Watershed Biogeochemical Processes Affecting Surface Waters in the Sierra Nevada with Emphasis on Snow Melt Episodes

Final Report
California Air Resources Board
ARB Contract Number AO32-116

Principal Investigators:
Aaron D. Brown and J. M. Melack

Contributing Scientist:
M. R. Williams

Marine Science Institute
University of California
Santa Barbara, CA 93106

September 1997

Abstract

Mass balances, mineral weathering, and the capacity to neutralize acidic snowmelt inputs were studied during the snowmelt periods of 1992 and 1993 in two small alpine catchments (2957 m) in Sequoia National Park, California. The catchments are 0.5 and 0.2 ha with 10 and 25% soil coverage, respectively, and are dominated by granodiorite rock outcrops. Between-catchment differences in the solute concentrations of both runoff and soil solutions indicate that soils are important factors in determining the chemical composition of surface runoff. Significant relationships of $[SO_4^{2-}]$ with base cations and Si in runoff, and the reconciliation of Ca^{2+} residuals in stoichiometric weathering reactions achieved by subtracting Ca^{2+} in the equivalent amount of SO_4^{2-} present, indicate that SO_4^{2-} is partially a product of weathering processes in these catchments. Sulfate flux was not attributed to SO_4^{2-} desorption processes. An ionic pulse of strong acid anions from the catchments was observed in runoff, but the timing of peak NO_3^- and SO_4^{2-} export was sometimes delayed until the late snowmelt period, indicating that soil processes may help regulate the timing of solute export in these alpine catchments. Cation exchange processes caused pH to decrease in response to a rain-on-snow event and applications of a LiBr tracer. The retention of Li^+ by predominately rock catchments suggests that acid neutralizing capacity is not compromised in areas with only sparse alpine soil cover, and rock surfaces may contribute to acid neutralization processes.

Acknowledgments

The authors wish to thank D. Graber, A. Esperanza the other research staff of the National Park Service at Ash Mountain for their support and permission to conduct this study within the confines of Sequoia National Park. This research was funded by the Air Resources Board of California (Contract No: A032-116) and NASA grant NAGW-2602.

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Conclusions and Recommendations

We observed that mineral weathering is the primary source of excess SO_4^{2-} from these alpine catchments. We observed significant relationships of SO_4^{2-} with solutes derived from mineral weathering, and negligible dry deposition of SO_4^{2-} and sulfate-desorption from soils. The reconciliation of Ca^{2+} in stoichiometric weathering reactions done by subtracting a contribution from sulfate-bearing rocks supports the our contention that mineral weathering is a source of SO_4^{2-} in these catchments. In addition to this finding, chemical data and water balances offer an unique opportunity to determine whether dry deposition, preferential dissolution of anorthite, or the presence of calcite, are factors responsible for incongruities in stoichiometric weathering reactions commonly found in alpine catchment studies. To accomplish this objective, we recommend the following: 1) a small plot (1 m^3) study in each catchment to determine summer and fall dry deposition inputs of solutes to these catchments, 2) a mineralogical survey of the catchments for evidence of sulfate-bearing rock (pyrite) and calcite, and 3) soil leaching experiments and measurements of cation exchange capacity (CEC) to determine the neutralization and leaching potential of the soils in these catchments. Lastly, we determined that even sparse soil coverage in alpine catchments plays an important role in the retention of chemical constituents in snowmelt runoff, and this finding has important implications for studies concerning the effects of acid precipitation in the Sierra Nevada.

Introduction

Alpine catchments of the Sierra Nevada have a snowmelt-dominated hydrologic cycle and limited capacity to neutralize acids (Melack & Stoddard 1991), which make these ecosystems particularly sensitive to the combined effects of acid deposition and climate warming. Most chemical fluxes occur during the early part of snowmelt runoff, producing an ionic pulse that is released from the snowpack (Williams & Melack 1991, Bales et al. 1993). Ionic pulses can result in rapid and significant changes in the chemical composition of lakes and streams. For instance, Sierran lakes are the most dilute group of lakes in the United States (Landers et al. 1987), and lowering their pH to below 5.5 could decrease the diversity of benthic invertebrate and algal communities (Kratz et al. 1994, Barmuta et al. 1990).

A variety of hydrologic and biogeochemical processes in shallow soils influence the composition of stream water in alpine catchments (Campbell et al. 1995, Williams et al. 1993, Williams et al. 1991). Important processes can include mineral weathering, cation exchange, SO_4^{2-} adsorption and desorption, and biotic reactions involving nitrogen compounds (Williams et al. 1996, Williams et al. 1995, Brown & Lund 1991). Mineral weathering influences the runoff chemistry of alpine catchments (Allen et al. 1993, Abrahamsen et al. 1979, Reuslatten & Jorgensen 1978, Feth et al. 1964), yet many geochemical studies done in the Sierra Nevada and Rocky Mountains are unable to reconcile stoichiometric residuals of Ca^{2+}, Si and deficits of HCO_3^- with measured concentrations (Campbell et al. 1995, Williams et al. 1993, Brown & Lund 1988, Clow 1987, Stoddard 1987). In some alpine catchments, preferential weathering of anorthite (Clayton 1988) or calcite (Drever & Hurcomb 1986) may serve as additional sources of Ca^{2+}. However, the preferential weathering of anorthite is speculative, and calcite is not present in appreciable quantities to attain stoichiometric balance of Ca^{2+} in the Emerald Lake

watershed (Williams et al. 1993). Dissolution of solid phases, biological activity, and sorption reactions may regulate Si concentrations in surface runoff (Brown 1993, Gaudet & Melack 1981).

Regulation of SO_4^{2-} concentration in surface waters has been shown to be an important component of alkalinity in Sierran lake systems (Brown et al. 1990a; Williams & Melack 1991). Sorption and desorption processes in soils possibly influence SO_4^{2-} concentrations in surface waters (Brown et al. 1990b, Nodvin et al. 1988), yet may not be the principal source or mechanism regulating the timing of relatively large fluxes of SO_4^{2-} from catchments (Likens et al. 1990, Johnson et al. 1986, Johnson & Henderson 1979). For instance, Lynch & Corbett (1989) determined that sulfate export in catchments can be regulated by overwintering mineralization of sulfur-rich reservoirs in soils and the staggered flushing of these reservoirs during the snowmelt period. Accurately predicting the chemical composition of surface runoff requires additional information on the dynamics (Hooper et al. 1990) and capacity (Brown et al. 1990b) of sulfate-regulating mechanisms in Sierran catchments.

Elucidating the geochemical processes that modify the solute composition of snowmelt runoff is difficult in large, minerologically and vegetatively heterogeneous catchments (Williams et al. 1991, Campbell et al. 1995). Moreover, staggered solute inputs from different contributing areas of a catchment during snowmelt runoff commonly confound observations concerning regulatory processes (Baron & Bricker 1987). Snowmelt runoff typically has short hydraulic residence times, and often is characterized by rapid flow (Bales et al. 1993), which suggests that some of the solutes in snowmelt runoff are not regulated by geochemical or biological reactions. Consequently, research is required to determine the extent to which certain geochemical and biological processes modify the chemical content of snowmelt runoff in Sierran catchments (Williams et al.

1993). For instance, small-scale catchments eliminate some of the spatial variability inherent in larger watersheds, and catchment comparisons are amenable to testing differential flowpaths and the relative importance of soil coverage in regulating solute export. Moreover, high frequency sampling (diel and daily) can reduce limitations of weekly to biweekly sampling, since missing diel and weekly variations in solute concentrations weaken possible inferences that can be made concerning regulatory processes affecting surface runoff. Similar research is necessary to assist in hydrochemical modeling and the regional and global scaling of biogeochemical processes in mountainous catchments. Such efforts will be successful only with the availability of long-term and high-quality hydrochemical data, and the determination of important biogeochemical processes regulating solute concentrations in surface runoff (Harrington et al. 1995, Wolford et al. 1996).

The motivation of this study was examine the hydrologic flowpaths and geochemical processes that regulate solute fluxes in alpine catchments, and how these affect acid neutralization processes in catchments with different amounts of soil coverage. Hence we measured the chemical composition of snow and surface runoff in two small (<0.5 ha) alpine catchments and make comparisons between catchments with different proportions of soil during two contrasting runoff periods. Tracer experiments using LiBr were conducted to analyze hydrologic flowpaths, and we compare Li^+ concentrations in snowmelt runoff to infer the amount of contact between snow melt and the soil or rock surfaces where acid neutralization processes occur. Our discussion of the geochemical mechanisms that regulate the export of solutes emphasizes those bearing on SO_4^{2-}, HCO_3^-, Ca^{2+}, and Si.

Study Site

The paired catchment area is at an elevation of 2957 m near Pear Lake in Sequoia National Park (36° 36' 26" N, 118° 39' 49" W). Catchment 1 (referred to as the rock catchment) is approximately 0.5 ha and dominated by bedrock outcrops, whereas catchment 2 (referred to as the soil catchment) is approximately 0.2 ha and contains about 25% soil coverage (Figure 1). Bedrock of the catchments is exfoliated granodiorite, which was glaciated within the last 10,000 years, leaving little colluvium or soil. Granodiorite of the Castle Creek (An_{24} plagioclase) and Emerald Lake (An_{42} plagioclase) Formations underlies about 15% of the adjacent Emerald Lake basin, and dark minerals comprise about 15% by volume of the granodiorite (Clow 1987). Soils are well drained Cryumbrepts and Cryorthents, and are derived primarily from weathering of the underlying bedrock. The average depth of the soils in the rock and soil catchments is several cm, although deeper areas (>30 cm) are located in the soil catchment. The catchment boundaries are well defined topographically.

Methods

Duplicate snow cores were collected weekly in each catchment in polyvinyl tubes that were acid cleaned and rinsed with deionized water (DIW). Samples were sealed and frozen in DIW rinsed polyethyene bags until melted for analysis (Brown 1995). Rain samples were collected in an Aerochemetrics Wet/Dry collector using polyethylene buckets that were rinsed with DIW. Runoff samples were collected automatically at least 4 times per day, up to a rate of 24 per day using Isco Model 3500 samplers. Soil solution samples were collected 1 to 3 times per day in suction samplers (Brown et al. 1990b). Soil profile samples were collected in sufficient replicates (n=4) to give a measure of variability for the parameters measured.

Some sample water was filtered using Nuclepore polycarbonate filters (0.4 μm nominal pore size) and stored in acid washed and DIW rinsed polyethylene bottles at about 4°C until analysis. Soil samples were stored field moist in sealed polyethylene bags at about 4°C. Unfiltered sample aliquots were obtained for analysis of pH, acid neutralizing capacity (ANC) and electrical conductance.

Analyses for pH, ANC, specific conductance, Si, and NH_4^+ were conducted at the University of California at Santa Barbara or Sequoia National Park. Other major constituents determined were Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-}, and Cl^-. Methods are described in detail elsewhere (Melack et al. 1989, Brown et al. 1990b) and are outlined briefly here. pH was measured using glass electrodes for measurement in low ionic strength solutions. ANC was determined by potentiometric titration with HCl (Gran 1950, 1952). Specific conductance was measured with a platinum conductance cell (k=0.1). Both pH and specific

conductance were temperature corrected to 25°C. Ammonium was measured colorimetrically using an indophenol blue method (Strickland & Parsons 1972). Sodium and K^+ were measured by flame atomic adsorption spectroscopy, and Ca^{2+} and Mg^{2+} were measured by flame atomic absorption spectroscopy using purified KCl or $LaCl_3$ as a matrix modifier to decrease interferences. Strong acid anions were measured by low pressure ion chromatography using a Dionex AS4-A separator column and dilute $NaHCO_3$ eluent. Silicon was measured colorimetrically as a silico-molybdate complex (Strickland & Parsons 1972). Quality assurance and control guidelines are given elsewhere (Melack et al. 1989).

The quantity of water stored in snow was measured weekly. The depth and extent of snow cover was measured by a survey of snow depths along pre-arranged transects. Snow pits were located in or near the study catchments for measurement of snow density.

Rain quantity and intensity was measured with either Qualimetrics or Sierra Misco tipping bucket rain gauges. Depths were checked with a standard non-recording rain gauge and with an Aerochemetrics Wet/Dry rain collector.

Evaporation was calculated by the energy balance method using specially collected meteorological data. These data were collected every 5 minutes and averaged over 15 minute intervals at a 3-5 m tower in the soil catchment. Data collected included: wind speed, humidity, air and snow temperature, and incident and reflected radiation.

