower stream flow between May 6 and May 10. Nitrate concentrations remained quite steady throughout the period at between 15 and $20 \mu\text{eq L}^{-1}$.

The decline in measured ANC in the stream was accompanied by a sharp increase in dissolved organic carbon (DOC) concentration (Figure 4e). DOC increased from 1.8 mg L^{-1} to a maximum of 4.9 mg L^{-1} on April 22. DOC remained above 4 mg L^{-1} until early May, when it began to decline. Aluminium also increased from $33 \mu\text{g L}^{-1}$ on April 17 to a maximum of $130 \mu\text{g L}^{-1}$ on April 27, and was significantly correlated ($r^2 = 0.93$, $p < 0.0001$) with DOC. Peaks in the concentrations of K, NO_2 , NH_4 , and PO_4 were observed during this same period (Figure 4f, g). These species reached their highest concentrations for the entire year at the beginning of the melt period, and concentrations of NO_2 and PO_4 dropped below the limit of detection ($3 \mu\text{g L}^{-1}$) for the rest of the year. Silica was initially concentrated in the streamwater (Figure 4h), dropped sharply during the first week of melt, then declined more gradually through the rest of the 3 mo period.

Changes in solute chemistry in the Loch Outlet in 1988 were similar to those in 1987, but their timing was somewhat different (Figure 5). The stream started flowing several weeks later than in 1987, and discharge remained low until mid-May (Figure 5a). Similarly, the ANC decline was much slower than in the previous year (Figure 5b), from $104 \mu\text{eq L}^{-1}$ on April 6 to a minimum of $31 \mu\text{eq L}^{-1}$ at the end of June. The pattern for pH was more similar to 1987, with a decrease from 6.79 on April 23 to 6.25 on April 26. The sum of base cations decreased throughout the 3 mo period, but the sum of the strong acid anions showed no such systematic change (Figure 5c). Sulfate and NO_3 concentrations were again high and steady during the early part of the melt (Figure 5d), then increased briefly in late May along with most other species as stream discharge declined in response to cold water.

Concentrations of DOC and Al were again closely correlated ($r^2 = 0.88$, $p < 0.0001$), but the increases in these species were not as steep as in 1987. DOC concentration increased from 1.2 to 4.6 mg L^{-1} between April 6 and May 18, then declined for the remainder of the snowmelt period. The concurrent increase in Al was from 12 to $120 \mu\text{g L}^{-1}$. As in 1987, peaks in concentration of most nutrient species were correlated with DOC and Al increases (Figure 5f-g). Increases in these parameters in 1988 were slower and more prolonged than in 1987. Concentrations of SiO_2 followed a similar pattern (Figure 5h), reaching a maximum of 3.0 mg

