

## Concentration-discharge relationships in runoff from a steep, unchanneled catchment

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**Abstract.** The observation that “old” water dominates storm runoff suggests that release of low-solute water from soils rather than rainwater must cause storm runoff dilution. This inference is supported by sprinkling experiments in an 860-m<sup>2</sup> catchment in the Oregon Coast Range, in which >200 mm of both high and low ionic strength precipitation produced similar concentration-discharge trends. Rainwater chemistry was buffered as it traveled through catchment soils: the amount of sprinkling-derived water in the runoff increased during long periods of steady discharge but was not accompanied by a change in runoff solute concentrations. Stored water plays a role in runoff dilution as well. Nearly all runoff from the catchment passes through underlying weathered bedrock rather than perching and discharging only through soil. Bedrock water composition appears to vary through storm events, as the average contact time of water with rock declines with increasing discharge, a behavior at odds with the concept of stable end-members.

### Introduction

The dissolved load in stream waters derives from geochemical and biological processes within the catchment area and from salts carried in rainwater. Variations of solute concentrations with discharge [e.g., *Bricker et al.*, 1968; *Kennedy*, 1971; *Miller and Drever*, 1977; *Neal et al.*, 1986; *Elwood and Turner*, 1989; *Mulholland et al.*, 1990] imply that the dissolved load reflects catchment hydrologic processes in addition to chemical processes. The ease of measuring concentration and discharge of runoff invites use of solutes as hydrologic tracers; because multiple factors control the solute load in runoff, however, it is difficult to decipher the effect of any individual process using only runoff chemistry [*Kirchner et al.*, 1993]. Similarly, in any catchment study of chemical weathering or of surface water acidification it is necessary to separate hydrologic controls on runoff chemistry from the chemical process of interest [*Bishop*, 1991].

The concentrations of most dissolved species in runoff decline during periods of high discharge, while a few increase in concentration or are unchanged. The precise pattern varies from catchment to catchment and from storm to storm [*Walling and Foster*, 1975]. Typically, products of mineral weathering (base cations, silica, alkalinity) decline in concentration with increased discharge, while hydrogen ion concentrations increase. Aerosol and rain-deposited anions (chloride, sulfate)

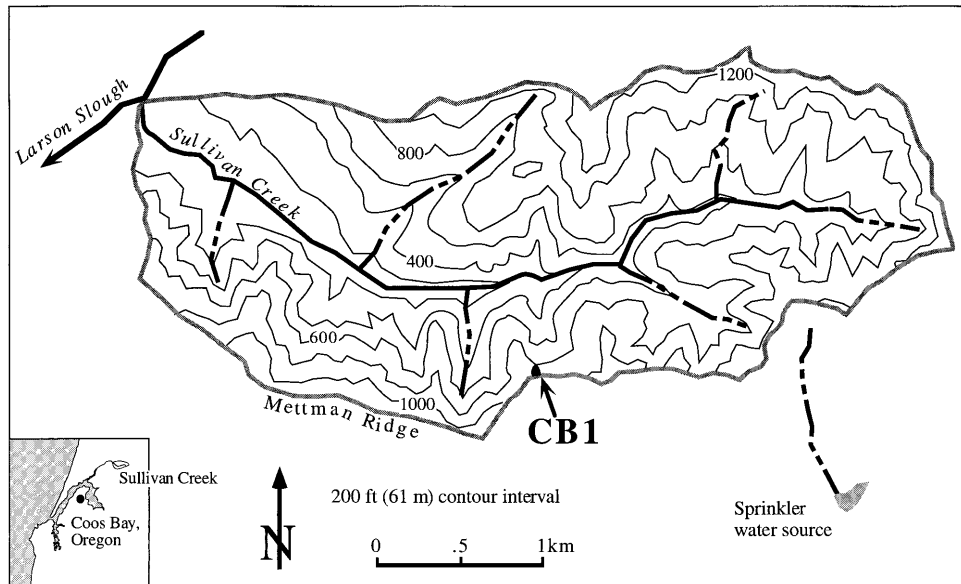
may display no trend with discharge. Biologically utilized species (potassium, nitrate) exhibit variable behavior.

A common explanation for these patterns is that runoff is diluted either with rainwater or with shallow soil water during periods of storm flow [e.g., *Johnson et al.*, 1969]. Dilution of runoff during storm flow is modeled conceptually as resulting from a conservative mixing relationship between a high-solute-concentration component, usually taken to be base flow, and a low-solute-concentration component:

$$Q_T C_T = Q_{Lo} C_{Lo} + Q_{Hi} C_{Hi} \quad (1)$$

where  $Q$  is discharge,  $C$  is solute concentration, and the subscripts  $T$ ,  $Lo$ , and  $Hi$  refer to the total runoff, the low-concentration component, and the high-concentration component, respectively. Several models exist in which waters that have had short contact times with soil comprise the low-concentration component [e.g., *Pilgrim et al.*, 1979; *Christophersen et al.*, 1982], leading to the conclusion that  $Q_{Lo}$  is water that has flowed rapidly through the catchment. Because Horton overland flow, an obvious source of rapidly delivered water, does not operate over most vegetated, humid catchments, much hydrologic modeling has focused on other fast processes such as saturation overland flow and macropore flow [*Dunne and Black*, 1970; *de Vries and Chow*, 1978; *Mosley*, 1979; *Smettem et al.*, 1991]. These flow mechanisms are characterized by high flow velocities and short residence times and are therefore expected to transmit rainwater through the catchment with only slight chemical modification. Concentrations of nonreactive species such as chloride, deuterium, and oxygen 18, however, tend to be considerably damped in runoff as compared to rainfall [*Hooper et al.*, 1988], which leads to the recognition that much storm runoff derives from “old” water from the catchment, rather than “new” or “event” water [*Sklash and*

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**Figure 1.** Map of the Sullivan Creek drainage basin in the Oregon Coast Range. The 860 m<sup>2</sup> CB1 and adjacent (not shown) CB2 catchments form the contributing area to ephemeral first-order channels and are typical of the headwaters of streams in humid, forested areas. Only channels delineated on the U.S. Geological Survey 7.5-foot quadrangles are shown; these do not include first-order channels. Water used for the sprinkling experiments was trucked from a stream outside the Sullivan Creek drainage.

Farvolden, 1982]. The dominance of old water in storm runoff implies the conundrum that solute concentration reductions must be attributed to release of low-solute water that had been stored within the catchment.

A three-component mixing model approach, developed by Christophersen *et al.* [1990] and Hooper *et al.* [1990], predicts stream water chemistry from varying mixtures of soil and ground water components identified within the catchment. This end-member mixing analysis (EMMA), applied to the Birkenes catchment, Norway, and Plynlimon catchment, Wales, has shown that unaltered rainwater does not contribute to stream chemistry. Instead, it proposes that waters of constant composition from different soil horizons within the catchment mix in varying proportions to yield observed variations in stream chemistry. This allows for old, low-concentration water in the runoff, rather than relying on dilution of storm runoff by new rainwater. EMMA does not require knowledge of hydrologic flow paths but does require identification of end-members within the catchment that have constant compositions [Jenkins *et al.*, 1994]. Is the constant composition requirement tenable? Soil water solute concentrations vary through storm events [Wilson *et al.*, 1991; Jenkins *et al.*, 1994] and may be nonuniform within the catchment [Bishop, 1991; Wels *et al.*, 1991]. Brief increases in solute concentrations in runoff at the onset of rainfall that have been attributed to “flushing” of salts from soils [Walling and Foster, 1975; Miller and Drever, 1977; Elsenbeer *et al.*, 1995] are not compatible with uniform composition water sources.

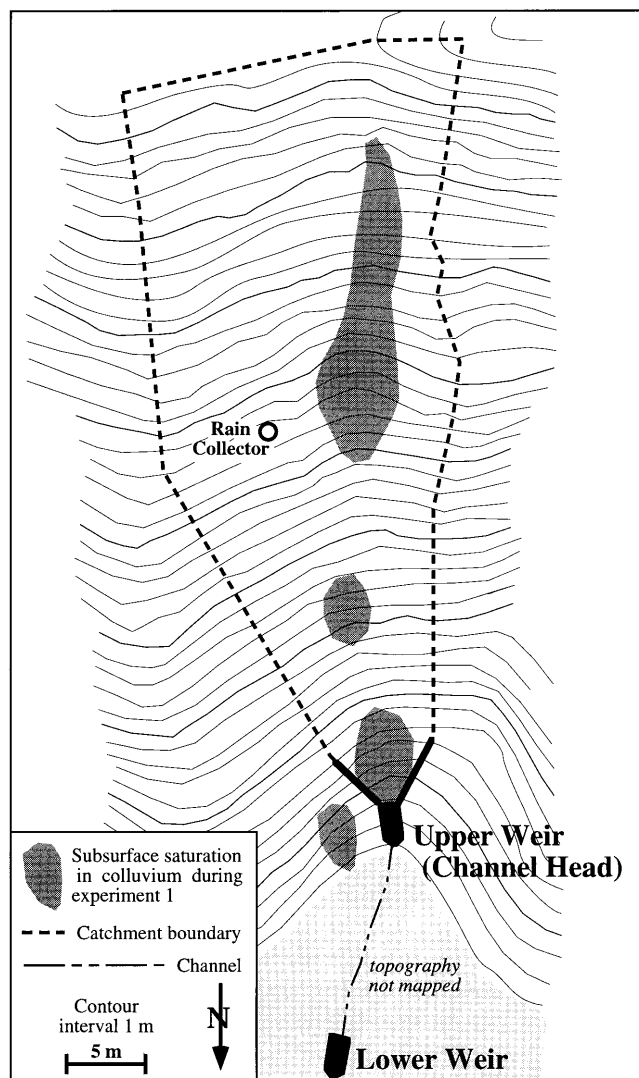
In this paper we present general findings on the hydrologic controls of runoff chemistry in a small catchment in the Oregon Coast Range. We conducted catchment-scale sprinkling experiments that combine hydrologic observations [Montgomery *et al.*, this issue; R. Torres *et al.*, The influence of the unsaturated zone on the hydrologic response of a small catchment, manuscript in preparation, 1996] (hereinafter referred to as R. Torres

*et al.*, manuscript in preparation, 1996), tracer studies, soil water sampling, and runoff monitoring. Here we report only runoff chemistry and discharge; in subsequent papers we shall explore soil water chemistry within the catchment and its relation to runoff chemistry. The sprinkling experiments allowed control of variables that are not normally adjustable: the rate, duration, and chemistry of the rain. In two sprinkling experiments, untreated water drawn from an impounded stream was the source of precipitation. In a third experiment, demineralized water was used in the sprinkler system. This offers the opportunity to document the runoff chemistry response to different input (precipitation) chemistries. The sprinkling experiments were of long duration at steady rainfall rates, which permitted observation of runoff chemistry during periods of nearly steady discharge and unchanging hydrologic flow paths. For comparison with these sprinkling experiments we present runoff chemistry and discharge during three periods of natural winter storm flow and base flow.