Runoff discharge was measured at precision-built H-flumes located at constrictions defining the outflows from the catchments. Stage-discharge relations for these flumes are well-known. Stage measurements were made every 5 minutes

and averaged over 15 minutes using Model II Stevens Depth Transducers or Druck pressure transducers. The transducers were calibrated several times each day throughout the season by direct measurement of stage in the flumes.

Hydrologic pathways and residence time were evaluated in each of the catchments using tracers at different times during snow melt. The chemical tracer LiBr was applied in a basin-wide grid at the base of the snowpack through access tubes driven vertically into the snow. The dosage of LiBr was determined for each application based on an estimate of discharge to minimize concentrations. The residence time of snowmelt water was estimated based on the time of initial appearance of Br^- at the flume and the disappearance of Br^- after, usually, several days.

Data analysis - Volume-weighted mean (VWM) concentrations were calculated for solutes in runoff both daily and for each water year. The equation for calculating VWM concentrations for n measured runoff samples can be represented as

$$VWM = \frac{\sum_{i=1}^{n} CiVi}{\sum_{i=1}^{n} Vi} \qquad (1)$$

where C_i = the observed concentration of instantaneous runoff i, V_i = discharge volume (m^3) for the Σ of half the period of time between the sample and its precursor, and that of the sample and its successor (represented as the period of

time i), and the denominator is the daily or water year Σ of discharge volume. VWM concentrations of solutes in snow samples were derived by weighting snow-core sections by their corresponding snow water equivalence (SWE).

Results

Catchment hydrology - Complete snowmelt-runoff hydrographs were obtained for both catchments in each year (Figures 2a and 3a). In both years, a small amount of water was already flowing at the rock catchment when measurements were initiated. Annual SWE of the bulk snowpack were 1420 m^3 and 5890 m^3 at the rock catchment, and 2300 m^3 and 3804 m^3 at the soil catchment in 1992 and 1993, respectively (Table 1). Runoff was 1150 and 4801 m^3 at the rock catchment, and 1070 and 2446 m^3 at the soil catchment. Runoff coefficients were in good agreement for the rock catchment in both years (0.81 and 0.82 for 1992 and 1993, respectively), and lower in the soil catchment (0.47 and 0.64, respectively; Table 1). The peak in snowmelt runoff for the rock catchment occurred approximately 10 and 20 days prior to that of the soil catchment in 1992 and 1993, respectively (Figure 2a), principally due to the different aspects of the two catchments (i.e. NW and SW aspects for the soil and rock catchments, respectively). Maximum daily runoff was about 80 m^3 in the soil catchment in both years, whereas it was about 70 and 100 m^3 in the rock catchment in 1992 and 1993, respectively.

Runoff chemistry - Water samples were obtained as a time series spanning the period of study. The temporal variation in VWM concentrations of the solutes measured in this study is shown in Figures 2a to 2c. Among the solutes measured, base cation, ANC, Si, and SO_4^{2-} concentrations generally had significant ($p<0.05$) inverse relationships to discharge (not shown). Only the 1993 snowmelt runoff period in the soil catchment had no significant discharge-concentration relationships. In a comparison of solute concentrations between catchments, most solutes were significantly higher in the soil catchment compared to the rock catchment (t-test, $p<0.05$), except for SO_4^{2-} in both years, and NO_3^- and NH_4^+ in 1993. Due to the large differences in snowmelt runoff between study years, solute

concentrations were generally significantly lower ($p<0.05$) in the 1993 water year than in 1992 for the same catchment. The chemical composition of runoff in both catchments was similar to streamwater chemistry of larger alpine watersheds in the Sierra Nevada (Melack et al. 1996).

We observed preferential elution of strong acid anions (Figure 2a). Preferential elution occurred also for Na^+ in 1993, but the flux of ions associated with preferential elution was not strong enough to counteract the influence of discharge on daily export values. For instance, gross, daily export of SO_4^{2-} in the rock catchment peaked in April 1992, well after the effects of solute elution were observed (Figure 3a). Gross, daily export of SO_4^{2-} in the soil catchment peaked as runoff peaked in May. The export of SO_4^{2-} in 1993 tracked runoff and was similar in both catchments, albeit with larger fluctuations in the soil catchment. Generally, the period of peak export for most solutes coincided with periods of peak discharge in both years, with notable exceptions being NO_3^- in the rock catchment (1992) and Si in the rock catchment (1993).

Mass balances - Pearson correlation analysis was conducted to determine the effect of LiBr additions on the flux of solutes from both catchments, and no solutes were influenced by the LiBr tracer for more than two days after each addition. The addition of LiBr generally increased the flux of base cations, with Ca^{2+} and Na^+ influenced most by the additions (Figure 4); the effect was larger in the rock catchment than in the soil catchment. We calculated the mass flux of solutes using only the chemistry from those days during snowmelt runoff that did not experience the effects of the LiBr additions.

All chemical constituents were first determined as volume-weighted mean (VWM) concentrations (Table 2) to facilitate comparison between the two catchments and minimize uncertainties in mass balances. Cation concentrations in

snow were usually $H^+ > Na^+ > Ca^{2+} > NH_4^+ > Mg^{2+} > K^+$, whereas the ranking of anion concentrations was less obvious than that of the cations because anion concentrations were similar to each other. In general, snow inputs were typical of high-elevation sites in the region [Melack et al. 1996]. The net exports of base cations, ANC and Si were consistent in both catchments (Table 3), which indicates that they were all produced by mineral weathering. Sulfate concentrations in runoff were about 3 times higher than in snow, and there was consistent net export of SO_4^{2-} from both catchments (Table 3). Chloride concentrations in runoff were similar to those measured in precipitation, and mass balances indicate that there were no appreciable sources or sinks of Cl^-. Nitrate concentrations were up to 10 times higher in snow than in runoff. Consequently, the export of NO_3^- in runoff was less than precipitation inputs, indicating a net sink of NO_3^- in these catchments.

LiBr additions - The chemical interaction of soils with runoff was evident in both the rock and soil catchments. Multiple applications of LiBr tracer showed that Li^+ is not conservative, and was retained by the soil cation exchange complex. The delay of Li^+ transport relative to Br^- is seen in both catchments (Figure 5). Moreover, when LiBr concentrations were high enough, some H^+ was released in exchange for Li^+, increasing H^+ concentrations in runoff. The effects was similar to that of the rain-on-snow event observed on May 5, 1992 (Figure 6). The retention of Li^+ by soil cation exchangers in both catchments indicates that even sparse alpine soil cover had an influence on runoff composition. Our study shows that the retention time for snow melt in alpine catchments was on the order of days, which gave ample time for many solid-solution reactions to occur and modify the composition of runoff.

Discussion

Possible errors in water balances - Water balances show a consistent deficit in the amount of water lost from the rock and soil catchments, possibly due to a combination of evaporation, storage, and leakage. The water balance for the rock catchment is reconcilable including a 20% loss due to snow ablation. In contrast, a similar calculation for the soil catchment indicates that there were discrepancies of about 50 and 35% in 1992 and 1993, respectively. Some of the difference between the catchments is due to evaporation, and part is associated with catchment boundaries which may shift when the surface topography of the snow differs from that of the buried rock surface; diversion of melt water across watershed boundaries by flow through the snowpack has been observed by Kattelmann (1986) in alpine catchments of the Sierra Nevada. Groundwater or rock fractures are also possible loss pathways. Hence, the difference in runoff between the two catchments may have been a combination of greater leakage in the soil catchment than in the rock catchment, but is also explainable in terms of different evaporative rates in catchments with distinctly different aspects.

The water balance in 1993 indicates that 18 and 36% of the snowpack losses in the rock and soil catchments are due to evaporation, or are unaccounted for. Mass balances of Cl^- show that there are no sources or sinks of Cl^- in these catchments (i.e. Cl^- is conservative), and indicate that the deficit in water budgets is a result of evaporation only, with negligible losses that can be attributed to either water storage in or leakage from the catchments. A method of determining evaporation is to estimate the amount of evaporative concentration in a catchment (Classen & Halm 1996, Classen et al. 1986). This method assumes that if an ion is conservative, then the ratio of its VWM input concentration (i.e. snow and rain) to its VWM output concentration (i.e. runoff) will be a measure of catchment's

evaporation. This technique can also be used to check for possible errors in water balances.

Our estimate of evaporation using this technique for the soil catchment is 48% of our total precipitation inputs, which is similar to that calculated using our estimate of the runoff coefficient (53%). The same calculation made for the rock catchment in 1992 indicates that there was negligible evaporation, since the VWM concentrations are the same, and is in contrast to evaporation calculated using our runoff coefficient (19%). However, an estimate of evaporative concentration for the 1993 water year indicates that evaporation for the rock and soil catchments was 15 and 38%, respectively, and these estimates are similar to those of 18 and 36% calculated from water budgets. Hence this analysis indicates that evaporation in these catchments is different, and that water balances have a high degree of accuracy in both catchments in the 1993 water year, and the soil catchment in the 1992 water year. We attribute the discrepancy of the evaporation estimate calculated using the runoff coefficient and that calculated from evaporative concentration for the rock catchment in 1992 to possible errors associated with the measurement of Cl^- in the bulk snowpack and small sample size (n=1).

The differences of evaporation for the two catchments is explainable in terms of the steeper slope in the rock catchment, which prevents the pooling of meltwater that is observed in the soil catchment, and the different aspects of the catchments which extend the snowmelt runoff period in the soil catchment later into the summer when temperatures are higher. Potential evaporation that occurs during this period can be relatively high (A. Leydecker, pers. com.). The soil catchment has a shallow groundwater reservoir that retains more water than that of the rock catchment, and this reservoir may serve as a partial explanation for the differences observed in runoff coefficients between catchments.

Error analysis of solute fluxes - Although the high frequency of sampling used to calculate the chemical composition of runoff samples in this study was representative, chemical measurements involved some degree of analytical error. While the error associated with measuring the concentration of a particular solute is generally low, the representativeness of mean solute concentrations derived from these measurements have inherently more uncertainty. Tukey's jackknife method (Sokal & Rohlf 1981) was used to evaluate the representativeness of solute means and the propagated error associated with solute export values. This technique estimates the variability of a mean solute concentration by iteratively computing the mean after removing single observations from the sample set. Variability of these values is used to calculate a standard error. In our study, the high frequency of sampling allowed the computation of daily VWM concentrations, which were used as individual points in the iterative computation of Tukey's standard error. For example, Si has an uncertainty of about 1% in the rock catchment in the 1992 water year calculated as the standard error of the population of sample means. Since baseflow discharge has an error of about 5%, propagating these errors gives an uncertainty of about 5% in the estimate of Si export (Table 2).

Hydrology and runoff chemistry - Snow melt drives the runoff hydrograph in these small catchments, and the chemical composition of snow melt is determined by the ionic pulse from the bulk snowpack and its interactions with soils and bedrock. In both catchments in both years, preferential elution of solutes from the snowpack caused the concentrations of solutes in early snowmelt runoff to be greater than in the bulk snowpack (Figures 2a to 2c), which is typical in alpine catchments (Johannessen et al. 1980, Johannessen & Henriksen 1978); this phenomenon has

been observed also at the Emerald Lake watershed (Williams et al. 1993, Williams & Melack 1991). Hydrologic flow paths and residence times determine the extent to which biogeochemical processes chemically alter snow melt as it moves through these alpine catchments. Snowmelt runoff that flows through the soil is influenced by chemicals generated by weathering (in stoichiometric proportions), whereas overland runoff has less contact with soils and is therefore chemically similar to snow melt. We assume that prior precipitation or residual groundwater reservoirs, that commonly influence the water budget in larger watersheds, are assumed to be absent in the study site due to small soil volumes measured.

In larger watersheds, temporally staggered contributions of water and chemicals to streamwater runoff from different areas of the watershed tend to dampen the temporal (daily and seasonal) variability observed in the streamwater composition. For example, lower elevations generally produce snowmelt runoff first due to warmer temperatures, while higher elevations generate meltwater later, as temperatures increase. At peak runoff, most of a watershed contributes, but some of the area is just beginning to melt and includes more concentrated snow melt than those areas that are in later stages of melting. Dampened chemical fluctuations that result from this process are probably less of a factor in individual catchments of this study since the elevation and aspect of the area contained in each catchment are similar. Hence the daily variability that occurs with respect to solute concentrations in the time series of these catchments (Figure 7) are more apparent than in time series of less intensive studies in larger catchments. Chemical responses of the two catchments to increasing temperatures are temporally different due to different warming trends as a result of having different aspects, with the rock catchment melting before the soil catchment (Figure 2a).