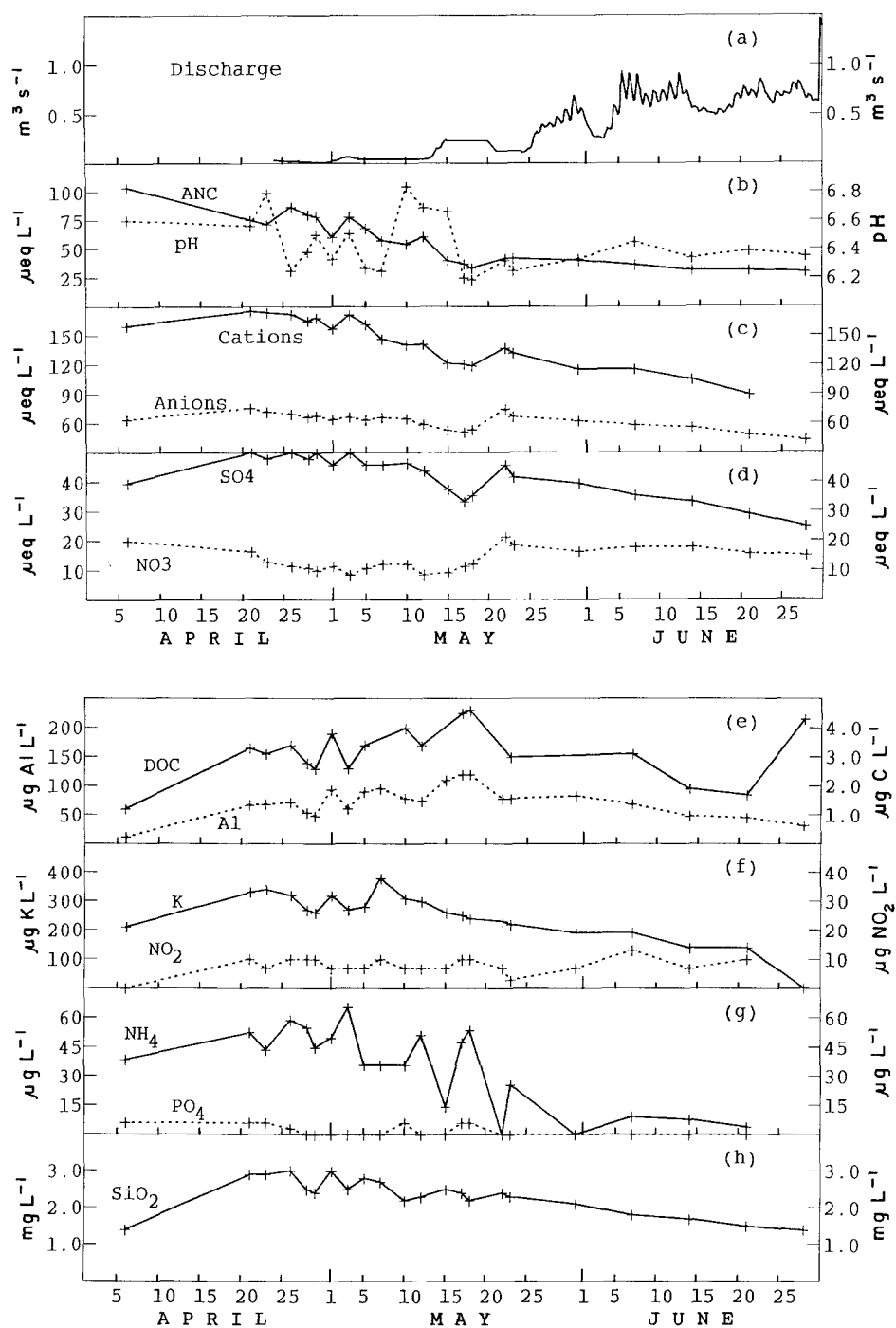


Fig. 5. Stream discharge and chemical parameters at the Loch Outlet, April through June of 1988.

L^{-1} on April 26, then declining gradually through the end of June.

3.3. SOIL SOLUTIONS

Soil solution composition was quite variable both spatially and temporally in tension and zero tension lysimeters. In many cases the standard deviations of analyte concentrations were greater than the means. Both arithmetic and volume-weighted mean (VWM) concentrations were calculated for each analyte for each lysimeter and are presented in Table I. In most cases, these VWM concentrations were greater than the simple mean concentration of all samples.

Variation in solute concentrations was much less between the two depths of zero-tension lysimeters than between the tension and the zero-tension lysimeters. The tension lysimeters consistently collected samples which were more concentrated in most analytes than the zero-tension lysimeters. Only NO_3 and NH_4 were more concentrated in zero-tension lysimeter samples.

Concentrations of Al, DOC, and SiO_2 were much higher in soil solution samples than in the surface water samples. Most soil solutions had DOC concentrations greater than 10 mg L^{-1} in zero-tension lysimeters, and the average DOC in tension lysimeter samples was more than four times as concentrated. Concentrations of Al in the tension lysimeters averaged about $900 \mu\text{g L}^{-1}$, and SiO_2 in these samples averaged about 8 mg L^{-1} .