### Field Site

We monitored runoff composition in the CB1 catchment within the Sullivan Creek drainage, near Coos Bay in the Oregon Coast Range (Figure 1). The CB1 catchment is a steep (40°–45°), small (860 m<sup>2</sup>) unchanneled valley (Figure 2). The mean annual rainfall is about 2.0 m yr<sup>-1</sup> [Anderson, 1995], and mean annual runoff is 1.6–1.8 m yr<sup>-1</sup> [Montgomery *et al.*, this issue]. We have focused on unchanneled valleys, the contributing area to channel heads, because they are complete watersheds that are small enough to characterize well and manipulate. Moreover, unlike plots, unchanneled valleys are a fundamental element of the landscape [Dietrich *et al.*, 1987]. The small size and steepness of CB1 are typical of headwater basins in the Oregon Coast Range [Montgomery and Dietrich, 1988].

The bedrock underlying the Sullivan Creek drainage is nearly flat-lying Flournoy Formation, an Eocene turbidite sandstone [Baldwin, 1974]. Organic-rich soils (average  $2.6 \pm 1.0\%$  carbon in 16 samples from two profiles) range up to 2.0 m deep, with the thickest accumulations found in the valley axis. The soils, mapped as Haplumbrepts by Haagen [1989], lack significant horizon development and are strongly disrupted by bioturbation. The average dry bulk density of the soils measured in two pits in the CB2 catchment (adjacent to CB1, Figure 1) was  $720 \pm 200 \text{ kg m}^{-3}$  (Table 1). The area was logged in 1987, 2 years before our monitoring began, and replanted with Douglas fir (*Pseudotsuga menziesii*) in 1988.



**Figure 2.** The CB1 catchment, outlined with heavy dashed line. During experiments, sprinkling was confined to the catchment area. Heavy solid lines show impermeable walls in colluvium feeding runoff into the upper weir. Dark shading depicts areas of subsurface saturation within the colluvium during the quasi-steady period of sprinkling experiment 1. The quasi-steady state areal extent of saturation within the colluvium was similar during experiment 3 and slightly greater during experiment 2. Although topography between the upper and lower weirs (light shading) was not mapped, the channel slopes  $30^\circ$  between the weirs. Topography and saturation are from Montgomery [1991].

**Table 1.** Soil Bulk Density  $\rho_b$  and Moisture Content by Weight ( $\theta_g$ ) and by Volume ( $\theta_v$ ) From Piston Core Samples Collected in Two Soil Pits in the CB2 Catchment on September 1, 1991

Depth, m	Density $\rho_b$ , $\text{kg m}^{-3}$	Moisture Content $\theta_g$ , wt %	Moisture Content $\theta_v$ , vol %
<i>Pit 1</i>			
0.32–0.40	560	29.0	16.2
0.55–0.70	720	32.9	23.5
0.80–0.95	750	31.9	23.8
1.05–1.20	950	35.5	33.8
<i>Pit 2</i>			
0–0.15	280	32.9	9.3
0.47–0.55	770	21.9	16.9
0.62–0.70	850	24.4	20.7
0.85–1.00	790	22.6	17.9
1.05–1.20	840	27.6	23.1
Average	$720 \pm 200$	$28.7 \pm 4.9$	$20.6 \pm 6.8$

One application of herbicide was made before planting, but no other treatments have occurred.

The soil in the catchment is so conductive ( $K_{\text{sat}}$  of order  $10^{-3} \text{ m s}^{-1}$ ) [Montgomery *et al.*, this issue] that neither is Horton overland flow produced nor is the soil saturated to the surface during rain storms. Rainwater infiltrates everywhere and percolates vertically through the soil (R. Torres *et al.*, manuscript in preparation, 1996). Local saturation develops within the colluvium only during rain storms and only in thin (maximum 0.3 m) disconnected patches along the axis of the catchment (Figure 2).

Two weirs at the outlet to the CB1 catchment allow separate monitoring of water at two points at the base of the catchment (Figure 2). The upper weir, a flume with v notch, is located at the channel head. The entrance to the flume is sealed to the bedrock. Plastic-lined walls through the colluvium, which are also sealed to the bedrock, extend roughly 3 m upslope from the entrance to the flume (Figure 2). These walls were designed to funnel all water from the colluvium into the upper weir. The lower weir, located 15 m downstream in the channel, underwent several manifestations during the period of monitoring. The first version, a makeshift lower weir, was constructed during sprinkling experiment 2 in 1990 when we realized that water balance was not obtained at the upper weir (Table 2) [Montgomery *et al.*, this issue]. This was replaced with a flume with v notch in the same location the following winter.

In 1990 the water discharging through the upper weir also passed through the lower weir. The discharge and water chemistry presented here for the lower weir in 1990 have been corrected, assuming conservative mixing (i.e., using (1)), to remove the input from the upper weir. Natural rain during the last day of sprinkling experiment 2 in 1990 produced runoff from the unchanneled catchment west of CB1 that also contributed to the runoff at the lower weir. No correction beyond the removal of the upper weir input was attempted to account for this additional source to the lower weir. By 1991 a diversion pipe was in place so that runoff from the upper weir and from the adjacent catchment was routed around the lower weir.

Both the lack of water balance at the upper weir and the patchy development of saturation in the colluvium (Figure 2) led us to recognize that most of the subsurface flow is con-

**Table 2.** Sprinkling Experiments at the CB1 Catchment

Experiment	Dates	Rainfall Rate, mm h <sup>-1</sup>	Upper Weir Steady State Discharge, mm h <sup>-1</sup>	Lower Weir Steady State Discharge, mm h <sup>-1</sup>	Total Rainfall, mm	Total Runoff, mm	Sprinkler Water Treatment
1	May 8–14, 1990	1.51 ± 0.32	0.56 ± 0.04	...	213 ± 45	NA	none
2	May 23–27, 1990	3.02 ± 0.48	0.95 ± 0.05 <sup>a</sup>	2.09 ± 0.27 <sup>a</sup>	290 ± 46	NA	none
3	May 27 to June 3, 1992	1.65 ± 0.20	0.54 ± 0.06	0.48 ± 0.08	275 ± 33	152	demineralized

NA, not available, because of missing or incomplete runoff from lower weir.

<sup>a</sup>Quasi-steady discharge before natural storm on May 26; lower weir corrected for upper weir input.

ducted through the bedrock, probably through fractures in the exfoliation zone [Montgomery *et al.*, this issue]. From a chemical perspective we therefore consider two water types: soil water, or water that traverses the soil in either unsaturated or saturated zones, and bedrock water. The upper weir was constructed to collect all water emerging from the colluvium above the channel head. Impermeable walls funnel soil water into the flume of the upper weir from the saturated area that develops upslope in storms and during our experiments (Figure 2). The lower weir receives water that exfiltrates from the bedrock in the region between the two weirs, as well as water from the very thin (<0.2 m) soil in this region. During sprinkling experiments the area between the weirs received very little input other than bedrock exfiltration because the sprinklers were located within the drainage basin outlined on Figure 2. Because of these physiographic characteristics, we consider the upper weir runoff to have a greater soil water influence and the lower weir to have a greater bedrock water influence during storm flow. As saturation disappears from the soil between storms, and only weak cross-slope lateral components to the downward unsaturated flow paths develop (R. Torres *et al.*, manuscript in preparation, 1996), base flow at both weirs is derived entirely from the bedrock.

## Methods

### Sprinkling Experiments

Two sprinkling experiments were conducted in CB1 catchment in May of 1990, and one was conducted in May and June of 1992 (Table 2 and Figures 3b and 3e). Rotating, pulse-type sprinklers delivered water to nearly the entire catchment area, in order to simulate a natural storm. All of these experiments were of long enough duration to bring the catchment into approximate hydrologic steady state; that is, the discharge stopped increasing and began oscillating on a diurnal basis. The oscillation was probably caused by evapotranspiration (T. W. Giambelluca and K. Loague, Evaporation estimate for the Coos Bay Experiment, manuscript in preparation, 1997) and wind-driven variation in rainfall rate. Approximately steady hydraulic head in the saturated zone (Figure 2) and discharge at the weirs (Figure 3) [Montgomery *et al.*, this issue] was reached after quasi-steady head conditions were established throughout the vadose zone in the colluvium (R. Torres *et al.*, manuscript in preparation, 1996). The discharge and hydraulic heads were maintained in this oscillating, approximately steady condition for several days during experiments 1–3. For brevity, hereafter these periods are described as hydrologic steady state. During this rare condition of steady flow, hydrologic parameters are nearly constant, and changes in runoff chemistry must arise from processes other than varia-

tions in flow paths. Natural rain fell during the final day of experiment 2, boosting both the rainfall rate and the discharge.

