

## **Chapter Three**

### **Solute Balances For Eight High Elevation Catchments in the Sierra Nevada**

**by**

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### 3. Chapter Three

#### 3.1. Introduction

Precipitation intercepted by watersheds in the Sierra Nevada undergoes many chemical alterations before exiting as streamflow. Previous studies of hydrochemistry in the Sierra Nevada have demonstrated that acid deposition is effectively neutralized by chemical reactions within the watersheds (Melack and Stoddard 1991; Sickman and Melack 1991; Melack et al. 1993). Chemical weathering of granitic minerals, cation exchange in soils and biotic activity are some of the mechanisms responsible for these alterations. However, the relative importance of these mechanisms in the neutralization of atmospheric acidity has been studied in only a few areas of the Sierra Nevada (Williams et al. 1993; Brown and Lund 1991; Melack and Stoddard 1991). Since the Sierra Nevada region is diverse with respect to geology, soils, precipitation quantity, vegetation and topography, more study is required before these geographically limited studies can be extrapolated throughout the range.

Watershed solute-balances have been used to quantify the influence of catchment processes on surface-water chemistry in a variety of settings (Paces 1985, Yurech and Balder 1988, Likens and Borman 1995). This approach utilizes comparisons between annual input/output budgets for major ions and nutrients to determine what biogeochemical reactions are altering water chemistry as it passes through a catchment.

We present data from solute balances for seven headwater catchments in the Sierra Nevada and for the upper Marble Fork of the Kaweah River. For the Crystal Lake, Lost Lake, Pear Lake and Topaz Lake watersheds, solute balances were constructed for water years 1990 through 1993. For the Emerald Lake, Ruby Lake and Spuller Lake watersheds, solute balances for water years 1990 through 1994 were computed. For the Emerald Lake watershed, data from earlier studies were used to construct solute balances for water years 1985 through 1987. A total of 36 solute balances are presented. Using these data we examine the relative influence of various biogeochemical mechanisms in controlling surface water chemistry in Sierran watersheds on both seasonal and annual time scales.

To quantify the hydrochemical changes that occur within a watershed, solute inputs to and losses from catchments must be accurately measured. Solute loading in the Sierra Nevada is the sum of solute contributed by wet and dry atmospheric deposition. Loss is the transport of dissolved and particulate material in the outflow streams of the catchments. For wet deposition, loading is a function of the volume of precipitation deposited and the concentrations of solutes present in the precipitation. For the outflow streams, efflux is a function of the discharge of the stream and the concentrations of solutes in the streamwater. Dry deposition varies with the concentration of solids and aerosols in the air and the quality and quantity of depositional surfaces in a specific area. In the present study we have focused our efforts on quantifying wet atmospheric deposition of solutes since determining the amount of dry deposition in the Sierra Nevada is problematic at best. However, dry deposition onto snow surfaces is included in the winter loading calculations since snowpits were used to measure winter deposition.

Details on the chemical and physical measurements of precipitation and streamflow in our study can be found in Chapters One and Two and in Melack et al. (1997). The

present chapter is divided into four sections. The first section summarizes the volume-weighted mean chemistry of the components of the solute balance, that is, winter precipitation (snow), non-winter precipitation, annual precipitation (sum of winter and non-winter precipitation) and outlet streamflow. In the second section we present the annual fluxes and net yield of solutes from the catchments along with a discussion of possible errors in the input-output budgets. The third section of the chapter examines the relationship between solute transport and water flux (e.g., winter loading versus SWE and outflow efflux vs stream discharge). The final section focuses on nitrogen dynamics within the study catchments since this is one of the least understood processes in Sierran watersheds. We will discuss the relative contribution of atmospheric and catchment source of N in the annual ionic pulse during snowmelt. In addition, we present a discussion of the current status of Sierran lakes with respect to the problem of nitrogen saturation.