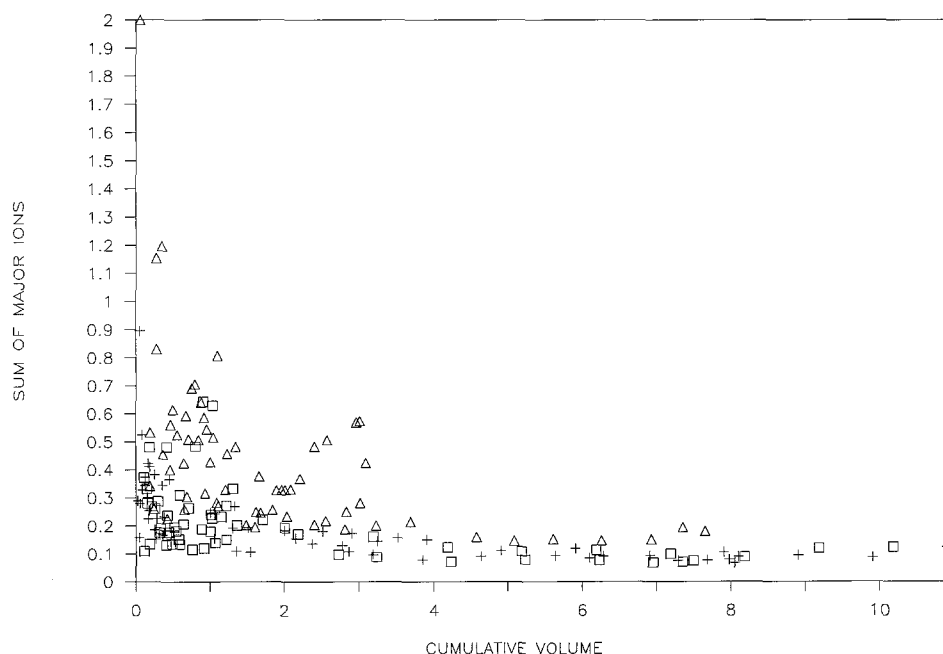


Fig. 6. Total ionic strength (meq L^{-1}) vs cumulative volume (K) for each lysimeter type in both years combined. Squares represent forest floor zero-tension lysimeters. Pluses represent B horizon zero-tension lysimeters. Triangles represent B horizon tension lysimeters.

TABLE I

	n	Min	Max	Med	Mean	SD	VWM
Zero-tension lysimeters: florest floor							
H	78	0.4	166	6	16	32	19
ANC	20	2	158	12	42	55	65
Ca	39	26	312	52	77	63	101
Mg	40	9	98	18	30	25	45
Na	42	8	152	13	28	37	47
K	42	<1	69	7	15	18	23
NH ₄	45	<1	164	<1	7	25	7
SO ₄	54	<2	94	16	25	18	32
NO ₃	54	<1	151	<1	10	26	21
Cl	54	<2	129	11	25	26	38
SiO ₂	21	1.4	5.6	2.1	2.3	0.8	3.1
Al	18	80	570	110	180	140	350
DOC	51	4.8	72.4	9.8	15.6	11.9	19.4
Zero-tension lysimeters: B horizon							
H	114	1	234	5.2	9.8	21	9.7
ANC	39	1	248	19	40	53	27
Ca	67	20	320	56	75	52	93
Mg	70	7	149	24	38	32	49
Na	79	7	152	21	32	25	37
K	79	2	71	10	13	12	19
NH ₄	68	<1	19	<1	<1	3	3
SO ₄	94	<2	106	20	28	20	29
NO ₃	93	<1	66	<1	3	9	8
Cl	94	<2	141	12	22	24	38
SiO ₂	46	0.4	26	2.8	3.8	3.5	6.7
Al	36	80	1400	230	350	270	370
DOC	75	3.7	78	11.3	16.3	13.4	19.6
Tension lysimeters: B horizon							
H	102	3	102	15	13	14	11
ANC	62	0	193	40	55	42	67
Ca	72	66	1008	206	271	205	373
Mg	82	26	251	58	70	42	83
Na	84	9	104	18	21	14	29
K	80	3	92	12	23	23	35
NH ₄	<1	<1	1	<1	<1	<1	<1
SO ₄	92	<2	493	41	65	76	83
NO ₃	92	<1	21	<1	1	3	3
Cl	92	<2	21	14	29	36	43
SiO ₂	67	1.5	26	6.2	6.6	4.5	8.1
Al	67	200	1900	900	900	400	920
DOC	93	<1	142	41	41	27	51

All concentrations in $\mu\text{eq L}^{-1}$ except SiO₂ in mg L^{-1} , and Al in $\mu\text{g L}^{-1}$. SiO₂ and Al were analyzed in 1987 only.

Samples from all depths showed declining concentrations during the melt period (Figure 6). Simple linear regressions of ionic strength vs cumulative volume collected for each lysimeter sample yielded highly significant negative correlations ($p < 0.0001$).

4. Discussion

In both years of the study pH and ANC in the stream water decreased at the beginning of the snowmelt period. Possible reasons for these declines are (1) titration of surface water ANC by strong acids in the meltwater; (2) the dilution of surface water ANC by meltwater; and (3) mixing of water from various sources upstream, including surface water, snowmelt water, and soil solution.