### Sprinkling Experiment Precipitation Compositions

The water source for all experiments was an impounded stream above a quarry located about 2 km from the CB1 catchment (Figure 1). During experiment 3 this water was demineralized before feeding it into the sprinkler lines by passing it through a 10- $\mu$ m particulate filter, activated carbon, and a series of anion, cation, and mixed-bed exchange tanks. The demineralized water had an average total dissolved solids concentration of  $7.6 \pm 6.4$  ppm, considerably lower than the  $60.6 \pm 3.2$  ppm dissolved solids in the untreated water. Most (88%) of the remaining solute in the treated water was silicon, which was inadvertently added to the water by the demineralization procedure during part of experiment 3, probably because of sediment buildup in the particulate filter.

### Natural Storms and Runoff

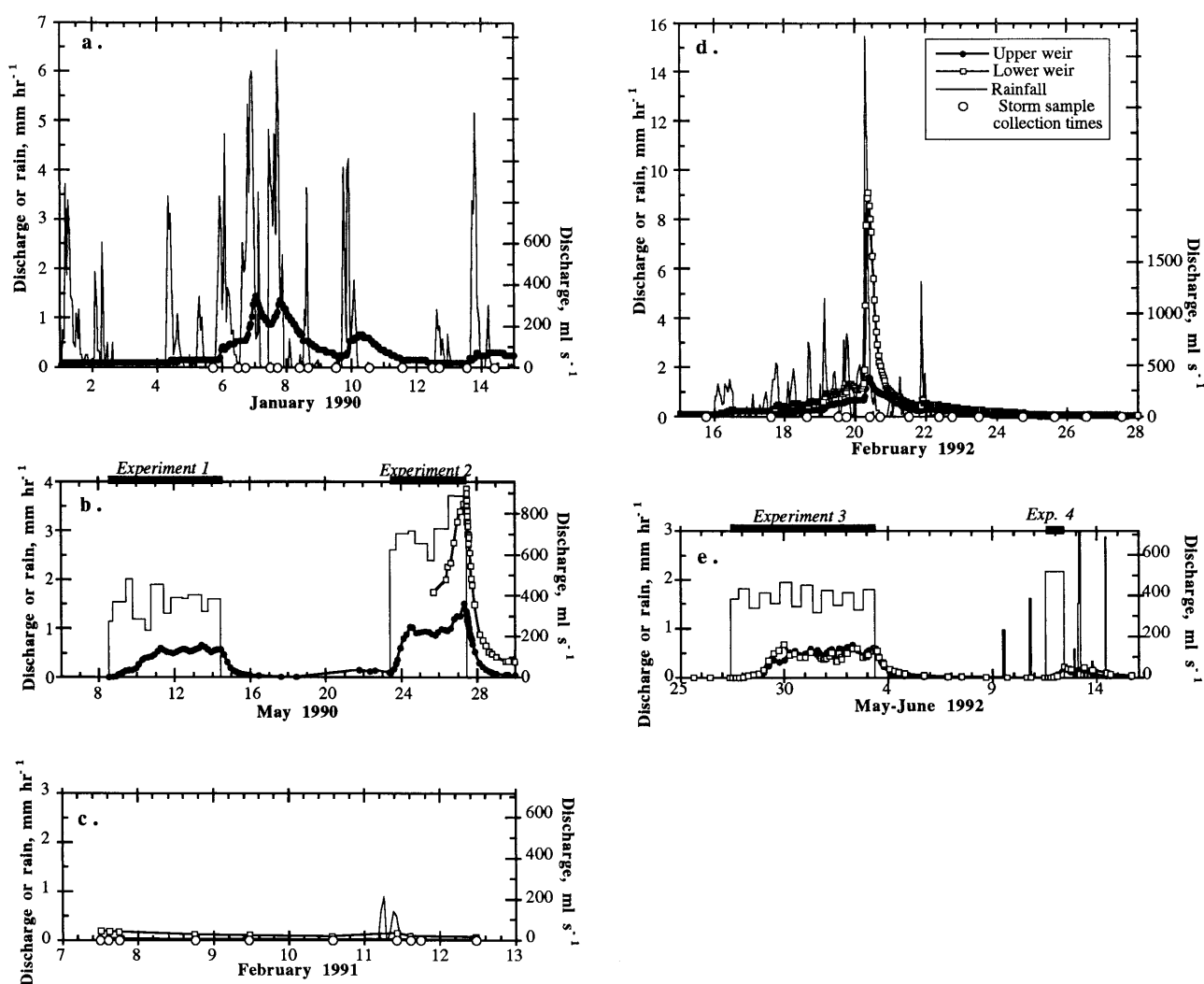
The runoff was sampled during two winter storms and one week of base flow over a 3-year period. Samples were collected between January 5 and 14, 1990, during a series of small storms (Figure 3a). A suite of samples were collected at winter base flow conditions in February 1991 (Figure 3c). In February of 1992 we sampled through a storm that crested with the highest discharge measured at CB1 since monitoring began in December 1989 (Figure 3d) [Montgomery *et al.*, this issue].

### Sample Collection and Analysis

Samples were collected at the weirs at 4-hour intervals during experiments 1 and 2 and at 6-hour intervals during experiment 3. The precipitation sampler was emptied twice daily. During natural rain storms, samples were collected one to two times each day from both the weirs and the precipitation sampler.

Water samples were collected in high-density polyethylene (HDPE) bottles at the weir. Filtration (0.45  $\mu$ m) and pH measurement were performed on site, usually within 24 hours of collection. Sample pH was measured with an Orion Ross Sure-flow combination pH electrode, calibrated with low-ionic strength buffers. Samples were treated with ionic strength adjuster and then stirred and read until a stable pH was obtained. Samples were split into two subsamples, one acidified (nitric acid) and one nonacidified, and were stored in acid-washed HDPE bottles under refrigeration (4°C) in the dark until analyzed.

In 1990, precipitation samples were collected twice daily with an HDPE funnel and bottle, following the method of Likens *et al.* [1967]. In subsequent years we abandoned the vapor barrier and tubing, owing to the low potential for evap-



**Figure 3.** Precipitation and discharge records from periods of water sampling: (a) Natural storms in January 1990. (b) Sprinkling experiments 1 and 2 in May 1990. (c) Base flow conditions, February 1991. (d) Natural storm in February 1992. (e) Sprinkling experiments 3 and 4 in May and June 1992. All plots have the same vertical scale, except Figure 3d, which is plotted at half scale. Samples were collected at regular 4- or 6-hour intervals during the sprinkling experiments (Figures 3b and 3e). Sample collection times during natural events are indicated with open circles along the x axis (Figures 3a, 3c, and 3d).

oration in the short (8–24 hour) collection intervals. Subsequent processing is as described above for weir samples.

The nonacidified subsamples were analyzed on a ion chromatograph (Dionex 2000i) for chloride, bromide (used as a tracer), nitrate, and sulfate. No phosphate was detected in any samples. Replicate analyses and duplicate samples yielded agreement within 0.2 ppm on average [Anderson, 1995].

The acidified subsamples were analyzed with ICP-AES inductively coupled plasma atomic emission spectrometer (ICP-AES) for aluminum, calcium, iron, magnesium, potassium, silica, sodium, and strontium. Samples collected in 1990 and 1991 were analyzed on a Perkin Elmer sequential analyzer. Eighty percent of the 1992 samples were analyzed on an ARL Fisons 3560 simultaneous collector ICP-AES, while the remainder were again analyzed on a Perkin Elmer sequential analyzer ICP-AES. Samples measured on both machines agree within 5%, except in aluminum, for which values obtained on the Perkin Elmer sequential analyzer were 2 times that obtained on the simultaneous collector machine. Replicate analyses and

duplicate samples yielded results reproducible to within 0.2 ppm. A standard riverine water reference material, SLRS-2 from the National Research Council of Canada, was run on the Perkin Elmer ICP with the 1992 samples; the analyses were within 3% of the certified values for Ca, Mg, and K and 9% for Na [Anderson, 1995].

A sulfuric acid titration with a Hach digital titrator was used for bicarbonate alkalinity determinations, using the Gran method [Stumm and Morgan, 1981] on unfiltered samples. Some of the alkalinity titrations were conducted in the field, but most were done in the laboratory 6 months to 1 year after the samples were collected. There is no obvious discontinuity in the data between the field measurements and the later laboratory measurements. Charge balance in runoff and precipitation samples was  $7 \pm 3\%$ . The generally positive charge balance errors probably reflect unmeasured organic anions.

At the time of sample collection, manual discharge measurements were made at the weir with a graduated cylinder or measuring cup and a stopwatch. These manual measurements

confirmed the weir rating curve and provided greater precision than the automated measurements, particularly at low discharge.

## Results

Most species displayed systematic variations with changing discharge during the sprinkling experiments, as shown by the runoff concentrations from experiments 1 and 2 (Figure 4). Although the rain in these experiments was untreated river water, which has solute concentrations greater than the base flow at the CB1 catchment, the concentrations of many species fell as the discharge increased at the beginning of the experiment, stabilized to a steady value at steady discharge, and then increased as the discharge fell at the conclusion of the experiment. At the soil-influenced upper weir this pattern was seen in calcium, sodium, magnesium, potassium, silica, alkalinity, and sulfate. The opposite behavior was observed in hydrogen ion, which increased in concentration with increasing discharge. The short record from the lower weir during experiment 2 shows higher total dissolved solids than at the upper weir. Although the lower weir intercepts deeper flow paths and receives very little water exfiltrating directly from the soil, concentrations of calcium, magnesium, sodium, silica, alkalinity, and nitrate varied inversely with discharge.