## 3.2. Methods

### 3.2.1. Volume-weighted Mean Chemistry

Annual volume-weighted mean concentrations (VWM) were calculated for each solute in winter and non-winter precipitation and outflow discharge. Volume-weighted means differ from simple arithmetic means in that solute concentrations are weighted in proportion to the amount of water-flux associated with them. For example, stream chemistry from a day with flow of 10,000 m<sup>3</sup> would be weighted 10 times more than chemistry from a day with only 1,000 m<sup>3</sup>. Similarly, a precipitation event of 20 mm would be weighted 4 times more than a storm of only 5 mm. For snow samples, the snow-water equivalence (SWE) of individual pit samples (derived from snow density measurements) was used to weight the samples. Volume-weighted means, therefore, give a truer estimate of average precipitation or stream chemistry and were used to calculate solute fluxes and yields. The general equation for calculating annual VWM solute concentrations for *n* measured events (i.e., the number of snowpit samples, rain storms or outflow samples collected during each water year) is given as:

$$C_{vwm} = \frac{\sum_{i=1}^n C_i V_i}{\sum_{i=1}^n V_i} \quad (1)$$

where:

$C_{vwm}$  = annual volume-weighted mean solute concentration (Eq m<sup>-3</sup>),

$C_i$  = solute concentration for event *i* (Eq m<sup>-3</sup>), and

$V_i$  = water flux associated with event *i* (m<sup>3</sup>).

For precipitation, the VWM calculations were fairly simple because the process of assigning volumes to chemistry samples was straightforward. However, for outflow chemistry, assigning volumes was more complicated since stream samples were not always contemporaneous with discharge. In calculating VWM outflow chemistry, several rules were used to distribute volume to the chemistry samples. Chemistry measured in a stream

sample would be used with the discharge for that particular day and when the time interval between stream samples was greater than one day, the midpoint of this interval ( $\pm 1$  day) was used as the division. For example, May 6 would be used as the division for samples collected on May 1 and May 11. Chemistry from May 1 would be used for flows from May 1 through 5 while chemistry from May 11 would be applied to streamflow from May 7 through 11 (further still if the next sample after May 11 was later than May 12). As a rule, streamflow for May 6 would be assigned chemistry from the earlier sample, May 1, unless there was some hydrologic event (e.g., rain storm, large increase or decrease in discharge) that led us to believe that flow for the midpoint date was, chemically, more similar to the later stream sample. If, samples were collected on May 1 and May 10, chemistry from May 1 would be used through May 5 and chemistry from May 10 would be used for the period of May 6 through 10.

The midpoint rule was always superseded if a hydrologic event of sufficient magnitude occurred between sample dates. These events included rainfall that increased streamflow, cold snaps that abruptly decreased streamflow and the initiation of snowmelt runoff. The date of the event was used as the division and, for these situations, chemistry from the later sample was used with streamflow on the day of the event.

### 3.2.2. Solute Loading

Solute loading in the Sierra Nevada is the sum of solutes contributed by wet and dry atmospheric deposition. For wet deposition, loading is a function of the volume of precipitation and the solute concentrations. Dry deposition varies with the concentration of solids and aerosols in the air and the extent and character of depositional surfaces in a watershed (for example, trees, rock, soil, etc.). In the present study we have focused our efforts on quantifying wet atmospheric loading since accurately determining the amount of dry deposition in the Sierra Nevada is nearly impossible.

Wet deposition was divided into two classes based on the timing and form (rain or snow) of the precipitation. Precipitation that occurred during the months of December through ~May was classified as snow deposition and is listed under snow in the data tables. Snow and rain that fell during the period of ~June through November was classified as non-winter precipitation and is listed under rain in the tables. Exceptions to these rules were rain events in May which were classified as non-winter precipitation and large snow-events in November that were classified as snow deposition. The logic behind the exceptions was that precipitation that falls as snow during large storms in May and November is chemically similar to winter snow. Conversely, rain that falls during May and November is chemically similar to summer and autumn rain. This classification scheme is less complicated than the one used in our report on wet deposition in alpine areas in the Sierra Nevada (Melack et al. 1997) and makes it somewhat easier to construct solute balances. It should also be noted that solute loading in the present study was computed on a water year of October 1 through September 30 while the water year in Melack et al. (1997) runs from November 1 through October 30.

Non-winter and winter solute loading was calculated by multiplying volume-weighted mean (VWM) solute concentrations by the amount of precipitation and then normalizing the product to watershed area:

$$L = (C_{vwm} \times P) / A \quad (2)$$

where:

- L = non-winter or winter solute loading ( $\text{Eq ha}^{-1}$ ),
- $C_{\text{vwm}}$  = VWM solute concentration in non-winter or winter precipitation ( $\text{Eq m}^{-3}$ ),
- P = volume of non-winter or winter precipitation deposited in catchment ( $\text{m}^3$ ), and
- A = area of catchment (ha).