Daily discharge ranged from 1 to over 70 m^3 in the both catchments, whereas daily VWM concentrations of most solutes generally varied by < 10 $\mu eq\ L^{-1}$ over

the snowmelt period. Since Si is assumed to be derived from mineral weathering, an increase in discharge due to snow melt would cause a proportional decrease of Si concentration in runoff if there were not proportionally larger contributions of Si from weathering with increasing discharge. However, the changes in daily VWM concentrations of Si during the snowmelt period were small compared to the changes observed in discharge, which indicates that chemical contributions from the mineral weathering of soils and bedrock influenced surface runoff concentrations.

Mineral weathering - The weathering of primary minerals was analyzed to determine if weathering is controlled by the equilibrium dissolution of minerals. We hypothesized that some of the previous difficulties in obtaining congruent weathering stoichiometry for alpine catchments of the Sierra Nevada were derived from errors associated with water and solute balances, the arbitrariness of the anorthite species selected, and an incomplete accounting of weathering sources in large watersheds, which are addressed in our study by the rigorous sampling of small-scale and geologically homogenous catchments. A mass balance approach to weathering, similar to that of Garrels and MacKenzie (1967), is applied to our data in Table 4. The plagioclase formula (An_{24}) chosen is representative of the granodiorite found in the vicinity of the study site catchments, and is the same as that used by Williams et al. (1993) for comparative purposes. Data from both catchments in both years are first corrected for inputs from precipitation, since this is the presumed source of annual inputs to the catchments. The resulting ionic composition is then consumed in the reconstruction of kaolinite to plagioclase, hornblende and potassium feldspar. Generally, some residual Ca^{2+}, HCO_3^- and Si remain, and can be attributed to a number of sources.

Calcium residuals or deficits may be due to using an average plagioclase composition that is different than that of the catchments. For instance, plagioclase as calcic as An_{80} can be found in areas of the Sierra Nevada (Sherlock & Hamilton 1958). More calcic hornblende (or augite) is also a possibility, as is Ca^{2+} resulting from the alteration of hornblende to chlorite (Sherlock & Hamilton 1958, Winchell 1945). Dissolution of carbonate minerals is another possibility, but seems unlikely (Drever 1988), and would not account for the remaining Si.

Other studies propose that excess Ca^{2+} is derived from calcite in alpine catchments (Williams et al. 1993, Mast 1992). Although we have not verified whether calcite is in the study site catchments, the source of the Ca^{2+} residuals in our stoichiometric weathering reactions is evidently from not from dry deposition, calculated using the methods employed above to determine the dry deposition of Cl^-. Because the relationships of Si with SO_4^{2-} and other weathering products suggest a weathering source of SO_4^{2-} in these catchments (Figure 8), we subtracted the equivalent concentration of Ca^{2+} in proportion to the amount of SO_4^{2-} present, which would account for the dissolution of gypsum and anhydrite, and the oxidation of pyrite. Calcium residuals and deficits determined using this procedure are reconcilable with possible errors associated in stoichiometric analyses (except the soil catchment in 1993), and is evidence that the weathering of sulfate-bearing rocks may contribute to SO_4^{2-} export in these catchments.

Stoichiometric analyses were conducted also using calculated ANC (defined as Σ cations minus Σ anions) opposed to measured ANC. This procedure was done to compensate for possible errors associated with Gran titrations in dilute natural waters and the bias that can result from the presence of organic acids (Lesack & Melack 1991). However, this procedure did not resolve our stoichiometric balance for ANC, and suggests that there are not appreciable biases or errors associated with our ANC measurements.

Other geochemical influences on runoff solute composition - The Si composition in our stoichiometric analyses is out of proportion to that of Ca^{2+}, and may result from the simplification of mineral compositions, deposition of Si during evaporation (Drever 1988), or any of the above suggestions which would increase the Ca^{2+} content of component minerals (and decrease the relative yield of Si in individual weathering reactions). The lack of congruity in our stoichiometric analyses suggests that constituents of mineral weathering are not controlled by equilibrium dissolution reactions alone. Alternatively, weathering may be combined with the diffusion of weathering products from fractured minerals, which would suggest that talus or bedrock surfaces are functioning similar to soils in regulating the chemistry of runoff.

We estimated that the hydrological residence time in these catchments was on the order of days, rather than hours, determined by the period of time required for LiBr to flush from the catchments after tracer additions (Figure 2c). Moreover, because soil volumes in these catchments are small, the changes in solute concentrations caused by snow melt could not be attenuated only by influxes of solutes from a reservoir of shallow groundwater or mineral weathering. Hence, relatively fast geochemical processes such as cation exchange, SO_4^{2-} adsorption or desorption, and the dissolution of amorphous aluminosilicates, which act on timescales of hours to days, are probably important factors in regulating runoff chemistry in these catchments.

Silicon reactions that involve the formation or dissolution of crystalline minerals are kinetically limited and could not regulate concentrations during large changes in discharge over a few days time. However, faster reactions (with timescales of hours to days) involving amorphous aluminosilicates may control Si concentrations in these catchments, such as has been documented by Paces (1978). The

dissolution of amorphous aluminosilicates is conceivably one reason for the high Si residuals measured in the stoichiometric weathering reactions above, and suggests that amorphous aluminosilicates may be important in regulating Si concentrations in the runoff of alpine catchments. Further evidence of amorphous sources of Si was documented by Clow (1992) in soil solutions of alpine plots in Loch Vale, which were slightly oversaturated during low-flow conditions and slightly undersaturated during high-flow conditions with respect to amorphous aluminosilicates. Our data show also the relative invariance of Si concentrations with variable discharge (particularly in the rock catchment (Figure 2 c)), which has been attributed to the dissolution of amorphous aluminosilicates in other studies (Kennedy 1971).

Cations produced by weathering were regulated in runoff, with small decreases in concentration to increasing discharge. Cation exchange reactions may partially control concentrations of these constituents similar to those observed at Emerald Lake, where cation exchange occurred in soils and talus, and was the principal control on base cation concentrations in streamflow throughout the snowmelt period (Williams et al. 1993).

Evidence of cation exchange processes occurring in these catchments was observed following a rain-on-snow event and its effect on runoff composition. A salt effect was observed in this study following the rain-on-snow event, and refers to the competitive displacement of exchangeable cations in soils with cations in deposition resulting in an equivalent transport of cations in runoff. The salt effect occurred in response to a rain-on-snow event in 1992 when concentrations of H^+, NO_3^- and SO_4^{2-} from the rock catchment increased and ANC decreased immediately following the rain (Figure 6). In contrast, there was a slight delay before the concentration of ANC decreased in runoff from the soil catchment, which is probably a moderating effect of the soil present.

Processes regulating the export of sulfate - Sulfate concentrations in runoff are about 3 times higher than those in snow. An explanation for the pattern observed for SO_4^{2-} concentrations in runoff in these catchments is that the ionic pulse of the snowpack could cause high concentrations of SO_4^{2-} during early snow melt and low concentrations during late snow melt; this pattern was observed in our study (Figure 2a). Daily, gross export of SO_4^{2-} in 1993 tracked runoff and was similar in both catchments, albeit with larger fluctuations in the soil catchment, which indicates that soils influence the transport of acid anions eluting from the snowpack in some years. Soils of the soil catchment possibly delayed the transport of anions until flows were high and, for SO_4^{2-}, the mechanism of retention may have been adsorption and desorption processes associated with changes in pH during snow melt.

In the Loch Vale watershed, adsorption and desorption reactions of SO_4^{2-} were not believed to play a major role in regulating SO_4^{2-} concentrations in stream water, because SO_4^{2-} retention is low in both mineral and organic components of soil (Baron et al. 1992). Evidence that SO_4^{2-} adsorption process are not responsible for the high net export of SO_4^{2-} in our study is the time series data of H^+ and SO_4^{2-} as modified by Si and Na^+ factors (Figure 7), which shows that SO_4^{2-} followed a flow-dilution pattern similar to Si and Na^+. Note that SO_4^{2-} and H^+ are positively related, which is in contrast to the sulfate-desorption processes that are observed with lower H^+ concentrations in other catchments (Nodvin et al. 1988). Moreover, pH changes in soil solutions throughout the snowmelt period of our study are relatively invariant and fluctuate about half a pH unit (5.2 to 5.7; Figure 9), indicating that SO_4^{2-} desorption processes are not occurring in the soils of these catchments.

There was consistent net export of SO_4^{2-} from both catchments that was second only to that of Ca^{2+} (Table 3). Dry deposition may be the source of excess SO_4^{2-} in runoff, but unless dry deposition of SO_4^{2-} is equal to or slightly greater than that of wet deposition, there appears to be a watershed source that is equal to or slightly greater than the precipitation source. Williams & Melack (1997) calculated that inputs of SO_4^{2-} from dry deposition at the Wolverton tower were as high as 37% of the annual inputs of SO_4^{2-} to catchments in the mixed-conifer zone. The higher aerosol scavenging potential of forests suggests that this value would be substantially lower in alpine catchments with little vegetation. Moreover, our stoichiometric analysis allowed for the congruent weathering of Ca^{2+} when a contribution of SO_4^{2-} from weathering was included in our calculations. Combined with the strong relationships of SO_4^{2-} to other weathering products observed in the runoff of both catchments (Figure 8), this evidence supports our contention that weathering is a source of SO_4^{2-} in these catchments. Hence, although the concentration of SO_4^{2-} in runoff is probably derived in part from antecedent summer and fall precipitation (including dry deposition initially) and snow melt, the majority is derived from the weathering of sulfate-bearing rocks.

Hydrologic Flowpaths and their Influence on Runoff Composition - Mass balance calculations for our study catchments show that there is net retention of H^+ in the rock catchment (42 and 69%), and both net retention and export of H^+ in the soil catchment (50 % retention and 13% export) in 1992 and 1993, respectively. Moreover, NO_3^- concentrations in snow are up to 32 times higher than those in runoff. Consequently, mass balances indicate that there is a sink of NO_3^- (Table 3), even allowing for evaporative concentration. Hence H^+ and NO_3^- in runoff are probably controlled by elution from the snowpack and the extent of neutralization

(for H^+) and potential biological processes (for NO_3^-) that occur along different hydrologic flowpaths.

Hydraulic conductivities of alpine soils in the study-site area are on the order of 1-10 m h^{-1} (Brown et al. 1990), suggesting that LiBr tracers in snowmelt water would be exported from these catchments within a few hours. However, Br^- sometimes took over a week to traverse a less than 100 m path through the soil catchment (Figure 2c). This delay is probably due to the migration of Br^- along convoluted flowpaths through soils, talus, and the retention of water in snow (Kattelmann 1986). The response of solute concentrations in runoff to LiBr additions included brief depressions in the pH caused by the release of H^+ from soil organic matter and minerals in exchange for Li^+ (similar to that observed in Figure 6). This resulted in the temporary retention of Li^+, which occurred in both catchments in both water years (Figure 5), and is further evidence that cation exchange processes influence the short-term, acid-base chemistry in these rocky, alpine soils.

The tracer concentration-time characteristics for these watersheds are log-normal (Figure 2c). Analysis of the tracer studies for both the rock and soil catchments show that the time to maximum concentration decreased throughout the snowmelt season, which probably occurred due to increased snowmelt runoff (until maximum flow) as the season progressed. Tracer analysis showed also that the length of time for each peak to pass (peak width) was similar between catchments, but sometimes greater in the soil catchment. The soil catchment contained more soil, so presumably there were more convoluted pathways for Li^+ to travel, increasing its residence time in the soil catchment. However, the relative differences of Li^+ retention times and peak widths between catchments are small, suggesting that they are determined also by hydrology. For example, because soil is likely to accumulate in areas of water flow, the rock catchment had a soil-

ladened depression about 100 m in length which channeled runoff to the flume (Figure 1). This channel probably increased the amount of contact between snowmelt runoff and soil in the rock catchment, and suggests that flow routing to soil-covered areas may be an important factor in determining between-catchment differences of runoff chemistry.

Retention of Li^+ by predominately rock catchments suggests also that potential acid neutralizing capacity is not compromised in areas with only sparse alpine soil cover. Moreover, small accumulations of soils in crevices or depressions, or rock surfaces themselves (Clow 1987, Abrahamsen et al. 1979, Meixner -pers. com.), may contribute to acid neutralization processes. Consequently, soil coverage designated only by large contiguous areas of soils is probably not a reliable indicator of a catchment's potential acid neutralization capacity at this scale. If the LiBr tracer additions are viewed as analogs to acidic pulses from rainstorms, the similar chemical retentiveness observed in both catchments implies that there is more time for infiltration and biogeochemical reactions to occur, which can modify the composition of runoff. Increased neutralization of acid precipitation is one possible consequence of this chemical retentiveness.