If titration was occurring, increases in the concentration of the strong acid anions should balance the decrease in ANC. Dilution of surface water ANC would be concurrent with decreases in the concentration of other species with similar declines in both acid anions and base cations. The data from this study show that decreases in streamwater ANC were greater than can be accounted for by changes in the concentration of major cations and anions (Figures 4 and 5). In 1987, the initial decrease in ANC by $78 \mu\text{eq L}^{-1}$ exceeded the decrease in the difference between acid anions and base cations by $50 \mu\text{eq L}^{-1}$. In 1988, the more gradual decrease in ANC of $73 \mu\text{eq L}^{-1}$ over the entire period was $47 \mu\text{eq L}^{-1}$ more than expected based on major ion concentrations. The resulting anion deficits were accompanied by elevated concentrations of DOC. Thus neither titration nor dilution explains the observed temporal patterns in surface water concentrations, and mixing of water from upstream sources must have had an influence on surface water concentrations.

Although all water in the study area is ultimately of meteoric origin, different hydrologic pathways can lead to large differences in residence time and chemical composition of the water in the system. Some studies have combined geochemical and hydrologic models to explain variations in surface water chemistry (Lam *et al.*, 1986; Bobba and Lam, 1988, 1989). Surface water can be represented as a mixture of water derived from a variety of sources with different solute compositions, with hydrologic controls of the mixing ratios among the source waters defining the overall solute concentrations. In this study, the possible sources of stream water were (1) lake water from The Loch, (2) snow meltwater, and (3) soil water. Solute levels in these three source waters were quite different (Figures 3, 4, 5; Table I), so changes in their relative contributions to stream discharge would result in changes in surface water chemical composition.

4.1. LAKE WATER CONTRIBUTION

The water in The Loch at the end of the winter was much higher in pH and ANC (Figure 4 and 5) than either of the other sources (Figure 3, Table I). The lake stratifies inversely under ice cover in winter, with denser bottom water at 4°C under colder water just beneath the ice. Previous studies have documented limited

mixing of early snowmelt runoff at or near 0 °C with denser bottom water under these conditions (Bergmann and Welch, 1985). Some mixing by turbulence and diffusion at the layer boundaries is inevitable however, so a contribution of deep, higher ANC lake water is expected.

In late winter, the volume of water in The Loch is less than 30 000 m³. The volume of water flowing through the lake during the decline in surface water ANC was much larger than this in both years. In 1987, the minimum pH and ANC occurred on May 2 (Figure 4) by which time the cumulative discharge from The Loch was about 140 000 m³ or nearly 5 times the volume of the lake. In 1988, 182 000 m³ had flowed through the flume by the time of the pH minimum. By this time, it is unlikely that much winter lake water remained, so we believe the lake to be a significant source of stream water only at the very beginning of the melt.

4.2. SNOW MELTWATER CONTRIBUTION

Meltwater percolating through a spring snowpack leaches solutes from crystal boundaries (Johannessen and Henricksen, 1978; Cadle *et al.*, 1984; Stein *et al.*, 1986; Semkin and Jeffries, 1988). This fractionation can produce meltwater early in the melt period which is much more acidic than the snowpack as a whole. Snowmelt samples collected in this study (Figure 3) exhibited higher concentrations during the first half of the melt period than in the second half.

Snowmelt was acidic (Figure 3), and if piped directly to surface waters would result in decreases in stream pH and ANC. Marsh and Woo (1984) showed that basal ice layers in the snowpack can create a pathway by which such pure meltwaters can be routed directly to surface waters. Pierson and Taylor (1985) documented a similar phenomenon due to impermeable ground frost. Stottlemeyer (1987) found that rapid meltwater production overcame the hydraulic conductivity of forest soils in a northern Michigan watershed and caused direct inputs to surface water by overland flow. Since stream samples in this study never became acidic or exhibited the low pH of the early meltwater samples (Figures 4 and 5), these direct pathways could not have been dominant. Unadulterated snow meltwater was not the dominant source of surface waters in this study.

Another important factor controlling the influence of meltwater inputs to stream waters was the timing of the melt. It seems unlikely to us that the melting process proceeded at the same rate throughout the watershed. Wind redistribution of the snow during the winter led to large differences in the depth of the snowpack, and differences in slope, aspect, and vegetative cover (shading) are likely to cause some areas to begin melting much earlier than other areas. The high-concentration early meltwater must have been flowing from some areas of the watershed even as later, more dilute water was being contributed from other areas. This spatial heterogeneity of meltwater production resulted in less acidic inputs to surface waters than would be expected if the entire snowpack ripened and released meltwater at the same time.