Annual solute loading was calculated as the sum of loading from non-winter and winter periods. In Equation (2), P is computed by multiplying precipitation depth (expressed in meters) by the area of the catchment (expressed in square meters). Calculations of solute loadings are simple computationally, however, because of gaps in data records, accounting for all deposition is problematic.

The spring snowpack integrates both wet and dry deposition during the period of December through March and yields an accurate measure of total solute loading during the winter (Berg et al. 1986). Snowpacks were sampled at all catchments during all years of the study, however, during the transitions between spring snow-surveys and operation of the rain collectors/gauges (April, May and November) some storms not measured. In order to more accurately estimate water flux into the catchments, data from nearby weather stations or study catchments were used to fill in any gaps in the precipitation records. Table III-1 summarizes the locations of rain gauges and collectors (both primary and alternate) used and the source for precipitation data (quantity and/or chemistry) during the transition months of April, May and November.

Filling in gaps in the precipitation record for a catchment was just the first step in estimating solute loading during these gaps. The chemical composition of the precipitation had to be extrapolated from an alternate station (e.g., Emerald Lake, Mammoth Mountain or Alpine Meadows which were equipped with rain collectors) or estimated in some other way. For missing non-winter precipitation (June through October), chemistry and, if needed, quantity from the alternate stations were used to calculate solute loading for the gaps. If chemistry was unavailable from the alternate station then the VWM chemistry of non-winter precipitation from the original station (computed from the subset of events sampled) was used. Table III-2 summarizes the amount of unsampled non-winter precipitation included in the solute balances for each catchment during water years 1990 through 1994. Lost Lake is not included in the table because no nearby station existed and no extrapolations of rain or snow were done. In most cases, no extrapolation of rain chemistry was required, however problems with equipment and logistics did result in the need for sizable extrapolations at Ruby and Spuller lakes. Extrapolations of rain chemistry were also considerable during water year 1990 because the rain-collector network was not installed until the summer of 1990.

Typically, VWM chemistry from the same catchment was used to fill gaps in the non-winter precipitation record. There were only 4 instances when chemistry data were extrapolated from an alternate station. Due to collector malfunction, two storms were not sampled at Emerald Lake during water year 1992 and chemistry data from a collector operated at the Mini-catchments was used. The two storms comprised 3% of non-winter precipitation at Emerald Lake during 1992. Another extrapolation was used to determine ammonium for a trace rain-event at the Eastern Brook Lake station during 1992 (this station was used for rain chemistry at Ruby Lake). Ammonium concentration from a rain sample on the same date at Mammoth Mountain station was used. The final case of

chemistry extrapolation occurred at Spuller Lake in 1994 when a significant rain event went unsampled. Chemistry for this storm, which contributed 35% of all non-winter solute loading in water year 1994, was extrapolated from the Mammoth Mountain station.

Chemistry for unsampled snow that fell in November, April or May was assumed to equal the volume-weighted mean concentration of the catchment snowpack (as sampled during the spring snow survey). Conversely, if unsampled precipitation during these months fell as rain and no chemistry was available from a nearby station, the volume-weighted mean concentration of non-winter precipitation for that catchment was used. Table III-2 summarizes the amount of unsampled snow in each catchment from water year 1990 through 1994. Of the eight catchments, only at Emerald Lake were storms that occurred in April, May and November routinely sampled. At this station snowboards were deployed and shallow snowpits were dug after storms to sample new snow. Also, operation of the Aerochemetrics collector began earlier and ended later than at the other catchments. In most cases, loading of solutes during these months was estimated from precipitation quantity measured at some nearby location and the volume-weighted mean chemistry of winter or non-winter precipitation measured at each catchment. With the exception of water year 1994 at Emerald and Spuller lakes, where sizable spring storms went unsampled for chemistry (SWE was determined), extrapolations of snow chemistry represented less than 10% of annual winter precipitation (Table III-2).