Figures 5 and 6 show concentrations in runoff plotted against discharge and concentrations in rainwater plotted against rainfall rate for all three sprinkling experiments and for natural storms. These plots show that the runoff composition is surprisingly insensitive to the rainfall composition. Runoff concentrations for most species cluster along negative to flat trends against discharge (see Table 3) that are broadly similar for all events. Hydrogen ion is the only species with a consistent positive trend with discharge. The trends during the January 1990 natural storm are similar, but concentrations are higher, and a few species (chloride, potassium, sulfate, nitrate) have trends that vary in sign between events; these deviations from the prevalent behavior will be discussed later. For all species except nitrate and potassium the spread in rainwater concentrations is greater than the scatter in runoff concentrations from all flows, particularly at high discharge.

Total dissolved solid (TDS) fluxes (concentration times water discharge) in the rainwater and in the runoff at the upper and lower weirs are plotted against rainfall and discharge, respectively, in Figure 7. For all experiments and natural events the TDS flux in runoff increases roughly linearly with discharge along trends that are broadly similar despite large differences in rainfall TDS fluxes.

## Discussion

The observed shift toward lower concentrations in runoff produced by both high-solute and low-solute rain suggests a strong buffering of runoff compositions. If chemically unaltered rainwater constitutes an important portion of the runoff, then, during the sprinkling experiments with untreated river water, runoff solute concentrations should have increased into the regions shaded in Figure 4. Changes in runoff concentrations are small relative to the changes in discharge; most species decline by less than 1 ppm (or roughly one tenth the concentration at a discharge of  $1 \text{ mm h}^{-1}$ ) with each tenfold increase in discharge (Table 3). Most species show remarkably little change in concentration during prolonged steady dis-

charge. The solute flux out of the catchment increases with discharge (as it must) but appears to be unrelated to the solute flux into the catchment from rain (Figure 7). These observations suggest that simple mixing of rainwater and base flow cannot account for runoff composition. Instead, they suggest that a large reservoir of water and solute within the catchment is the source of most runoff or that rapid chemical buffering of water occurs as it passes through catchment soils.

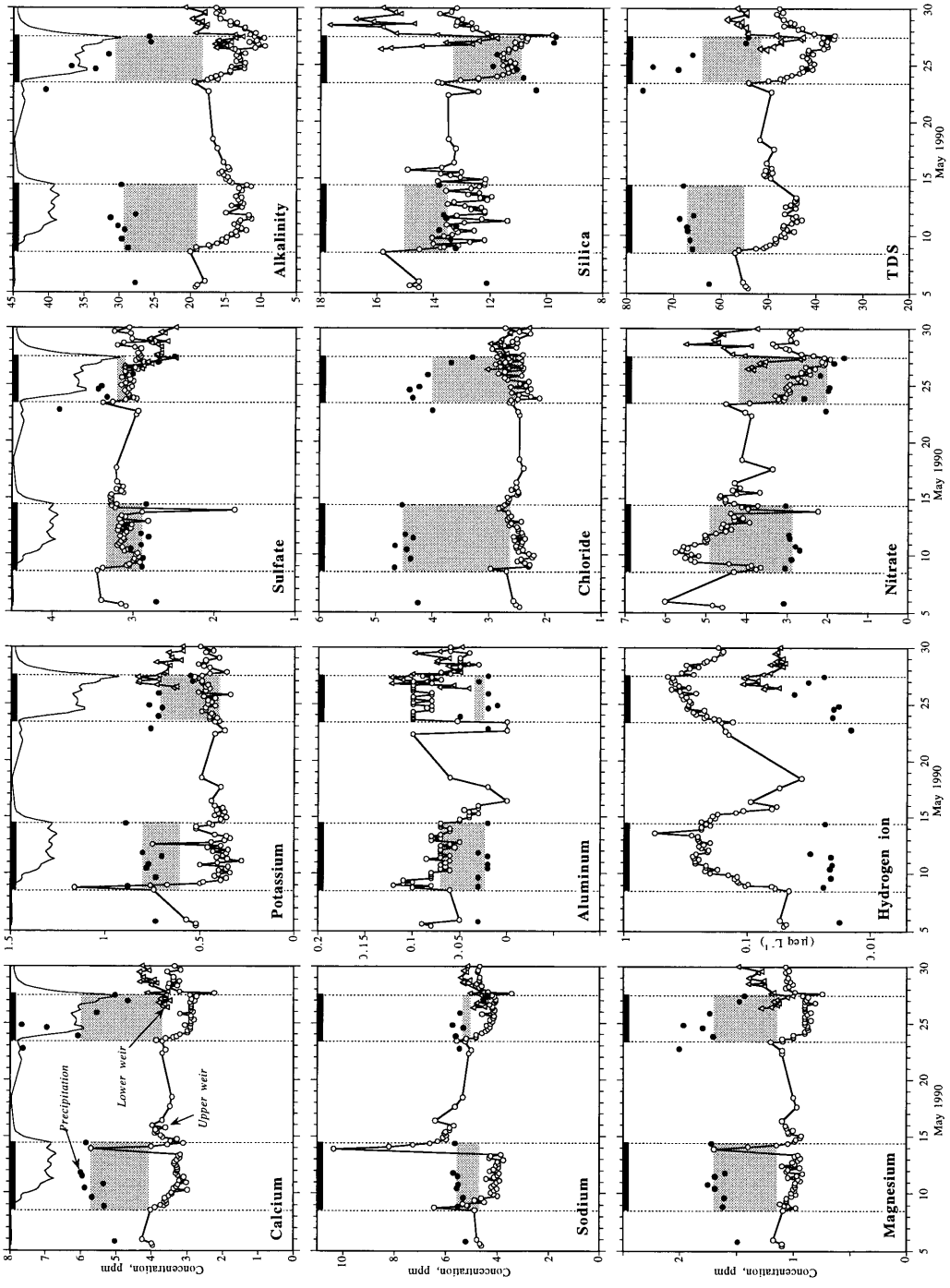
Two mechanisms can explain the similarity of runoff composition during all of the sprinkling experiments and natural storms. First, if rainwater does constitute an important fraction of the runoff, then its chemical composition must be rapidly buffered by the regolith in the catchment. Alternatively, if rainwater does not contribute directly to storm runoff, then dilute water from within the catchment must cause the reduction in solute concentrations in storm runoff.

One way to distinguish these potential mechanisms for solute concentration reduction is to identify the sources of storm runoff. Where does the water leaving the catchment through the weirs come from? First, we look at the total water balance during the sprinkling experiments in order to constrain conservatively the amount of new water likely to be in the runoff. Then we use chloride concentrations in sprinkler water and runoff to constrain the contribution of new water in the runoff. These calculations, along with the differences between the two weirs and a consideration of concentration transients in the runoff, lead to a discussion of the mechanisms controlling solute variations in the runoff.