4.3. SOIL SOLUTION CONTRIBUTION

Soil solutions sampled in this study exhibited large differences in solute chemistry depending on the collection method (Table I). Samples collected in the zero-tension lysimeters were generally more dilute than those collected in the tension lysimeters. Some workers have reported sample contamination from the ceramic material of the porous cup lysimeters (Litaor, 1988), but never with the model used in the present study. These problems tend to produce concentrations of K, Al, and SiO_2 as much as an order of magnitude higher than the natural soil solutions collected. The data from this study do not show such extreme values.

It is more likely that tension and zero-tension lysimeters collected different fractions of the soil solution. Tension lysimeters may preferentially collect water from soil micropores, whereas the zero-tension lysimeters preferentially sample macropore flow (Schaffer *et al.*, 1979; Wang, 1984; Arthur, 1990). By this reasoning, micropore water is more tightly held by capillary pressure, and requires tension to collect. Seepage rates are much slower for micropore flow, and the contact time of this water is therefore longer than for solutions in soil macropores. Longer contact times, and the presumably greater surface area of the micropore space, result in the higher concentrations for these samples. This is further suggested by the fact that concentrations in the tension lysimeter samples were generally closer to those measured on a 1:1 soil-water paste in the laboratory (Walthall, 1985).

Concentrations of Al in soil lysimeter samples were more than an order of magnitude higher than expected for equilibrium between dissolved inorganic Al species and a solid phase such as $\text{Al}(\text{OH})_3$ at the pH of these samples (Drever, 1988). Fulvic acids, produced by the decomposition of organic material in the soil, can form strong complexes with Al (Driscoll, 1985; Lawrence *et al.*, 1986; Backes and Tipping, 1987; Plankey and Patterson, 1987; Abrahams *et al.*, 1988). High concentrations of DOC found in the soil lysimeter samples support the hypothesis that such organic Al complexes are the reason for the increased Al solubility in these soils.

Concentrations of Al in early surface water samples (Figures 4 and 5) are more than two orders of magnitude higher than the theoretical solubility at pH 6 (Drever, 1988). Complexation of Al with F or SO_4 ions could account for some increase in inorganic Al concentrations, but not enough at the low concentrations of these ions found in the soil solutions in this study. Significant correlation between dissolved Al and DOC in these samples suggests organic Al complexes formed in the soils as a source of this material. The peaks of nutrient concentrations in the surface waters at the beginning of the melt also support the idea that soil solution was flushed at that time (Figures 4 and 5). Flushing of nutrients from the soils at the beginning of the melt indicates a decoupling of these species from their biological cycles. Soils in the study area rarely freeze, so organic decomposition probably proceeded slowly under the snowpack throughout the winter, and decomposition products may have accumulated in the soil solution. Reduced biological activity

under the snow would have prevented rapid uptake of these nutrients. When water from the melting snow infiltrated in the spring, these species were flushed into surface waters. Declining total ionic strength through the melt period in both years (Figure 6) further support the hypothesis that soil solution was flushed rapidly by infiltration of meltwater. A similar pattern was reported by Johannesssen *et al.* (1980). These authors categorized the runoff into three phases: early piston flow, peak concentrations from snowpack solute release, and dilution.

By the time of the peak discharge in mid-June, DOC and Al concentrations declined to pre-snowmelt levels in both 1987 and 1988. This decline reflects dilution of the soil solution component in the stream by the much larger inputs from melting snow. Most ions in the surface waters reached their annual minimum concentrations by mid-June (Baron and Bricker, 1987).

The relatively strong influence of forest soil drainage on stream composition at the beginning of the melt season is somewhat surprising given the small areal soil coverage of the watershed. Mast *et al.* (1990) have shown that on an annual basis, weathering of primary minerals in the bedrock of LVWS can explain nearly all of the flux of ions from the basin. We hypothesize that snowpack in the lowest (forested) parts of the watershed melts earliest, and that asynchronous melting causes surface waters to exhibit the characteristics of a forested catchment with well-developed soils in the early spring. Later in the season meltwater inputs from higher areas of the basin dominate, and solute chemistry reflects the predominantly alpine character of the watershed. By late spring the soil drainage component is difficult to detect.