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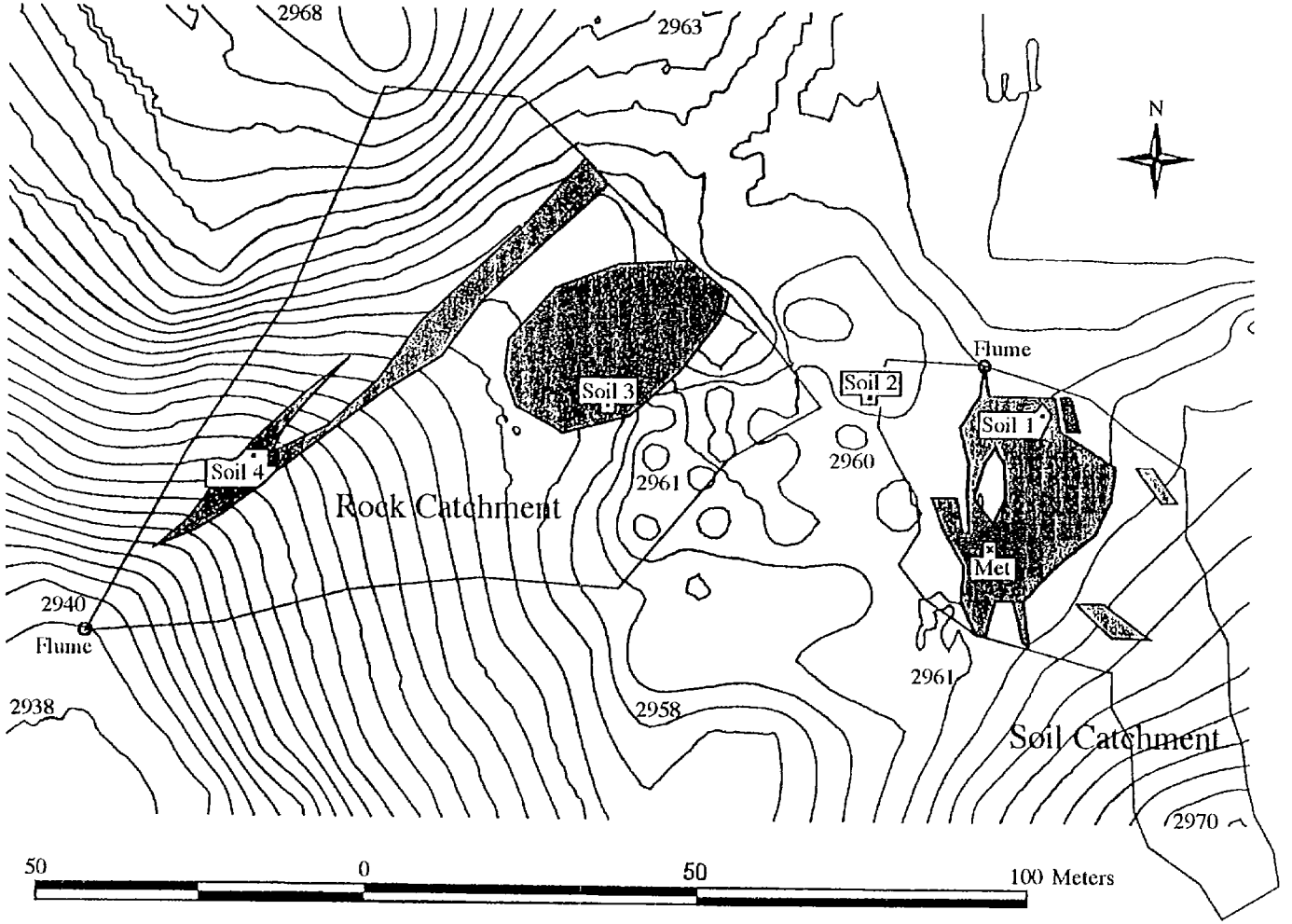
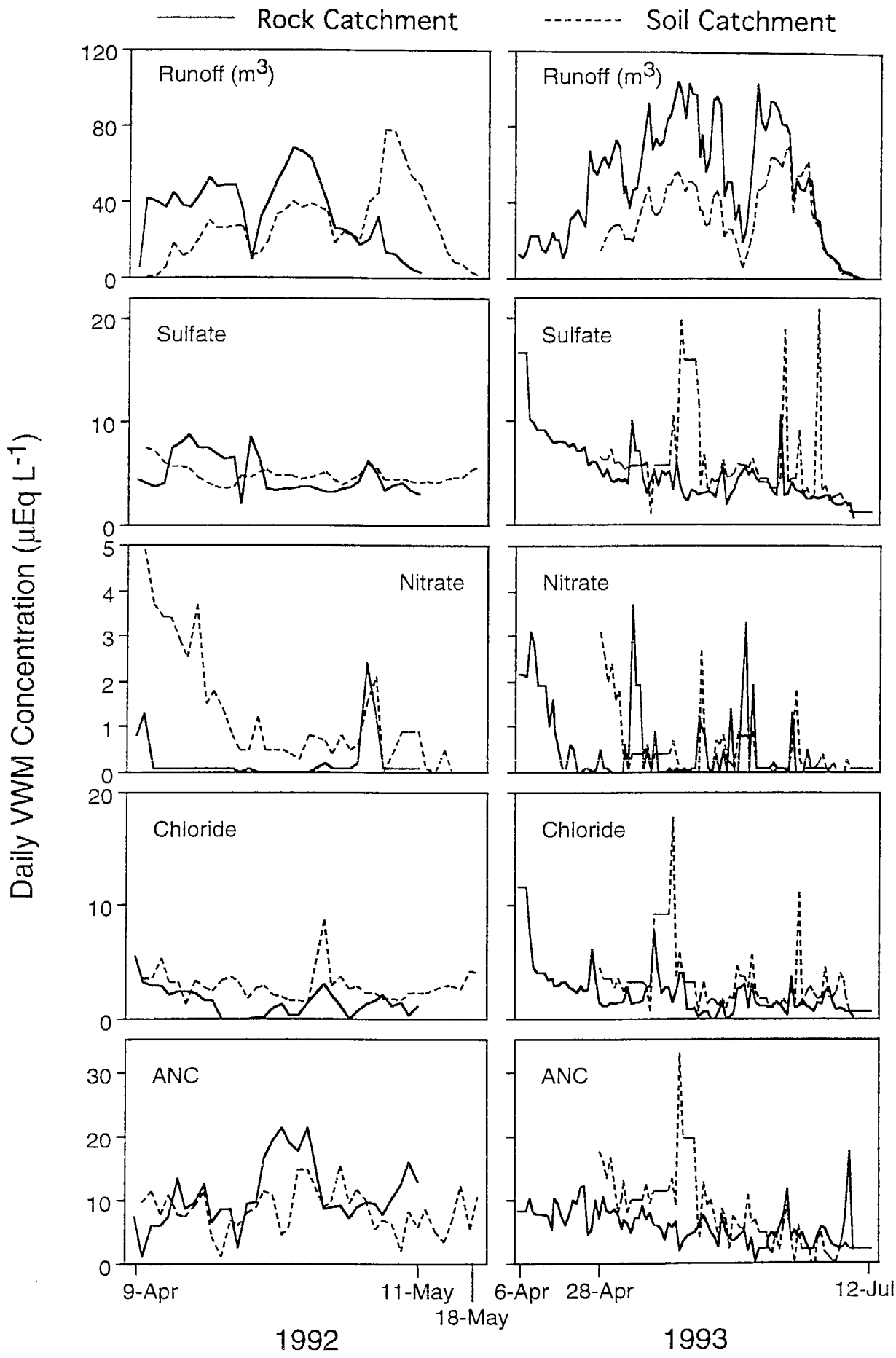
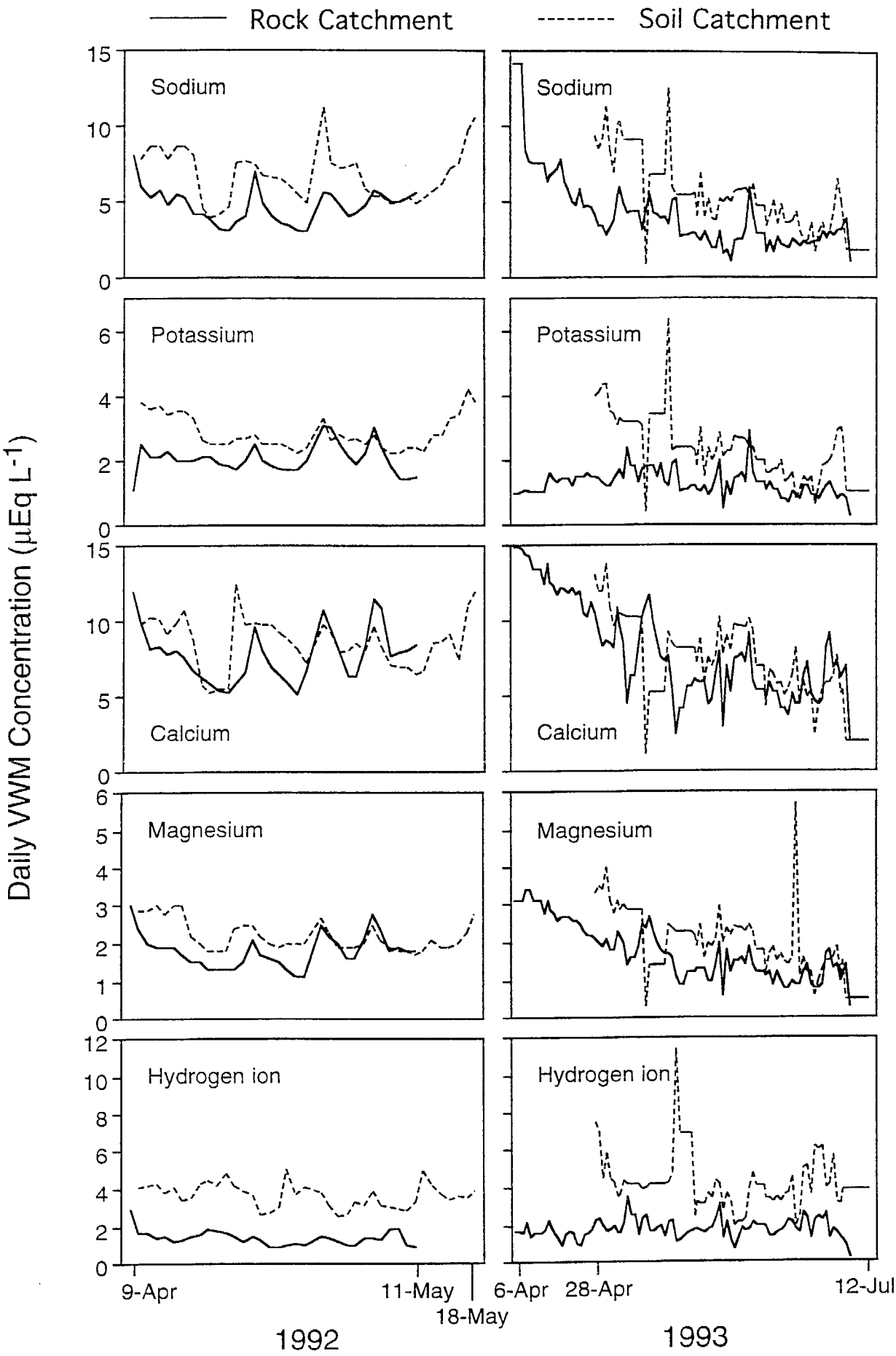
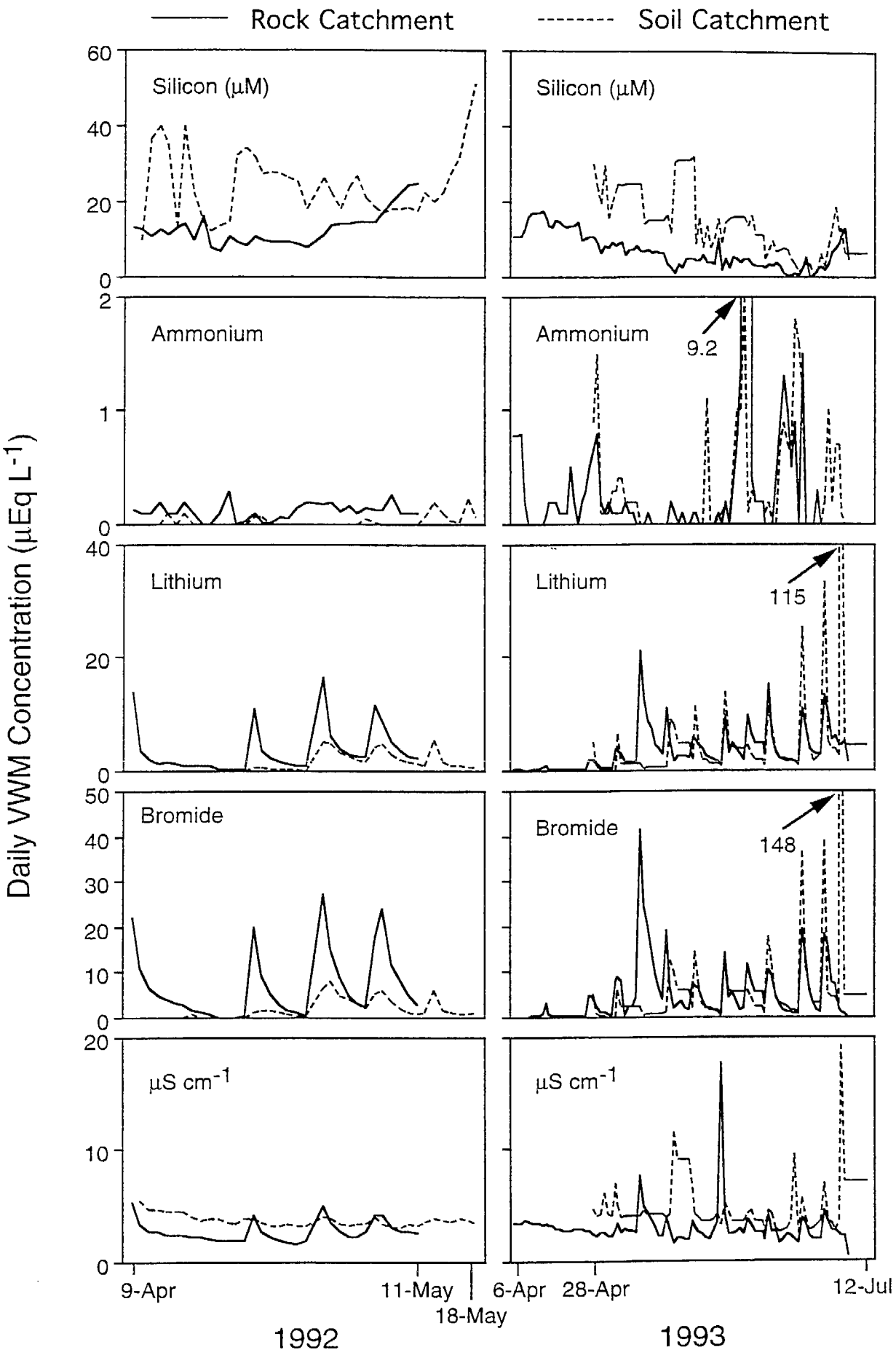
Figure 1. Map of the study-site catchments in Sequoia National Park, California. The larger catchment to the west is the referred to as the "rock" catchment because it has a the larger exposed rock area than the adjacent, "soil" catchment, which is to the east and has a proportionally larger soil-covered area than the "rock" catchment. The meterological tower is designated by "Met", soil lysimeters are numbered 1-4, and the H-flumes used to measure runoff quantity at the catchment outlets are labeled "flume". Shaded areas represent soils inside the catchment boundaries.