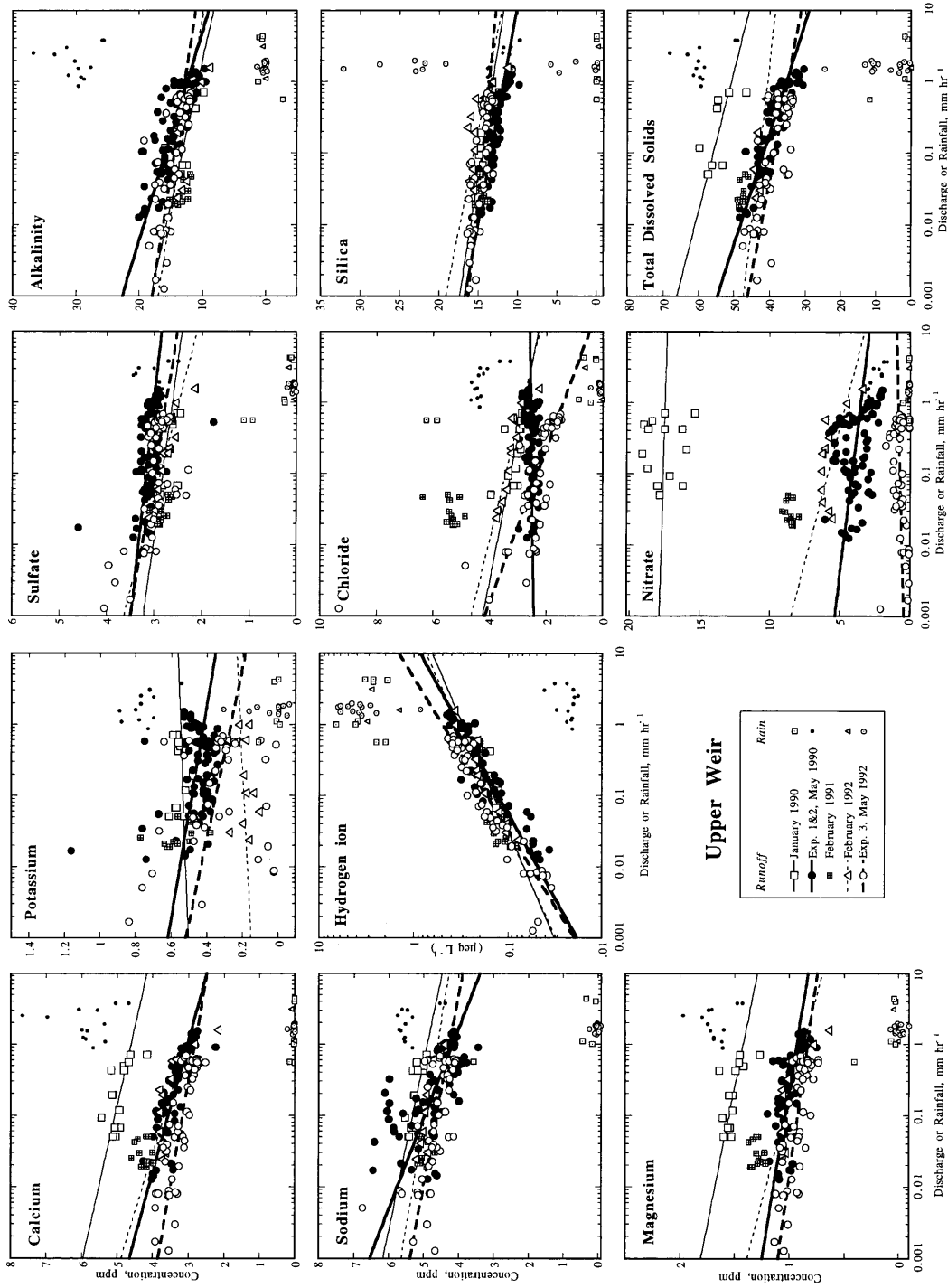
### New Water in Runoff

The rainfall during each of the sprinkling experiments totaled 213–290 mm (Table 2). Was this sufficient rainfall to expect a significant component of rainwater in the runoff due to plug-flow displacement of stored water? Or put another way, how much water is stored within the catchment in comparison to the total rainfall? One may compute the amount of water stored within a catchment from the product of the soil thickness and the water content. The water content of soil samples collected 1 week after the first heavy rain at the end of the dry season in the CB2 catchment was  $20.6 \pm 6.8\%$  by volume (Table 1), and the soil-water retention curve shows a residual soil-water content of 18% at pressure heads below  $-0.7 \text{ m}$  (R. Torres et al., manuscript in preparation, 1996); 20% is therefore a reasonable estimate of the water content of well-drained soil in the catchment. Soil thickness measured in 104 logged borings ranges from 0.1 to 1.98 m; the mean depth in these borings is  $0.7 \pm 0.4 \text{ m}$ . Thus the soils hold about 140 mm ( $0.20 \times 700 \text{ mm}$ ) of water when fully drained. The rainfall during the three sprinkling experiments exceeded by 70–145 mm this estimate of the drained water content in the catchment soils, and therefore, given a plug-flow model for displacement of water from the catchment, a minimum of 70–145 mm of the runoff could have been new rainwater.

In this first estimate of stored water in the catchment prior to the sprinkling experiment we have ignored the actual antecedent water contents for the experiments, water storage in weathered bedrock beneath the regolith, and evapotranspiration during the experiments. The 70- to 145-mm excess of sprinkling relative to water storage therefore yields a maximum estimate for the contribution of new rainwater to runoff (assuming plug flow). Antecedent moisture conditions for each experiment undoubtedly differed from the fully drained esti-

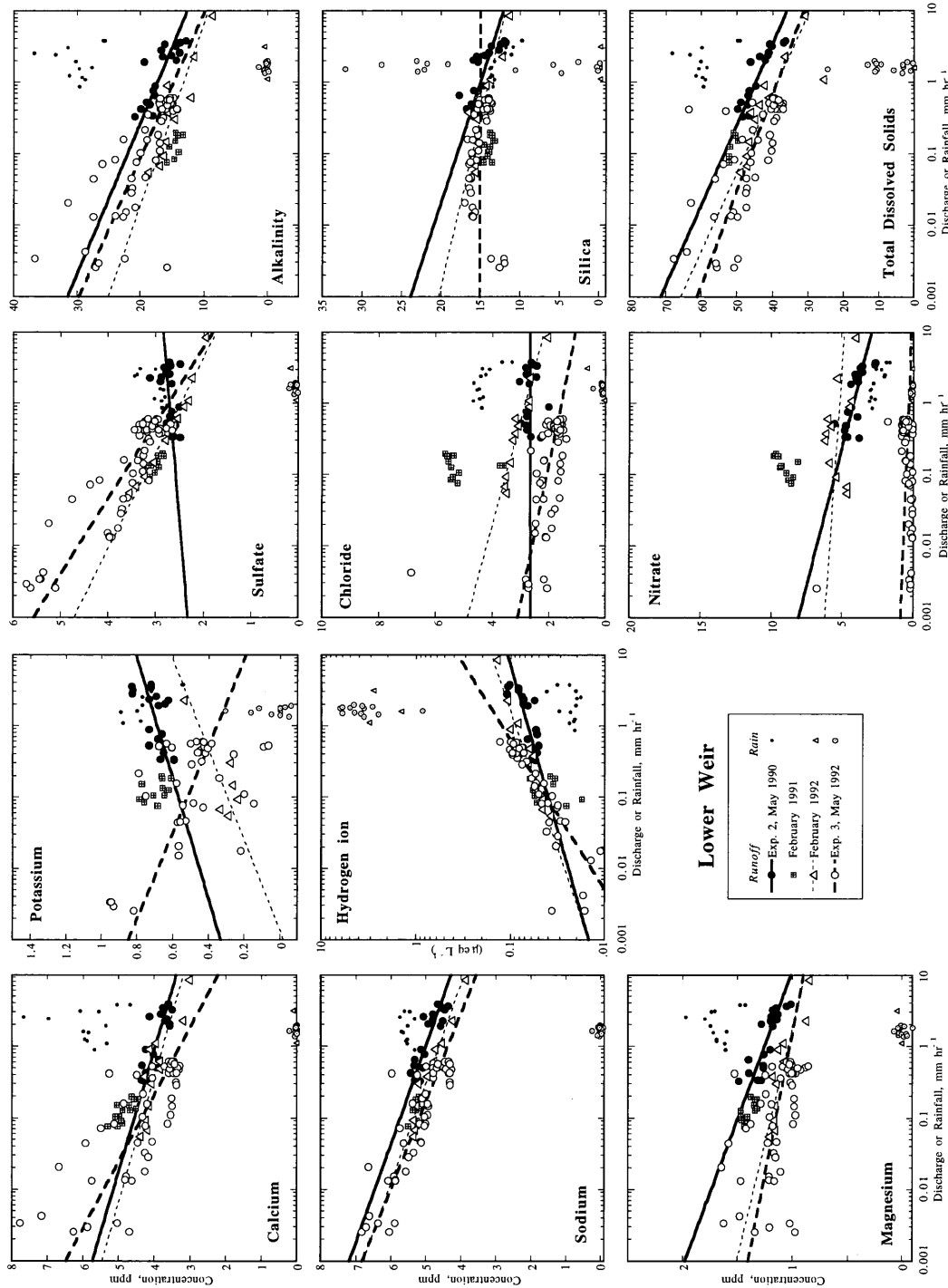


**Figure 4.** Runoff chemistry during sprinkling experiments 1 and 2 in May of 1990. Heavy bar at the top of each panel indicates when the sprinklers were running; the upper weir hydrograph (arbitrary scale) is plotted with discharge increasing downward in the top panels. Open symbols show runoff chemistry. Solid circles show rainwater chemistry. Hydrogen ion is in microequivalents per liter on log scale, while all other species are reported in parts per million. Shading shows range of compositions expected if runoff at the upper weir is a mixture of preexperiment runoff and average sprinkled water. The concentration peaks in many species on May 13–14 were caused by injection of sodium bromide for a tracer experiment. This injection clearly perturbed the exchange complex as sodium replaced other cations, leading to enhanced concentrations in the runoff over a period of about 2 days.



**Figure 5.** Precipitation chemistry and concentration-discharge relationships at the upper weir during events shown in Figure 3. Solid symbols are sprinkling experiments with untreated water (experiments 1 and 2). Open symbols are sprinkling experiments with demineralized water (experiment 3) and natural storms. Precipitation compositions are shown with smaller versions of the symbols used for the corresponding runoff and are plotted as a function of rainfall rate. Regressions are listed in Table 3.





**Figure 6.** Precipitation chemistry and concentration-discharge relationships at the lower weir during events shown in Figure 3. Symbols are as in Figure 5. Regressions are listed in Table 3.