5. Conclusions

Direct collection of meltwater from the base of the snowpack in 1987 indicated that an 'acidic pulse' of concentrated melt water was produced by the snowpack. Variations in release times of acidic inputs across the watershed caused the pulse at The Loch Outlet to be less acidic than snowmelt released from a given location in the pack.

Reductions in surface water ANC at the beginning of the 1987 and 1988 snow-melt season resulted from the replacement of concentrated winter surface waters, not from titration by acidic meltwater inputs. Soil solutions flushed by melting snow were a significant component (perhaps as much as 45%) of the more dilute water which fills The Loch as the winter water was flushed out. These solutions carried the accumulated products of decomposition of soil organic matter, which built up during the winter when biological nutrient cycles were suppressed. The strong relation between DOC and Al in surface water samples suggests that humic substances are an effective agent for the complexation of Al in the soil, and organically-bound Al functions as an effective tracer of soil drainage in surface waters. Soil drainage contributed humic substances and Al to stream outputs throughout the flow season in LVWS, but water from melting snow dominated

the stream discharge by mid-May.

Chemical and hydrologic processes on LVWS during the two years of this study prevented significant degradation of surface water quality during the snowmelt period. In both years the hydraulic conductivity of the forest soils was sufficient that infiltration of acidic meltwater buffered these inputs. Meltwater produced later from alpine areas was diluted by snowmelt from areas which had already lost most of their chemical constituents. The consistently positive ANC values in surface waters imply that episodic acidification of Loch Vale Watershed during snowmelt is unlikely at the present levels of atmospheric loading.

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References

- Abrahams, P. W., Tranter, M., Davies, T., and Blackwood, I. L.: 1988, *Water, Air, and Soil Pollut.* **43**, 231.
- Arthur, M. A.: 1990, 'The Effects of Vegetation on Watershed Biogeochemistry at Loch Vale Watershed, Rocky Mountain National Park, Colorado', Ph. D. Dissertation, Cornell University, Ithaca, NY.
- Backes, C. A. and Tipping, E.: 1987, *Water Resour. Res.* **21**, 221.
- Baron, J. and Bricker, O. P.: 1987, 'Hydrologic and Chemical flux in Loch Vale Watershed, Rocky Mountain National Park', in R.C. Averett and D. McKnight (eds.), *Chemical Quality of Water and the Hydrologic Cycle*, Lewis Publishers, Ann Arbor, MI, pp. 141-156.
- Baron, J. and Walthall, P. M.: 1985, 'The Nature of Precipitation, Soil, and Surface-Water Chemistry in a Subalpine Ecosystem', in D. E. Caldwell, J. A. Brierley, and C. I. Brierley (eds.), *Planetary Ecology*, Van Nostrand Reinhold Co., Inc., New York, NY, pp. 497-508.
- Bergmann, M. A. and Welch, H. E.: 1985, *Can. J. Fish. Aquat. Sci.* **42**, 1784.
- Bobba, A. G. and Lam, D. C. L.: 1988, *Can. J. Fish. Aquat. Sci.* **45**, 81.
- Bobba, A. G. and Lam, D. C. L.: 1989, *Water, Air, and Soil Pollut.* **46**, 261.
- Cadle, S. H., Dasch, J. M., and Grossnickle, N. E.: 1984, *Water, Air, and Soil Pollut.* **22**, 303.
- Cole, C. J.: 1977, 'Geology of East-Central Rocky Mountain National Park and Vicinity, with Emphasis on the Emplacement of the Precambrian Silver Plume Granite in the Longs Peak-St. Vrain Batholith', Ph.D. Dissertation, Univ. Colorado, Boulder. 344 pp.
- Drever, J. I.: 1988, *The Geochemistry of Natural Waters*, 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, NJ.
- Driscoll, C. T.: 1985, *Env. Health Perspective* **63**, 93.
- Fishman, M. J., and Friedman, L. C.: 1985, 'Methods for Determination of Inorganic Substances in Water and Fluvial Sediments', in *Techniques of Water Resources Investigations of the U.S. Geological Survey*, Book 5, Ch. A6, U.S. Government Printing Office, Washington, DC.
- Haines, T. A.: 1981, *Trans. Am. Fish. Soc.*, **110**, 669.
- Harte, J. and Hoffman, E.: 1989, *Conserv. Biol.* **3**, 149.
- Jeffries, D., Cox, C., and Dillon, P.: 1979, *J. Fish. Res. Bd. Canada* **36**, 640.
- Johannessen, M. and Henriksen, A.: 1978, *Water Resour. Res.* **14**, 615.
- Johannessen, M., Skartveit, A., and Wright, R. F.: 1980, in D. Drablos and A. Tollen (eds.), *Proc. Int. Conf. Ecol. Impact Acid Precip.*, SNSF Project, Oslo, pp. 224-225.
- Lam, D. C. L., Boregowda, S., Bobba, A. G., Jeffries, D. S., and Patry, G. G.: 1986, *Water, Air,*