### **3.2.3. Solute Exports**

Solute losses from the catchment were determined by accurate gauging of the outflow stream and intensive monitoring of stream chemistry during the snowmelt period. Outflow discharge was measured hourly at the automated gauging stations located in each catchment. When gaps in these records occurred (due to equipment malfunction), discharge was estimated by either of two methods. The first, linear interpolation, was used when the gap was of relatively short duration, i.e., a few hours. The linear interpolation used the last known discharge before and the first known discharge after the gap. For longer gaps ( $\geq 1$  day), hourly discharge measurements immediately before and after the gap were regressed against discharge at a nearby catchment for the same period. Regression equations were used to estimate the missing data from discharge measured at the nearby station. The technique successfully filled large gaps since there is a high degree of correlation ( $r^2 > 0.9$ ) between discharge in adjacent catchments. These estimation techniques were used infrequently since data capture at all stations was greater than 95%. Data capture during snowmelt runoff was nearly 100% and large gaps were confined to non-snowmelt periods because the watersheds were not visited as frequently during these periods.

Prior to 1990, the outflow from the study catchments (with the exception of Emerald Lake) was not sampled at sufficient frequency during snowmelt to accurately measure annual solute exports (Table III-3). Beginning in water year 1990, outflow chemistry during the snowmelt period was sampled more intensively. For the snowmelt period (March through August) the number of outflow samples collected at each catchment ranged from 7 to 18. With the introduction of automated stream-samplers (ISCO model 2900) the number of samples that could be collected increased considerably. During 1993 and 1994, 95 and 82 samples, respectively, were collected from the outflow

at Emerald Lake. These totals include ~ 50 samples collected during the peak runoff months of May and June. In contrast, the next most intensive sampling of the Emerald Lake outflow occurred in 1986 and 1987 when 21 and 27 samples, respectively, were collected. Of these totals only 8 to 10 samples were collected the peak runoff months. Solute balances for Emerald Lake during 1993 and 1994 represent the most detailed input-output budgets measured for a high elevation catchment in the Sierra Nevada.

Annual solute export  $E_A$  was calculated as the product of outflow discharge and VWM solute concentration:

$$E_A = (C_{vwm} \times Q_A) / A \quad (3)$$

where:

$E_A$  = annual solute export (Eq ha<sup>-1</sup>),

$C_{vwm}$  = annual VWM solute concentration in outflow (Eq m<sup>-3</sup>),

$Q_A$  = volume of annual outflow discharge (m<sup>3</sup>), and

$A$  = area of catchment (ha).

No attempt was made to interpolate stream chemistry between sampling dates because, during snowmelt runoff, day to day variations in stream chemistry were usually small. In addition, simple linear interpolation ignores changes in hydrologic conditions (rain events, sharp increases or decreases in discharge) and does not appreciably improve the accuracy of the solute balances. Discharge-dependent interpolation is useful for storm-dominated catchments (see Lesack 1993) but were not warranted for the present study since storm flow contributes a negligible amount of runoff from Sierran catchments.

#### 3.2.4. Solute Yields

Solute loading and outflow losses were computed using Equations (2) and (3) and annual watershed solute yield ( $Y_A$ ) was computed as:

$$Y_A = (E_A - L_A) \quad (4)$$

where:

$E_A$  = the annual flux of dissolved constituents in outflow discharge (from Equation 3), and

$L_A$  = is the annual solute loading (calculated as the sum of winter and non-winter solute loading which were computed separately using Equation 2)

Yields are expressed in equivalents per hectare of catchment area (Eq ha<sup>-1</sup> yr<sup>-1</sup>). Solute yields greater than zero mean that losses exceeded inputs and the catchment is a source for that particular solute. Conversely, yields less than zero indicate that inputs exceeded losses and that the watershed is a net sink. Yields near zero indicate the solute behaves conservatively with respect to watershed processes. Fluxes were normalized to catchment area so that comparisons could more easily be made among the eight study sites which varied in area by nearly in order of magnitude.

### 3.3. Results and Discussion

#### 3.3.1. Precipitation and Outflow Chemistry

Volume-weighted mean (VWM) chemistry was calculated for each component of the solute balance in all catchments. These components include non-winter precipitation, winter snowfall, annual precipitation (sum of winter and non-winter precipitation) and outflow

In the following section we will describe the VWM chemistry of solute balance components and attempt to compare and contrast these data across study sites and years. Both statistical and non-statistical comparisons are included. In the case of non-winter precipitation, we make non-statistical comparisons because: (1) some sites share non-winter precipitation chemistry (e.g., Emerald, Pear and Topaz lakes) and (2) annual non-winter precipitation is highly influenced by the mix of spring/summer/autumn storms, making year to year comparisons spurious. Thus, statistical tests among study sites and among years was inappropriate for non-winter precipitation. Instead, the standard errors (SE) of the volume-weighted means (shown in parentheses in Tables III-6 through III-13) were used as the basis for comparisons among years and between solutes when appropriate (see Section 3.3.4.). If a mean  $\pm 2$  SE did not overlap another mean  $\pm 2$  SE then the means were assumed to be different;  $\pm 2$  SE is a reasonable approximation of the 95% confidence interval for a sample size  $> 15$  (Sokal and Rohlf 1981).