**Table 3.** Curve Fits to Concentration-Discharge Observations Shown in Figures 5 and 6

Species	Data Set	Upper Weir					Lower Weir				
		$C_*$ , ppm	$m$	$r$	lev. sig. <sup>a</sup>	$n$	$C_*$ , ppm	$m$	$r$	lev. sig. <sup>a</sup>	$n$
Ca	storms, Jan. 5–14, 1990	4.6	-0.45	0.649	>99%	15	...	...	...	...	...
	experiments 1 and 2, May 1990	3.0	-0.54	0.831	>99%	88	4.0	-0.59	0.801	>99%	19
	storm, Feb. 19–28, 1992	3.0	-0.61	0.766	>99%	16	3.8	-0.57	0.865	>99%	12
Mg	experiment 3, May–June 1992	2.8	-0.34	0.811	>99%	52	3.3	-1.07	0.766	>99%	54
	storms, Jan. 5–14, 1990	1.4	-0.13	0.614	>99%	15	...	...	...	...	...
	experiments 1 and 2, May 1990	0.9	-0.10	0.680	>99%	89	1.2	-0.24	0.827	>99%	19
Na	storm, Feb. 19–28, 1992	0.9	-0.17	0.765	>99%	16	1.0	-0.16	0.869	>99%	12
	experiments 3 and 4, May–June 1992	0.8	-0.09	0.741	>99%	53	1.0	-0.13	0.498	>99%	54
	storms, Jan. 5–14, 1990	4.9	-0.42	0.729	>99%	15	...	...	...	...	...
K	experiments 1 and 2, May 1990	4.2	-0.79	0.662	>99%	86	5.0	-0.72	0.860	>99%	19
	storm, Feb. 19–28, 1992	4.6	-0.34	0.878	>99%	12	4.6	-0.72	0.973	>99%	12
	experiments 3 and 4, May–June 1992	4.2	-0.38	0.654	>99%	52	4.4	-0.81	0.879	>99%	54
H <sup>b</sup>	storms, Jan. 5–14, 1990	0.6	0.02	0.122	n.s.	15	...	...	...	...	...
	experiments 1 and 2, May 1990	0.4	-0.07	0.326	>99%	91	0.7	0.12	0.644	>99%	19
	storm, Feb. 19–28, 1992	0.2	0.02	0.234	n.s.	12	0.4	0.16	0.827	>99%	7
Si	experiments 3 and 4, May–June 1992	0.3	-0.08	0.332	>95%	39	0.4	-0.16	0.560	>99%	39
	storms, Jan. 5–14, 1990	0.30	0.32	0.737	>99%	12	...	...	...	...	...
	experiments 1 and 2, May 1990	0.33	0.42	0.900	>99%	92	0.06	0.22	0.791	>99%	19
Alkalinity	storm, Feb. 19–28, 1992	0.34	0.35	0.958	>99%	12	0.09	0.26	0.948	>99%	12
	experiments 3 and 4, May–June 1992	0.49	0.47	0.948	>99%	54	0.12	0.47	0.953	>99%	54
	storms, Jan. 5–14, 1990	6.1	-0.65	0.742	>99%	15	...	...	...	...	...
Cl	experiments 1 and 2, May 1990	5.5	-0.76	0.808	>99%	93	7.0	-1.37	0.719	>99%	19
	storm, Feb. 19–28, 1992	6.4	-0.82	0.749	>99%	16	6.5	-0.98	0.859	>99%	12
	experiments 3 and 4, May–June 1992	6.3	-0.41	0.745	>99%	54	7.0	-0.01	0.008	n.s.	52
SO <sub>4</sub> <sup>2-</sup>	storms, Jan. 5–14, 1990	10.7	-2.46	0.668	>95%	8	...	...	...	...	...
	experiments 1 and 2, May 1990	12.4	-3.41	0.796	>99%	88	17.2	-4.71	0.817	>99%	19
	storm, Feb. 19–28, 1992	12.5	-1.01	0.479	>99%	11	13.2	-3.93	0.909	>99%	11
NO <sub>3</sub> <sup>-</sup>	experiments 3 and 4, May–June 1992	12.7	-1.70	0.747	>99%	52	14.7	-4.96	0.768	>99%	54
	storms, Jan. 5–14, 1990	2.8	-0.48	0.615	>95%	14	...	...	...	...	...
	experiments 1 and 2, May 1990	2.6	0.04	0.141	n.s.	95	2.7	0.01	0.010	n.s.	18
NO <sub>3</sub> <sup>-</sup>	storm, Feb. 19–28, 1992	2.8	-0.60	0.850	>99%	17	2.8	-0.67	0.964	>99%	12
	experiments 3 and 4, May–June 1992	1.4	-0.91	0.681	>99%	69	1.6	-0.51	0.528	>99%	68
	storms, Jan. 5–14, 1990	2.6	-0.20	0.417	>99%	14	...	...	...	...	...
NO <sub>3</sub> <sup>-</sup>	experiments 1 and 2, May 1990	3.0	-0.16	0.353	>99%	96	2.7	0.13	0.335	n.s.	19
	storm, Feb. 19–28, 1992	2.5	-0.38	0.867	>99%	17	2.5	-0.74	0.980	>99%	12
	experiments 3 and 4, May–June 1992	2.8	-0.25	0.628	>99%	65	2.7	-0.94	0.897	>99%	68
NO <sub>3</sub> <sup>-</sup>	storms, Jan. 5–14, 1990	17.5	-0.14	0.046	n.s.	14	...	...	...	...	...
	experiments 1 and 2, May 1990	3.5	-0.61	0.326	>99%	96	4.2	-1.28	0.722	>99%	19
	storm, Feb. 19–28, 1992	4.5	-1.31	0.737	>99%	17	5.2	-0.34	0.284	n.s.	12
NO <sub>3</sub> <sup>-</sup>	experiments 3 and 4, May–June 1992	0.8	0.14	0.255	>95%	69	0.3	-0.19	0.152	n.s.	67

$C = C_* + m \log Q$ , where  $C$  is species concentration in runoff in parts per million,  $C_*$  is a fitted parameter equal to the concentration at  $1 \text{ mm h}^{-1}$  discharge,  $m$  is the fitted slope, and  $Q$  is the discharge in millimeters per hour.

<sup>a</sup>Level of significance of the correlation coefficient  $r$  (n.s., not significant).

<sup>b</sup>Concentration for hydrogen ion is in micrograms per liter; regression is  $\log C = C_* + m \log Q$ .

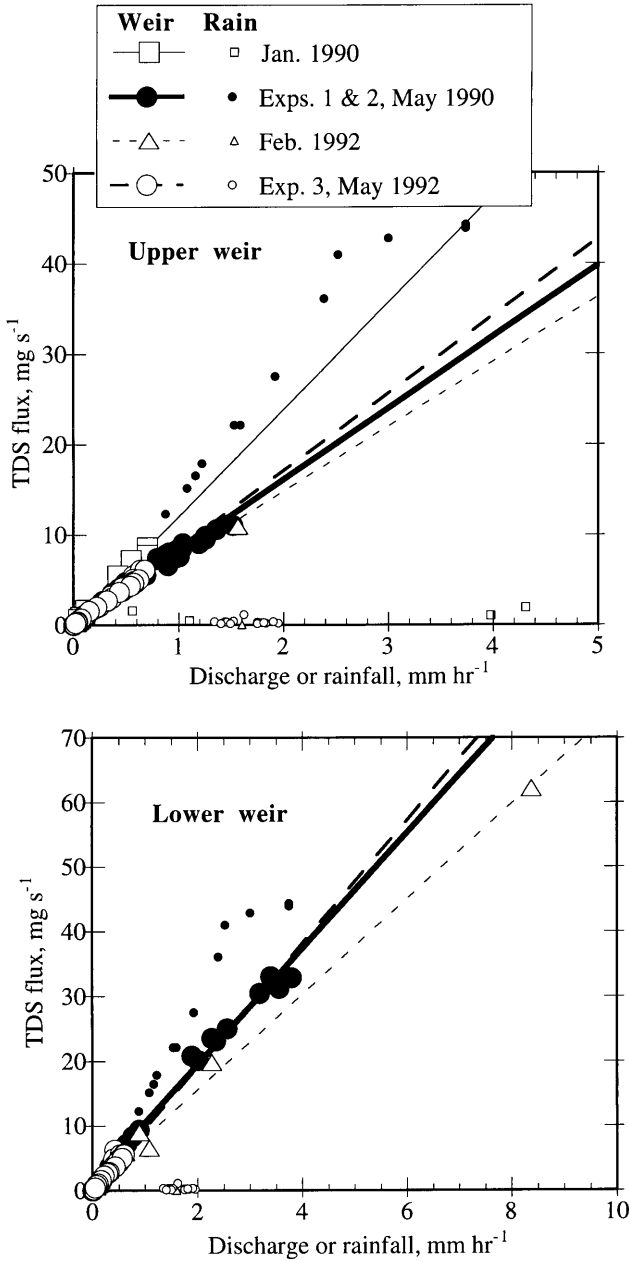
mate. Experiments 1 and 2 were preceded by 17- to 19-mm events from sprinkler test runs and natural rain, respectively, 3 days before the start of the experiments. Both of these occurrences probably boosted water contents above the fully drained estimate. Only one, half hour long, sprinkler test was conducted before experiment 3, and just 3.2 mm of rain had fallen in the preceding 26 days. Thus the fully drained water content estimate probably describes well the start of experiment 3. The runoff in experiment 3, the only one for which we have complete data from both weirs, was 152 mm. This overlaps with the 140-mm estimate of fully drained water content for the soil, suggesting that runoff may have consisted entirely of displaced old water. Storage in bedrock may comprise a significant additional reservoir of water within the catchment, for which we have no estimate at present.