2968
2963
N
Flume
Soil 3
Soil 2
Soil 1
Soil 4
2960
2961
Rock Catchment
Met
2940
Flume
2961
2938
2958
Soil Catchment
2970
50
0
50
100 Meters

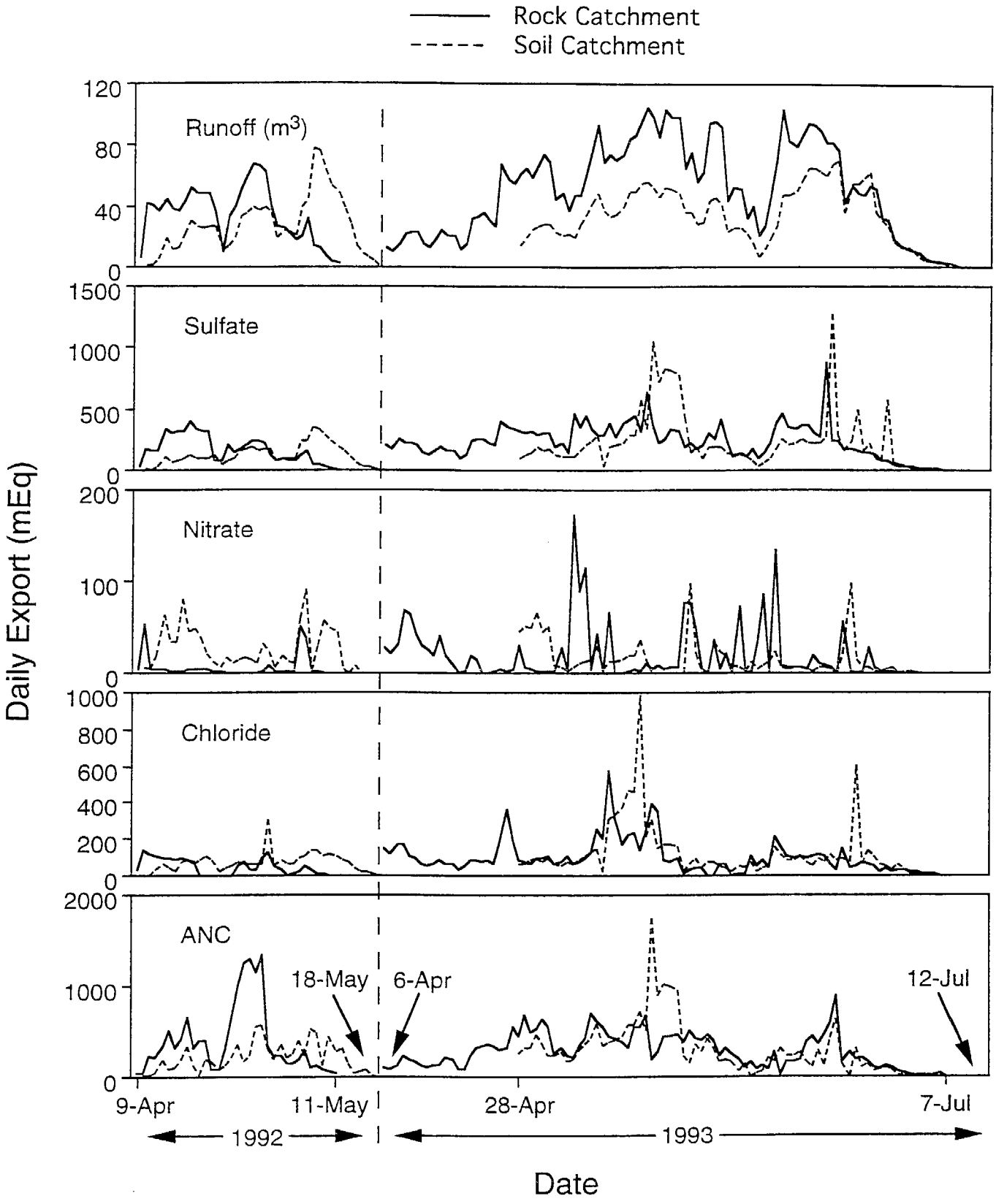
Figures 2a to 2c. Daily mean and daily volume-weighted mean (VWM) concentrations of runoff in the soil and rock catchments during the period of study.

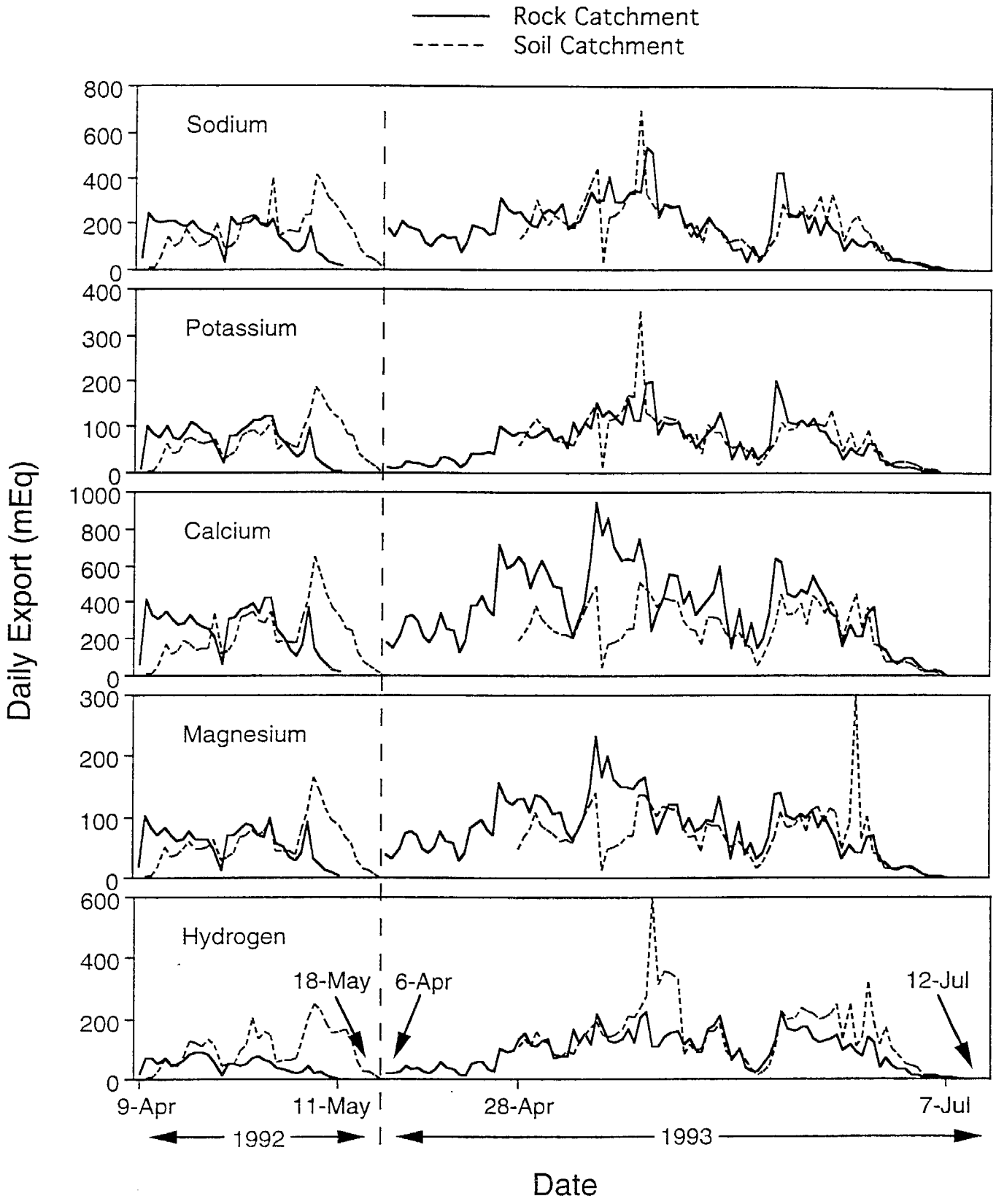

Rock Catchment
Soil Catchment
Runoff (m3)
Runoff (m3)
Sulfate
Sulfate
Nitrate
Nitrate
Chloride
Chloride
ANC
ANC
Daily VWM Concentration (µEq L-1)
120
80
40
0
20
10
0
5
4
3
2
1
0
20
10
0
30
20
10
0
9-Apr
11-May
18-May
6-Apr
28-Apr
12-Jul
1992
1993


Rock Catchment
Soil Catchment
Daily VWM Concentration (µEq L-1)
Sodium
Potassium
Calcium
Magnesium
Hydrogen ion
9-Apr
11-May
18-May
6-Apr
28-Apr
12-Jul
1992
1993


Rock Catchment
Soil Catchment
Daily VWM Concentration (μEq L-1)
Silicon (μM)
Silicon (μM)
Ammonium
Ammonium
9.2
Lithium
Lithium
115
Bromide
Bromide
148
μS cm-1
μS cm-1
9-Apr
11-May
18-May
6-Apr
28-Apr
12-Jul
1992
1993

Figures 3a to 3c. Daily mean runoff and daily export of the solutes measured during the snowmelt periods of 1992 and 1993.