- and Soil Pollut.* **31**, 149.
- Landers, D. H., Eilers, J. M., Brakke, D. F., Overton, W. S., Kellar, P. E., Silverstein, M. E., Schonbrod, R. D., Crowe, R. E., Linthurst, R. A., Omernik, J. M., Teague, S. A., and Meier, E. P.: 1987, *Characteristics of lakes in the Western United States, Vol. I: Population Descriptions and Physico-Chemical Relationships*, EPA-600/3-86/054a, U.S. Environmental Protection Agency, Washington, DC.
- Lawrence, G. B., Fuller, R. D., and Driscoll, C. T.: 1986, *Biogeochemistry* **2**, 115.
- Litaor, M. I.: 1988, *Water Resour. Res.* **24**, 727.
- Marsh, P., and Woo, M.: 1984, *Water Resour. Res.* **20**, 1853.
- Mast, M. A.: 1989, 'A Laboratory and Field Study of Chemical Weathering with Special Reference to Acid Deposition', Ph.D. Dissertation, Department of Geology and Geophysics, University of Wyoming, Laramie, WY, 174 pp.
- Mast, M. S., Drever, J. I., and Baron, J.: 1990, *Water Resour. Res.* **26**, 2971.
- NADP/NTN National Atmospheric Deposition Program/National Trends Network: 1989, NADP/NTN Coordination Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.
- Peden, M. E.: 1986, *Methods of Collection and Analysis of Wet Deposition*, Illinois State Water Survey, Report No. 381, Champaign, IL.
- Pierson, D. C. and Taylor, C. H.: 1985, *J. Glaciology* **31**, 190.
- Plankey, B. J. and Patterson, H. H.: 1987, *Environ. Sci. Technol.* **21**, 595.
- Schaffer, K. A., Fritton, D. D., and Baker, D. E.: 1979, *J. Environ. Qual.* **8**, 241.
- Schofield, C. L., Galloway, J. N., and Hendrey, G. R.: 1985, *Water, Air, and Soil Pollut.* **26**, 403.
- Semkin, R. G., and Jeffries, D. S.: 1988, *Can. J. Fish. Aquat. Sci.* **45**, 38.
- Stein, J., Jones, H. G., Roberge, J., and Sochanska, W.: 1986, 'The Prediction of both Runoff Quality and Quantity by the Use of an Integrated Snowmelt Model', in E. M. Morris (ed.), *Modelling Snowmelt-Induced Processes*, IAHS Publication No. 155, pp. 358-374.
- Stoddard, J.: 1987, *Limnol. Oceanogr.* **32**, 825.
- Stottlemeyer, R.: 1987, *Can. Fish. Aquat. Sci.* **44**, 1812.
- Turk, J. T. and Spahr, N. E.: 1991, Rocky Mountains: Controls on Lake Chemistry', in D. Charles (ed.), *Acid Deposition and Aquatic Ecosystems*, Springer-Verlag, New York.
- Vertucci, F. A.: 1990 'Methods for Detecting and Quantifying Lake Acidification', *Proceedings of the International Mountain Watershed Symposium, Subalpine Processes and Water Quality*, in I. G. Popoff, C. R. Goldman, S. L. Loeb, and L. B. Leopold (eds.), Tahoe Resource Conservation District, P.O. Box 10529, South Lake Tahoe, CA.
- Walthall, P. M.: 1985, 'Acidic Deposition and the Soil Environment of Loch Vale Watershed in Rocky Mountain National Park', Ph.D. Dissertation, Department of Agronomy, Colorado State University. 148 pp.
- Wang, D.: 1984, 'Fire and Nutrient Dynamics in a Pine-Oak Forest Ecosystem in the New Jersey Pine Barrens', Ph.D. Dissertation, Yale University, New Haven, CT.