Another way to gauge new rainwater contributions to runoff is with chloride concentrations, assuming conservative behavior. The sprinkling experiments with high-chloride rain (experiments 1 and 2) and with low-chloride rain (experiment 3)

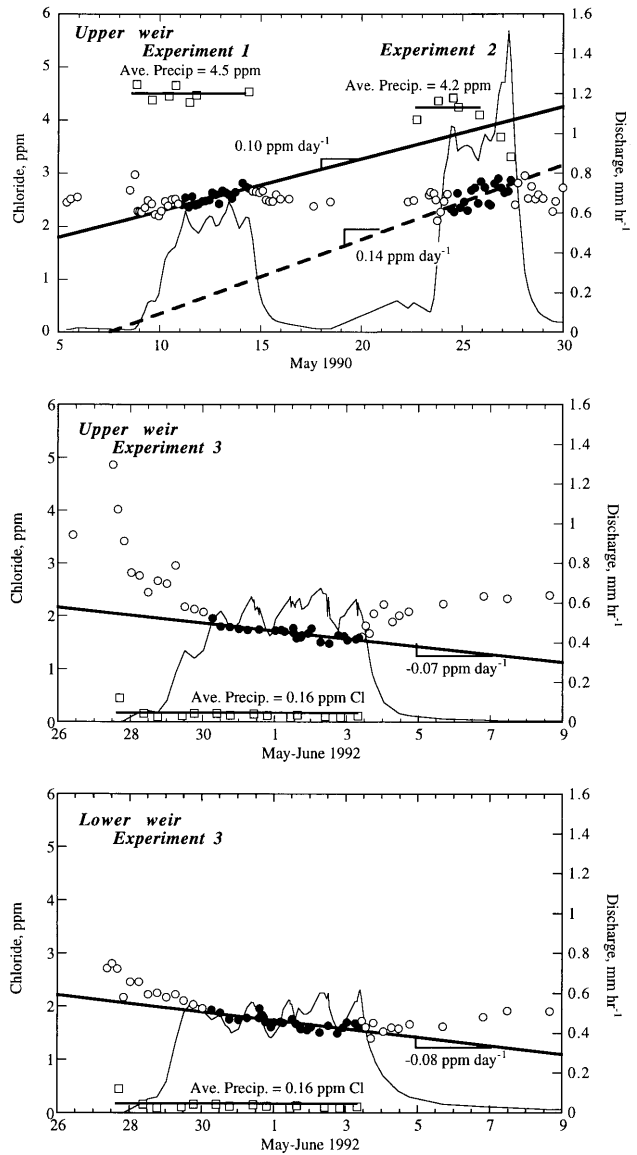
provide two different realizations of this test. Once steady discharge is reached, the flow paths contributing to runoff stabilize and therefore changes in chloride concentration can be attributed to changes in the composition of water emerging from these flow paths. Figure 8 shows the chloride concentration in the runoff at the upper weir during the three sprinkling experiments and from the lower weir during experiment 3 (the lower weir record from experiment 2 was too short to include in the following analysis). In all three experiments the chloride concentration moved toward the concentration in the rainwater during the time of steady state hydrology. The chloride concentration rose in response to untreated water (high chloride) sprinkling in experiments 1 and 2 and fell in response to demineralized water (low chloride) sprinkling in experiment 3. On the recession limbs, chloride concentrations (plotted with open symbols on Figure 8) moved away from the rainwater compositions, falling at the ends of experiments 1 and 2 and rising at the end of experiment 3. During the rising limb of the experiments, chloride concentrations did not consistently ap-

proach the rainwater composition, in contrast to the response expected if new water is the source of increased discharge.

On the rising limbs of sprinkler experiments 1 and 2, chloride concentrations changed little from base flow concentrations of about 2.5 ppm, despite sprinkling water with 4.5 ppm chloride. This contrasts with the steep decline in chloride concentrations on the rising limb of experiment 3, when the average sprinkling water was 0.16 ppm chloride. Evaporation associated with drier antecedent conditions may have caused the initially high chloride concentrations for experiment 3. Chloride fluxes from catchments often exceed the input from rain



**Figure 7.** The flux of total dissolved solids (the sum of measured species) in runoff follows similar trends with discharge for different storm and sprinkler events, in which the flux of total dissolved solids in the rainwater varied significantly. Rainwater fluxes are plotted with smaller symbols than the corresponding runoff for each event. Linear regressions fit the runoff fluxes at the weirs.



**Figure 8.** Chloride concentrations during sprinkler experiments 1–3, used to demonstrate increasing contributions of new rainwater to runoff as the experiment progressed. Runoff samples collected during the steady discharge periods are shown with solid circles, while samples from other times are shown with open circles. Open squares show rainwater concentrations; the average for each experiment is indicated with horizontal bar. Regressions lines, with slopes indicated, fit only the concentrations during steady discharge (solid circles). Discharge curves are shown for reference.

and snow [Hem, 1992], suggesting that chloride is leached from rocks and sediments. A bedrock source for chloride at our site, which is possible given that the sandstone is marine in origin, could produce high concentrations of chloride in the CB1 base flow and lower chloride concentrations within the more leached soil. The rising limb concentrations of chloride during the experiments would then represent varying mixtures of these water sources, with the different trends observed in the experiments arising from differences in the antecedent soil water. Extensive sprinkler tests with high-chloride water preceded experiment 1 but not experiment 3, and therefore the stored water composition is likely to have been different for

**Table 4.** Fractions of Old and New Water in the Runoff at the Time of Sprinkler Shut-Off, Calculated Using (3)

	Fraction Old Water	Fraction New Water
Upper weir		
Experiment 1	0.84	0.16
Experiment 2	0.77	0.23
Experiment 3	0.82	0.18
Lower weir		
Experiment 3	0.81	0.19

these two experiments. Without knowledge of soil water compositions, the role of new water in producing the concentration trends during the rising limbs of the experiments remains ambiguous. The opposing concentration trends on the falling limbs are probably due to a decrease in the proportion of runoff from shallow flow paths, characterized by more new water, toward deeper flow paths characterized by older water.

If chloride behaves conservatively, meaning that it has no sources or sinks within the catchment over the timescale of the experiments, then the concentration trends during steady discharge must arise from increasing proportions of new rainwater in the runoff with time. Slopes are shown in Figure 8 from linear regression of the chloride concentration as a function of time during the steady discharge portions (the solid data points) of the experiments. Similar magnitude, but opposite sign, slopes of 0.1 and  $-0.07 \text{ ppm d}^{-1}$  were obtained for experiments 1 and 3, which had nearly identical rainfall rates of about  $1.5 \text{ mm h}^{-1}$  (Table 2). A greater slope of  $0.14 \text{ ppm d}^{-1}$  was obtained for the higher rain intensity experiment 2 ( $3 \text{ mm h}^{-1}$ ). This suggests that the rate at which new water moves through the catchment is related to the intensity of the rainfall. Since flow rates in the vadose zone are controlled by rainfall rates, this behavior is expected if the vadose zone controls the delivery of new water through the catchment (R. Torres et al., manuscript in preparation, 1996).

We use chloride concentrations and the mixing model of (1) to constrain the change in new water contribution to runoff from the beginning to the end of the steady discharge periods of the sprinkling experiments. We assume that the runoff during steady discharge is a mixture of uniform old water, whose chloride concentration is given by the runoff at the start of the period of steady discharge, and of new water, whose chloride concentration is that of the rain. As discussed above, runoff during the rising limbs of the experiments may be a mixture of new water and water previously stored in the catchment, and therefore using the runoff composition at the beginning of steady discharge for the old water component may underestimate the actual amount of new water in the runoff. The mass balance for chloride concentration in the runoff,  $C_r$ , is

$$C_r = X_o C_o + (1 - X_o) C_n, \quad (2)$$

where  $C_o$  and  $C_n$  are the chloride concentration in old water and new rainwater, respectively, and  $X_o$  is the fraction of old water contributing to the runoff. This can be solved for  $X_o$ :

$$X_o = \frac{C_r - C_n}{C_o - C_n}. \quad (3)$$

The fraction of new water contributing to runoff increased steadily, reaching 16–23% by the end of the period of steady discharge in the experiments (Table 4). These estimates are

conservative, in that they attribute all of the runoff at the beginning of the period of steady discharge to old water. They are smaller, by almost a factor of 2, than the estimate of new water runoff based on water balance. Nonetheless, these numbers illustrate that new water contributions can be significant in a prolonged storm and that new water contributions to runoff increase through a storm becoming progressively greater as the total amount of rain increases.

Although new rainwater does contribute to the runoff, in amounts that increase with the duration of the rainfall, the concentrations of many species other than chloride remain constant during steady discharge. Moreover, the composition of runoff does not depend on the chemistry of the rainwater. These observations imply that new water is buffered in its chemical composition as it moves through the catchment. The soil is the likely site of new water buffering during storms through mechanisms such as ion exchange or adsorption/desorption reactions. Is this soil-buffered rainwater the source of dilute water in the runoff during high flow, or are there other possible sources for dilute water in the catchment? We can make some inferences from our understanding of the hydrology of the site and fine-scale features in the runoff chemistry.

#### Flow Paths and Runoff Chemistry

Intensive monitoring of the head fields in unsaturated soil (R. Torres et al., manuscript in preparation, 1996), saturated soil, and underlying bedrock [Montgomery et al., this issue] has shown that a large proportion of all storm runoff from the CB1 catchment is water that exfiltrates from the weathered bedrock. A thin and patchy saturated zone develops within the soil during rainfall. The patch of partial soil saturation that is in contact with the upper weir makes up less than 10% of the total catchment area, and therefore water that has been in contact with soil, but not with bedrock, can account for no more than 10% of the water flux during the steady discharge portions of our sprinkler experiments. Base flow must be generated solely from exfiltration from the bedrock or from water that flows in a very thin layer over the bedrock. It is clear therefore that high-solute concentrations in base flow reflect mineral weathering reactions in the weathered bedrock or at its top surface. Because such a small proportion of storm runoff is water that has traveled only through the soil, the lower solute concentrations in runoff during storm flow conditions must also be generated from water that has traveled through bedrock.

Hydrologic and topographic considerations suggest a greater deep, weathered rock flow contribution to the lower weir than the upper weir [Montgomery et al., this issue], an interpretation supported by the greater solute concentrations at the lower weir (Figures 4–6). If this is the case, then the lower weir should show little or no change in chemical composition with discharge because of the smaller role of soil water there. However, concentration-discharge regression slopes for the lower weir are as steep, and often steeper, than for the upper weir (Table 3). This suggests that the composition of water exiting the bedrock may also change as the discharge from the bedrock changes, becoming more dilute at high flow and more concentrated at low flow.