Rock Catchment
Soil Catchment
Runoff (m3)
120
80
40
0
Sulfate
1500
1000
500
0
Nitrate
200
100
0
Chloride
1000
800
600
400
200
0
ANC
2000
1000
0
18-May
6-Apr
12-Jul
9-Apr
11-May
28-Apr
7-Jul
1992
1993
Daily Export (mEq)
Date


Rock Catchment
Soil Catchment
Sodium
Potassium
Calcium
Magnesium
Hydrogen
Daily Export (mEq)
800
600
400
200
0
400
300
200
100
0
1000
800
600
400
200
0
300
200
100
0
600
400
200
0
18-May
6-Apr
12-Jul
9-Apr
11-May
28-Apr
7-Jul
1992
1993
Date

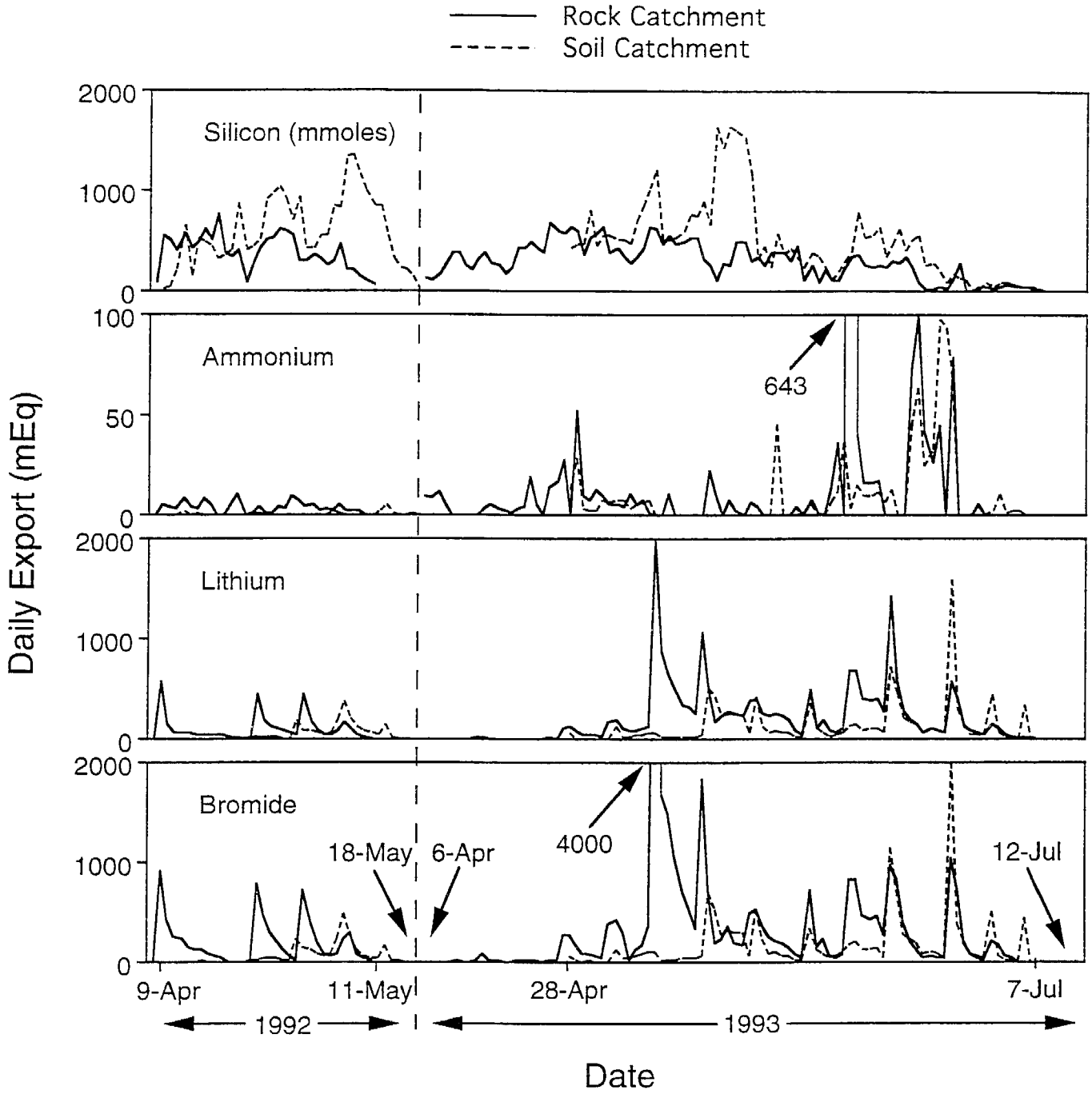

Rock Catchment
Soil Catchment
Silicon (mmoles)
Ammonium
643
Lithium
Bromide
18-May
6-Apr
4000
12-Jul
Daily Export (mEq)
2000
1000
0
100
50
9-Apr
11-May
28-Apr
7-Jul
1992
1993
Date

Figure 4. Comparison of VWM concentrations of solutes in runoff for the rock and soil catchments with and without the influence of LiBr additions.

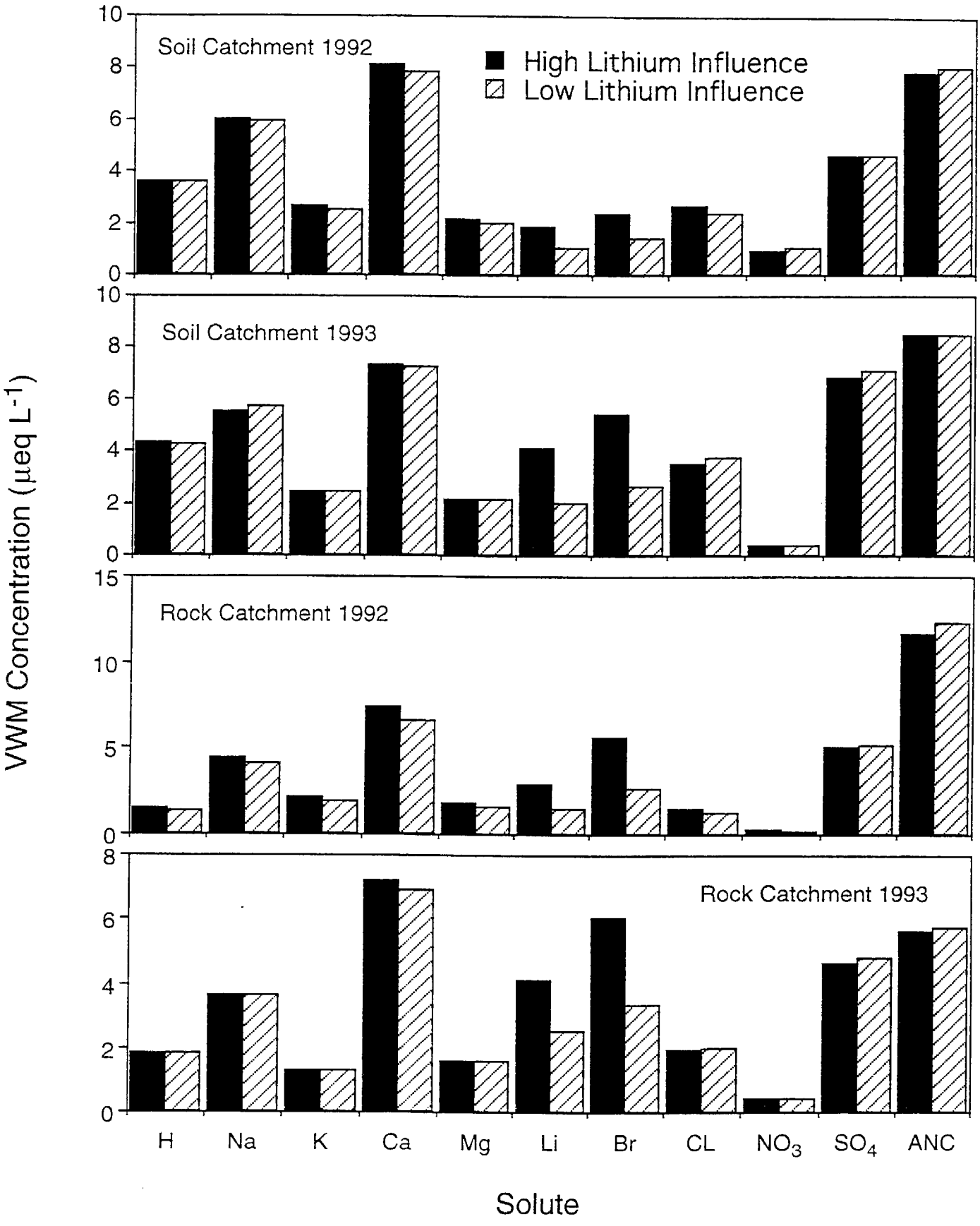

Soil Catchment 1992
High Lithium Influence
Low Lithium Influence
Soil Catchment 1993
Rock Catchment 1992
Rock Catchment 1993
VWM Concentration (μeq L-1)
H
Na
K
Ca
Mg
Li
Br
CL
NO3
SO4
ANC
Solute

Figure 5. Relationships of Li to Br in the rock and soil catchments in 1992 and 1993.

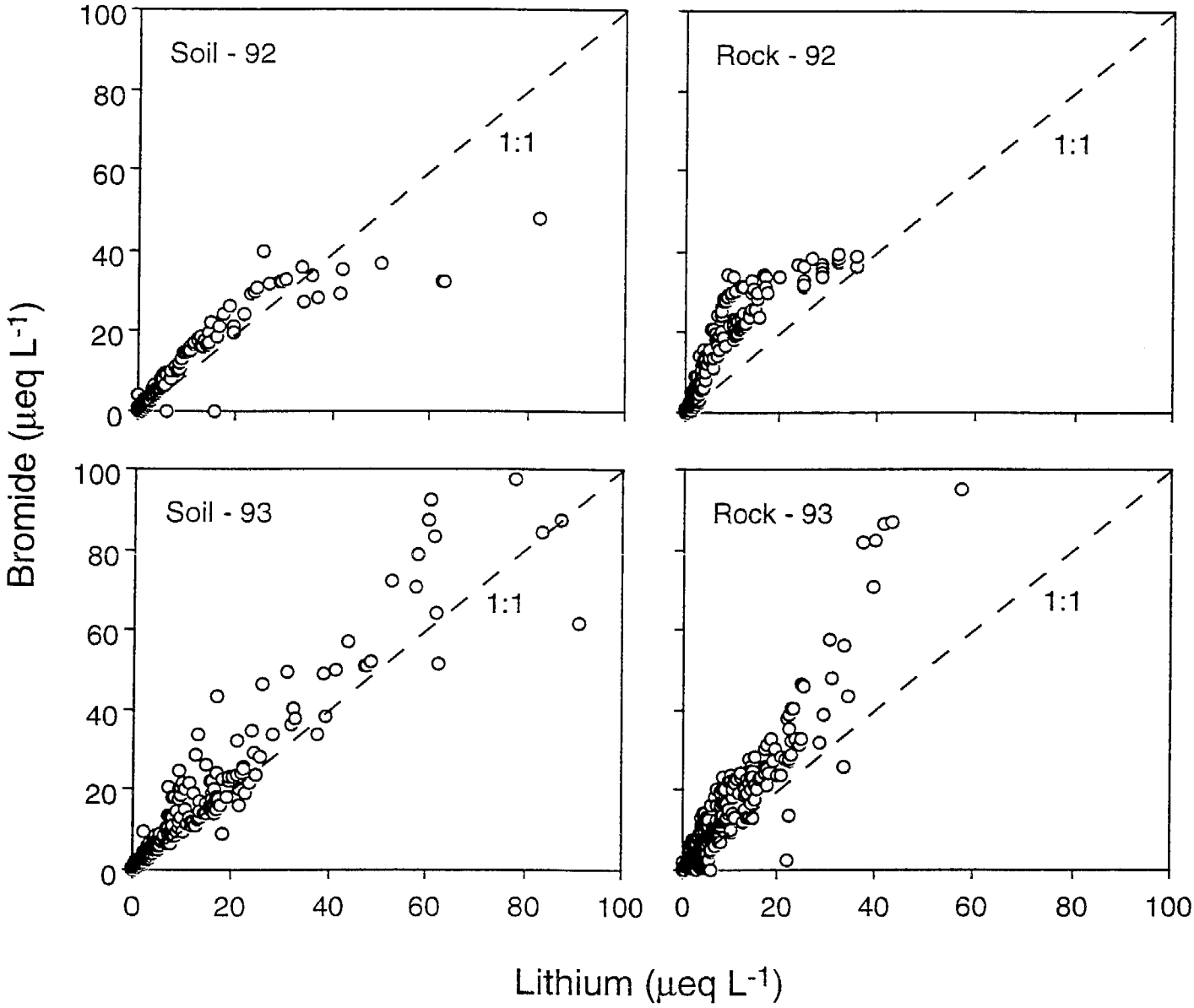

Soil - 92
Rock - 92
Soil - 93
Rock - 93
1:1
Bromide (µeq L-1)
Lithium (µeq L-1)
0
20
40
60
80
100

Figure 6. The effect of a rain-on-snow event on the concentrations of strong acid anions, hydrogen ion, and acid neutralizing capacity (ANC). The rain event occurred the evening of May 5, 1992.

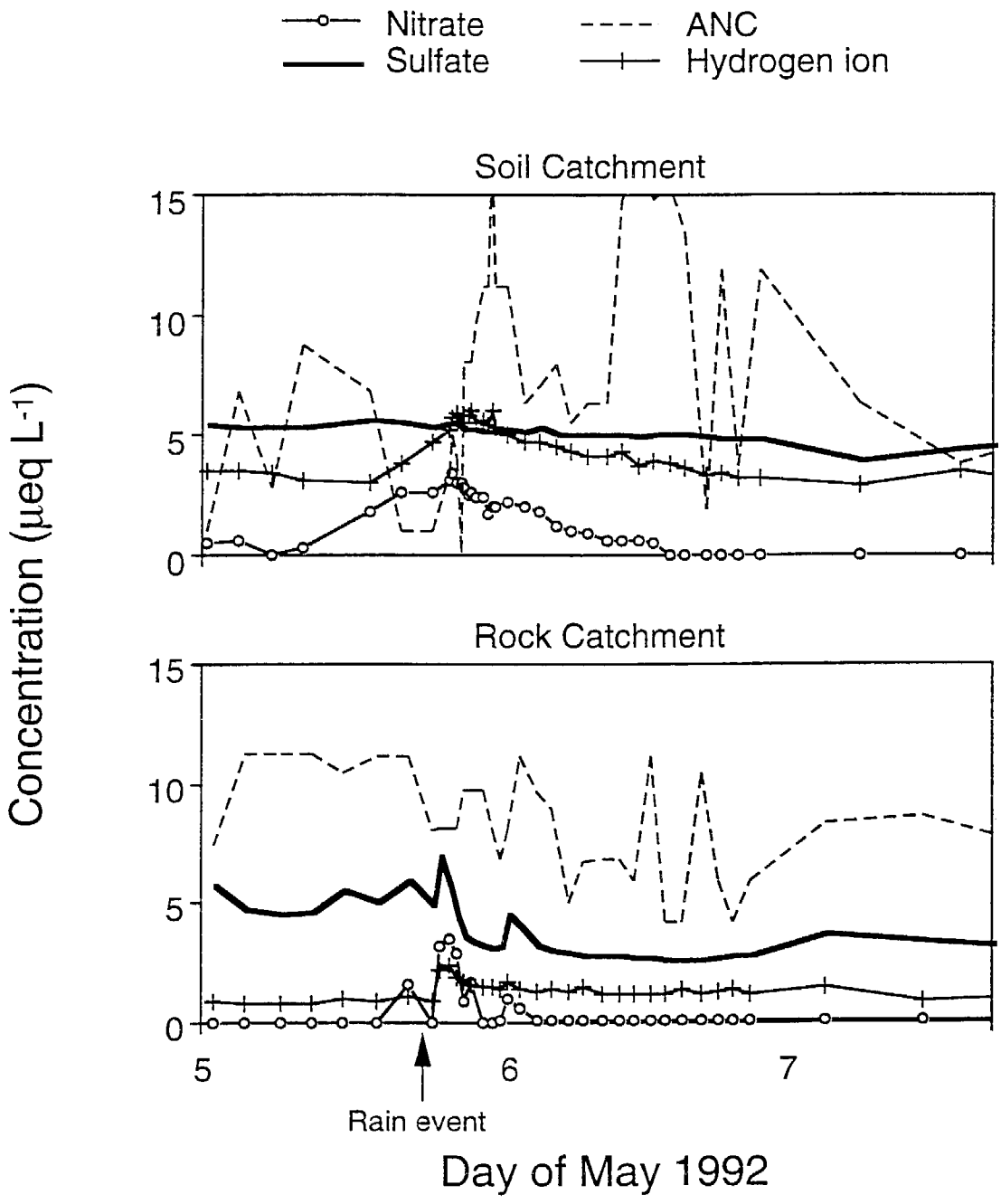

Nitrate
Sulfate
ANC
Hydrogen ion
Soil Catchment
Rock Catchment
Concentration (μeq L-1)
15
10
5
0
5
6
7
Rain event
Day of May 1992

Figure 7. Time series of ions divided by both silicon and sodium factors to determine their relationships to the products of mineral weathering. The panels selected from the rock catchment in 1992 are representative for both catchments in both years.

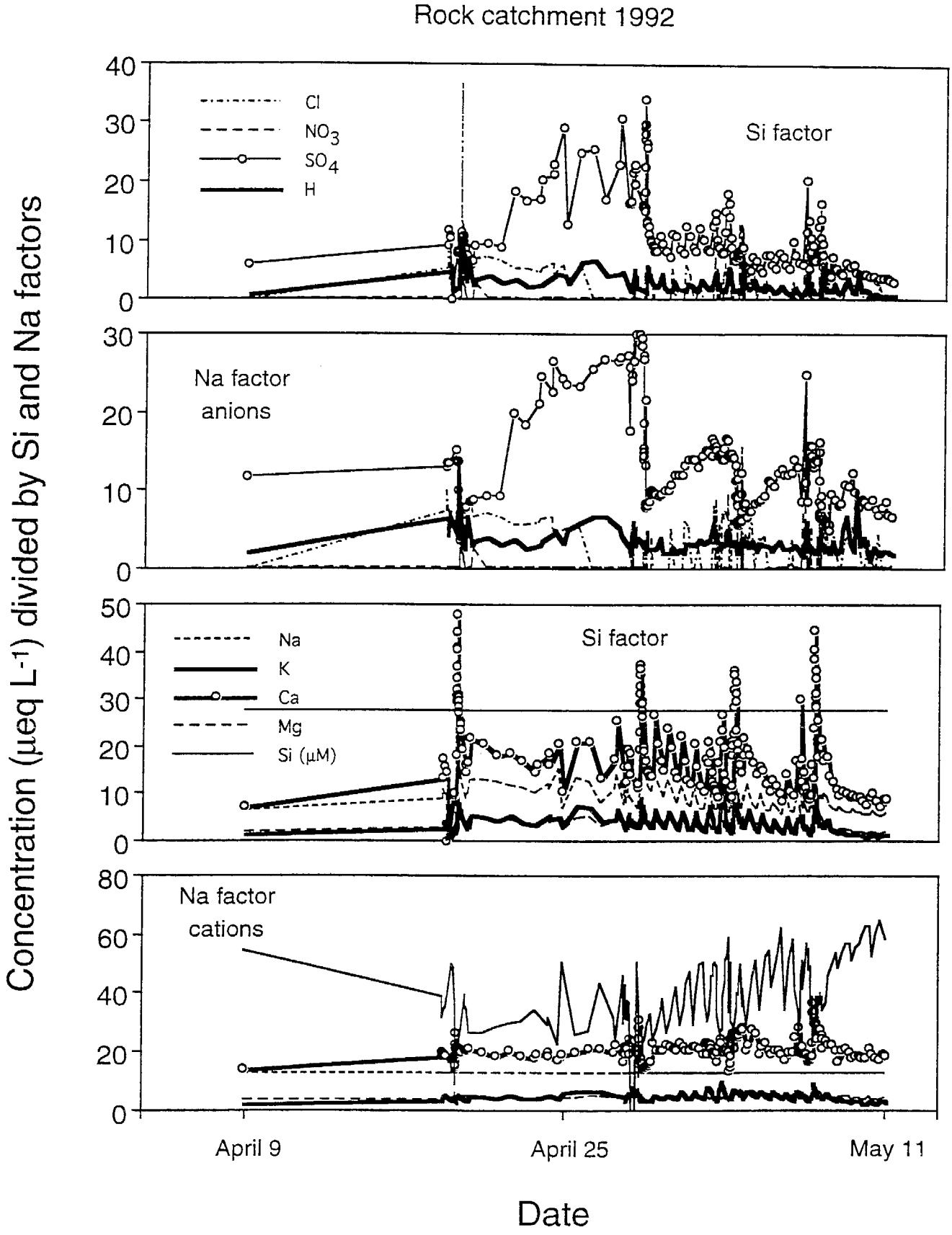

Rock catchment 1992
Concentration (μeq L-1) divided by Si and Na factors
Cl
NO3
SO4
H
Si factor
Na factor
anions
Na
K
Ca
Mg
Si (μM)
Si factor
Na factor
cations
April 9
April 25
May 11
Date

Figure 8. The relationships of silicon and sodium to sulfate in the rock and soil catchments in 1993. The relationships are all significant ($p<0.05$), and are similar to those observed in the soil catchment in 1992. Similar relationships in the rock catchment in 1992 are not significant.

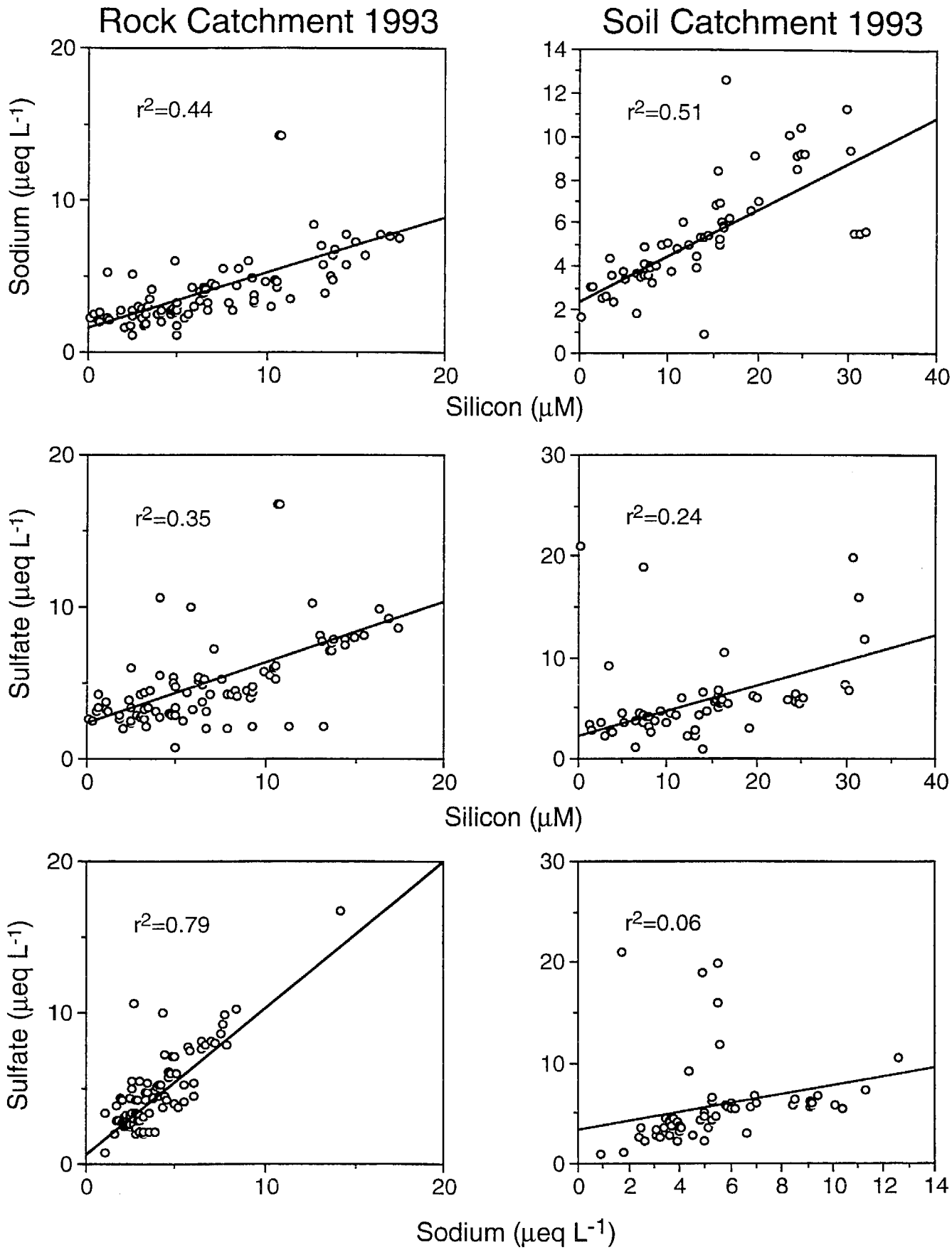

Rock Catchment 1993
Soil Catchment 1993
Sodium (µeq L-1)
r2=0.44
r2=0.51
Silicon (µM)
Sulfate (µeq L-1)
r2=0.35
r2=0.24
Silicon (µM)
Sulfate (µeq L-1)
r2=0.79
r2=0.06
Sodium (µeq L-1)

Figure 9. Time series of the concentrations of selected solutes in soil lysimeters in the rock and soil catchments in 1992. Lysimeter designations for different areas of the rock and soil catchments are labeled in Figure 1. Lysimeters 1a and 1b in the soil catchment are at 10 and 30 cm depths below the soil surface, respectively.