Water from the soil enters bedrock over nearly the entire area of the CB1 catchment, adding newer, more dilute buffered soil water to the older, more evolved water already within the bedrock. The near-surface rock in the catchment is fractured, and therefore flow velocities through the bedrock will increase

dramatically during storm flow. As the chemistry of water in the bedrock depends on reaction kinetics, flow velocity, and distance along the flow path [Freeze and Cherry, 1979, p. 296], rapid fracture flow should lower the mineral-weathering-derived solute concentrations in water exfiltrating from the bedrock during storms. Thus at least a portion of the observed decline in concentrations in runoff at both the upper and lower weirs may be due to changes in bedrock water compositions.

The interaction of water in different pore sizes may also alter the composition of water exiting the bedrock during rain events. We observed transient concentration increases in sodium, potassium, and chloride, and to a lesser degree silica and sulfate, at the beginning of the sprinkler experiments. Solute concentration increases during the rising limb have been noted by others and attributed to "flushing" of solutes from soil [Walling and Foster, 1975; Miller and Drever, 1977; Luxmoore and Ferrand, 1993]. During experiment 1, increased concentrations were seen after 6 hours of sprinkling (9 mm of rain) (Figure 4), accompanied by a barely perceptible discharge increase from 0.013 to 0.016 mm h<sup>-1</sup>. These initial increases in concentration were muted at the start of experiment 2 but were again observed at the beginning of experiment 3 in these species as well as in alkalinity, calcium, and magnesium [Anderson, 1995].

These transient increases in runoff solute concentration precede significant changes in saturated hydraulic head [Montgomery *et al.*, this issue] and hence precede alteration of the flow paths contributing runoff. Because the proportions of runoff from bedrock and soil flow paths probably have not changed over this time interval, piston flow displacement of water should produce water of the same composition as before the rain began. The change in runoff composition cannot be attributed to new rainwater bypassing the soil because concentration increases are seen both in experiment 1, with high-solute untreated rain, and in experiment 3, with low-solute demineralized rain. Instead, shortly after the onset of rain, some mechanism must mobilize high-solute concentration water that had been relatively immobile before rain began. This has been observed in soils, where enhanced transport of high-concentration water from small pores into large pores occurs during rain events [Jardine *et al.*, 1990]. Because exfiltration from weathered bedrock is the source of base flow in CB1, the high-concentration water probably comes from small pores in the bedrock, in which solute concentrations are high owing to both the high mineral surface area to water volume ratio and the low water velocities of the smallest pores. The water in these small pores may participate in flow out of the bedrock if there is a rapid increase in the effective porosity (i.e., the pore space in which water is mobile) through linking of pores when rain begins [Luxmoore and Ferrand, 1993]. At CB1 this appears to happen before increases in water content of the bedrock occur. The short timescale over which concentration rises in the runoff occur implies that the high-solute concentration water in the runoff derives from areas near the weirs, but presumably this effective porosity increase occurs throughout the catchment. Solute concentrations in the runoff eventually decline with continued rain, as more dilute water from the soil enters the bedrock and the rapid fracture flow system develops. Initial concentration increases in the runoff were not as apparent in experiment 2, probably because of wetter antecedent conditions and the short time since experiment 1.

These two lines of reasoning, based on the our understanding of the hydrology of the catchment and our observations of

short-lived concentration increases in several species in runoff following the onset of rain, both suggest that the composition of water emerging from the bedrock changes through the course of a storm. Although concentrations decline with increasing discharge, bedrock exfiltration remains more concentrated than soil water, as evidenced by the difference in chemistry between the upper and lower weirs.

These observations lead to a conceptual model for concentration-discharge relationships in the runoff from the CB1 catchment. Solute concentrations in runoff depend on the proportions of runoff from the soil and from the rock and from small and large pores, both of which vary as a function of discharge. Rainwater chemistry is buffered, probably within the soil, so that runoff chemistry cannot be characterized as a simple mixture of rain and preevent water. Water in the bedrock varies in composition through storms as the mean residence time of water in the rock changes. At low flow the water exfiltrating from the rock has had longer, more intimate contact with the bedrock on average and therefore has high solute concentrations. At high flow, water has shorter contact times with the rock on average and therefore runoff reflects the lower solute concentrations resulting from reactions in the overlying soil. Rain appears to enhance exchange of water and solutes between small and large pores, allowing solutes produced between rain events to be swept out during rain events.

#### Nutrient Species

Two nutrient species, potassium and nitrate, have concentration variations with runoff that do not follow the general trends discussed previously. Potassium concentrations are low in the runoff, and analytical uncertainties are high. The potassium regression lines, which have very low slopes (Table 3) and are the least significant of all the concentration-discharge relationships, tend to be positive (increasing concentration with increasing discharge) during winter storms and negative during the springtime experiments. The seasonality suggests that potassium uptake by plants and microbes during the growing season plays a role in regulating potassium exports from the catchment. Nitrate concentrations in runoff have shown wide variation on annual, seasonal, and sprinkling experiment timescales. Measured nitrate concentrations were highest during January 1990 and were successively lower in each of the two following winters (Figure 5). Presumably, the high concentrations during the winter of 1990 are from the effects of logging in 1987 and herbicide treatment in 1988. These types of disturbances are known to increase the export of nitrogen in the form of nitrate from the forest soil [Vitousek *et al.*, 1982]. The decline in nitrate over subsequent winters suggests the recovery to a balance between nitrate production and uptake by plants and microorganisms. Concentrations also rose and fell on a seasonal scale: winter runoff concentrations were higher than those measured in our late springtime sprinkling experiments in 1990 and 1992. The difference between the 17.5 ppm nitrate at 1 mm h<sup>-1</sup> discharge in January 1990 and the 3.5 ppm nitrate at the same discharge 5 months later, in May 1990, can probably be attributed to uptake by plants and microorganisms. High nitrate concentrations caused high concentrations of base cations, particularly calcium and magnesium, and reduced alkalinity in the runoff in January 1990 (Table 5).

Nitrate concentrations followed a distinctive pattern during the sprinkling experiments (Figure 4). Concentrations rose sharply to a maximum within one and a half days after the sprinklers were turned on in experiment 1 and then declined

**Table 5.** Effect of Nitrate and Charge Balance on Upper Weir Runoff Composition in January 1990 and May 1990

Species	January 1990	May 1990
NO <sub>3</sub> <sup>-</sup>	-282	-56
Ca <sup>2+</sup>	230	150
Mg <sup>2+</sup>	115	74
Na <sup>+</sup>	213	182
K <sup>+</sup>	15	10
Alkalinity	-175	-203
Cl <sup>-</sup>	-79	-73
SO <sub>4</sub> <sup>2-</sup>	-54	-62
Charge balance	-1.5%	+2.7%

Calculated for a discharge of 1 mm h<sup>-1</sup> from regressions in Table 3. Values are given in microequivalents per liter.

steadily through the rest of the sprinkling experiment. Experiment 2 lacked the initial rise in concentrations but again showed steady decline through the experiment. The experiment 1 pattern was repeated during experiment 3, albeit at lower overall nitrate concentrations [Anderson, 1995]. These temporal patterns during the course of the sprinkling experiments may reflect the dynamics of the biota. The initial sharp rise in concentration may show the increased efficiency of nitrogen mineralization (nitrate production) with the onset of rain, and the subsequent decline in concentration reflects either increased uptake by growing plants and microbes or exhaustion of the mineralization source. Because these biodynamics are not coupled to the flow paths in the catchment, nitrate does not show the same variations with discharge that inorganic species do.

## Conclusions

Runoff composition at the CB1 catchment followed concentration-discharge trends that were independent of rainwater composition during sprinkling experiments with untreated, high-solute-concentration water, with demineralized water, and during natural winter storms. This similarity in runoff chemistry during events with high and low ionic strength incoming rainwater argues against a direct dilution of runoff by rainwater, in agreement with observations from Birkenes and Plynlimon catchments [Christophersen *et al.*, 1990].

New rainwater contributes to runoff in proportions that increase with continuing rainfall. Conservatively, new rain contributed 16–23% of the runoff after 6–7 days of continuous, steady sprinkling. Despite the growing contribution of new rainwater to the runoff during long periods of steady discharge, runoff solute compositions remained relatively steady. This and the similarity in runoff compositions no matter what the rainwater composition is imply that the soil in the CB1 catchment buffers the composition of water that passes through it. This buffering capacity was not exhausted by rain totaling >250 mm.

In addition, two lines of reasoning suggest that it is probably incorrect to characterize water in the bedrock with a stable composition. First, concentrations varied with discharge at the lower weir, where bedrock exfiltration is the primary source of runoff. The fractured nature of the bedrock leads to greater flow velocities with increased hydraulic gradients and higher water tables during storms. Shorter contact times in the bedrock during storm flow can explain the lower solute concentrations at the lower weir during storm flow. Second, concen-

trations of several species rose during the first hours of sprinkling experiments, before saturated flow paths were established in the soil. These apparent changes in the composition of water exfiltrating from bedrock can be explained if the onset of rain forges links between small, unconnected pores and fractures, in which solute concentrations are high, and larger connected voids with lower solute concentrations. The high-solute water is then mobilized into the connected porosity. The reservoir of both water and solutes within the bedrock must be large, however, given that runoff compositions were steady during steady discharge.

These observations suggest that at our study site, the widely observed inverse relationship between runoff and solute concentration results from consistent differences between soil water and bedrock water chemistry and from variations in water contact time within the bedrock. The bedrock flow path control on runoff chemistry may be fairly common, as bedrock in unglaciated terrain is seldom hydrologically tight.

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