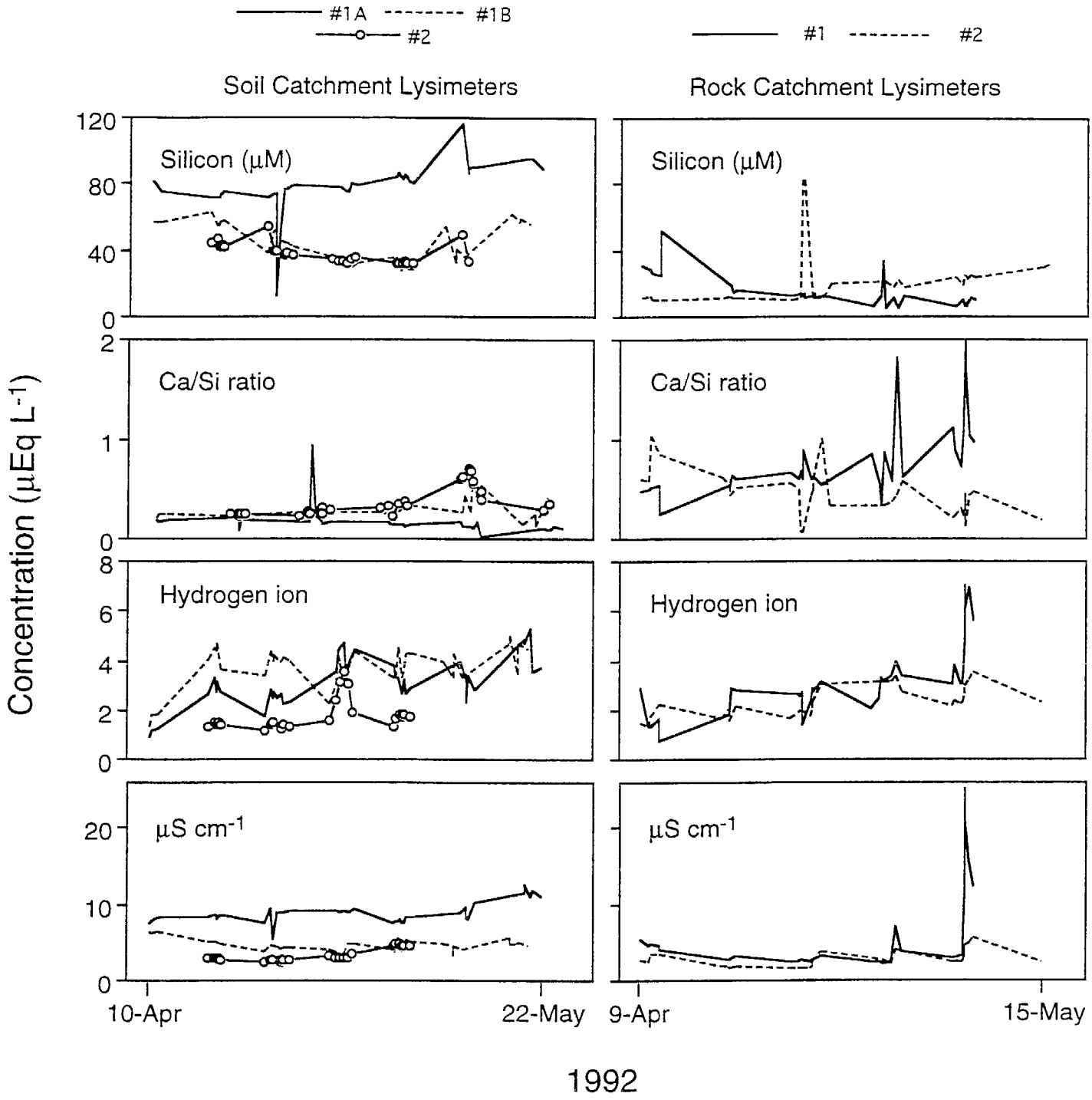

#1A
#1B
#2
#1
#2
Soil Catchment Lysimeters
Rock Catchment Lysimeters
Silicon (µM)
Ca/Si ratio
Hydrogen ion
µS cm-1
120
80
40
0
2
1
0
8
6
4
2
0
20
10
0
10-Apr
22-May
9-Apr
15-May
1992
Concentration (µEq L-1)

Table 1. Comparison of precipitation inputs and runoff outputs for the rock catchment (Rock) and the adjacent soil catchment (Soil) in 1992 and 1993. Runoff coefficients are the fraction of precipitation inputs that leave the catchments in the form of surface runoff.

Solute	Soil (1992)	Soil (1993)	Rock (1992)	Rock (1993)
Inputs (m^3)	2300	3804	1420	5890
Outputs (m^3)	1070	2446	1150	4801
Runoff coefficients	0.47	0.64	0.81	0.82

Table 2. Comparison of solute concentrations in runoff for the study-site catchments. Data are from the rock catchment (Rock) and the adjacent soil catchment (Soil) in 1992 and 1993. Silicon concentrations are in units of μM; electrical conductivities (EC) are in units of μS cm^{-1}. All other solutes are in units of μeq L^{-1}. DEF designates anion deficit, defined as the sum of cations minus the sum of anions (not including Li^+ or Br^-). Tukey's standard error of the population of daily VWM concentrations for selected solutes are given in parentheses.

Solute	Soil (1992)	Soil (1993)	Rock (1992)	Rock (1993)
H^+	3.6 (0.01)	4.2 (0.03)	1.3 (0.02)	1.8 (0.03)
pH	5.44	5.38	5.89	5.74
Li^+	1.0	2.0	1.4	2.5
Na^+	5.9 (0.03)	5.7 (0.04)	4.0 (0.03)	3.6 (0.03)
K^+	2.5 (0.01)	2.4 (0.01)	1.9 (0.01)	1.3 (0.01)
Ca^{2+}	7.8 (0.03)	7.2 (0.03)	6.6 (0.04)	6.9 (0.03)
Mg^{2+}	2.0 (0.01)	2.1 (0.01)	1.5 (0.01)	1.6 (0.02)
NH_4^+	0.0 (<0.01)	0.3 (<0.01)	0.1 (<0.01)	0.2 (<0.01)
Br^-	1.4	2.6	2.6	3.3
Cl^-	2.3 (0.07)	3.7 (0.05)	1.2 (0.04)	2.0 (0.04)
NO_3^-	1.0 (0.03)	0.4 (0.01)	0.01 (0.03)	0.4 (0.03)
SO_4^{2-}	4.6 (0.02)	7.1 (0.03)	5.2 (0.03)	4.8 (0.03)
ANC	8.0 (0.06)	8.5 (0.05)	12.3 (1.01)	5.7 (0.09)
Cations	22.8	23.9	16.8	17.9
Anions	17.3	22.3	21.4	16.2
Total ions	40.1	46.2	38.2	34.1
DEF	5.5	1.6	-4.6	1.7
Si	21.7 (0.19)	14.8 (0.15)	10.9 (0.13)	5.8 (0.06)
EC	3.5	4.5	2.2	2.7

Table 3. Comparison of mass balances for the rock catchment (Rock) and the adjacent soil catchment (Soil) in 1992 and 1993. All units are in equivalents except for silicon, which is in moles.

Solute	1992 Soil Input	1992 Soil Output	1992 Soil Balance	1993 Soil Input	1993 Soil Output	1993 Soil Balance	1992 Rock Input	1992 Rock Output	1992 Rock Balance	1993 Rock Input	1993 Rock Output	1993 Rock Balance
H^+	7.9	3.9	4.0	9.1	10.3	-1.2	4.9	1.5	3.4	15.3	8.6	6.7
Na^+	4.5	6.3	-1.8	12.3	13.9	-1.6	2.8	4.6	-1.8	13.2	17.3	-4.1
K^+	0.3	2.7	-2.4	1.2	5.9	-4.7	0.2	2.2	-2.0	0.7	6.2	-5.5
Ca^{2+}	3.7	8.3	-4.6	7.6	17.6	-10.0	2.3	7.6	-5.3	8.8	33.1	-24.3
Mg^{2+}	0.6	2.1	-1.5	1.3	5.1	-3.8	0.3	1.7	-1.4	0.9	7.7	-6.8
NH_4^+	2.4	0.0	2.4	2.7	0.7	2.0	1.5	0.1	1.4	6.8	1.0	5.8
Cl^-	2.6	2.5	0.1	9.0	9.1	-0.1	2.2	1.4	0.8	10.1	9.6	0.5
NO_3^-	3.6	1.1	2.5	3.2	1.0	2.2	3.0	0.1	2.9	8.8	1.9	6.9
SO_4^{2-}	3.2	4.9	-1.7	7.2	17.4	-10.2	2.2	6.0	-3.8	9.7	23.0	-13.3
ANC	0.0	8.6	-8.6	0.0	20.8	-20.8	0.0	14.1	-14.1	0.0	27.4	-27.4
Silicon	0.0	23.2	-23.2	0.0	36.2	-36.2	0.0	12.5	-12.5	0.0	27.8	-27.8

Table 4. Source minerals of annual catchment runoff (moles) in 1992 and 1993. Deficits and residuals in the final products of this procedure are designated by negative and positive numbers, respectively.

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Si
Rock catchment (1992)						
Solute export	3.80	0.85	4.60	2.20	14.10	12.50
Minus snow inputs	1.15	0.15	2.80	0.20		
Minus Kao to Hornblend	0.56	0.70	0.10	0.05	2.72	1.65
Minus Kao to K Feldspar				1.95	1.95	3.90
Minus Kao to Palgioclase	0.53		1.70		2.79	3.43
Final product and	1.56				6.64	3.52
percent residual (Calcium)	(59%)					
Minus sulfate contribution	1.86					
Corrected final product and	-0.30				6.64	3.52
percent residual	(-11%)				(47%)	(28%)
Rock catchment (1993)						
Solute export	16.55	3.85	17.30	6.20	27.40	27.80
Minus snow inputs	4.40	0.45	13.20	0.70		
Minus Kao to Hornblend	2.84	3.40	0.48	0.23	13.20	8.04
Minus Kao to K Feldspar				5.30	5.30	10.60
Minus Kao to Palgioclase	1.13		3.62		5.93	7.30
Final product and	8.18				2.97	1.86
percent residual (Calcium)	(67%)					
Minus sulfate contribution	6.58					
Corrected final product and	1.6				2.97	1.86
percent residual	(13%)				(11%)	(7%)
Soil catchment (1992)						
Solute export	4.15	1.05	6.30	2.70	8.60	23.20
Minus snow inputs	1.85	0.30	4.50	0.30		
Minus Kao to Hornblend	0.63	0.75	0.11	0.05	6.60	4.02
Minus Kao to K Feldspar				2.35	2.35	4.70
Minus Kao to Palgioclase	0.53		1.69		2.77	3.41
Final product and	1.14				-3.12	11.07
percent residual (Calcium)	(50%)					
Minus sulfate contribution	0.94					
Corrected final products and	0.20				-3.12	11.07
percent residual	(9%)				(-36%)	(48%)
Soil catchment (1993)						
Solute export	8.80	2.55	13.90	5.90	20.80	36.20
Minus snow inputs	3.80	0.65	12.30	1.20		
Minus Kao to Hornblend	1.59	1.90	0.27	0.13	7.38	4.49
Minus Kao to K Feldspar				4.57	4.57	9.14
Minus Kao to Palgioclase	0.41		1.33		2.18	2.68
Final product and	3.00				6.67	19.89
percent residual (Calcium)	(60%)					
Minus sulfate contribution	5.1					
Corrected final products and	-2.1				6.67	19.89
percent residual	(-42%)				(32%)	(55%)