In the case of inter-station and inter-year comparisons of winter precipitation and outflow chemistry, more rigorous statistical tests were used (see Tables III-4 and III-5). Testing for station-to-station differences was not done on an annual basis, but instead all years of data were combined for the analysis. Likewise, station data were combined when testing for inter-annual differences. In both cases data analyses were restricted to the seven lake-basins for water years 1990 through 1993; 1994 data were unavailable at most sites and only data from 1993 and 1994 were available for the Marble Fork. An one-way ANOVA was used to determine if statistically significant ( $p < 0.05$  unless otherwise indicated) differences in VWM chemistry existed among the catchments. If significant differences were found, a multiple-comparisons test (Student-Newman-Keuls method) was used to isolate the differences. Occasionally, the data did not conform to a normal distribution and a non-parametric ANOVA on ranks was used to determine significant differences ( $p < 0.05$ ). In the following sections, statistically tested differences are explicitly identified and all other differences should be assumed to be of a non-statistical nature.

##### 3.3.1.1. Emerald Lake Watershed

Volume-weighted mean concentrations for the solute balance components were calculated for water years 1985 through 1994 at Emerald Lake watershed (Table III-4). Data are omitted for 1988 and 1989 when gauging of the outflow was interrupted and non-winter precipitation records were incomplete. Also missing are organic anion data from earlier years of the project (1985 through 1990) when these constituents were not routinely measured in precipitation.

At Emerald Lake the two classes of precipitation had very different chemistry (Table III-4). In most cases, solute concentrations in winter precipitation were

significantly lower ( $p < 0.05$ ) than in non-winter precipitation, reflecting the dilute nature of snowfall in the Sierra Nevada and high concentrations of solutes in summer rain (Melack et al. 1997). Annual VWM pH ranged from 4.7 to 5.5 for non-winter precipitation and from 5.3 to 5.6 for winter snow (Table III-4). Nitrate and ammonium were found in relatively high concentrations in both winter and non-winter precipitation. VWM ammonium ranged from 6.0 to 67  $\mu\text{Eq L}^{-1}$  in non-winter precipitation and from 0.9 to 4.6  $\mu\text{Eq L}^{-1}$  in winter snowfall. The VWM concentration of nitrate in precipitation varied from 5.4 to 45.8  $\mu\text{Eq L}^{-1}$  in non-winter periods and from 1.7 to 4.2  $\mu\text{Eq L}^{-1}$  in winter. Similarly, VWM sulfate concentrations ranged from 4.1 to 39.8  $\mu\text{Eq L}^{-1}$  in non-winter precipitation and from 1.2 to 3.0 in the winter. Concentrations of organic anions (acetate and formate) were typically ca. 0.5 to 1.0  $\mu\text{Eq L}^{-1}$  in winter snow and ranged from 2.1 to 19.6 for non-winter periods. Formate usually exceeded acetate in non-winter precipitation; levels of the organic anions were similar in winter snowfall. Other important solutes in Sierran precipitation were calcium and sodium. Levels of magnesium and potassium were low.

The wide range of VWM chemistry for non-winter precipitation at Emerald Lake (and at the other stations as well) is caused by large interannual variability in the quantity and timing of deposition. Summer rain in the Sierra Nevada can have solute concentrations from 2 to 10 times greater than in spring or autumn snowfall (Melack et al. 1997). Thus, for any year the VWM chemistry of non-winter precipitation depends on a mixture of rainstorms (usually summer and autumn) and snowstorms (usually spring and autumn). In a year with relatively abundant summer rain, the VWM solute concentrations for non-winter precipitation will be higher than in a year with little summer precipitation.

In contrast to precipitation, the annual VWM chemistry for the Emerald Lake outflow varied relatively little (Table III-6). The volume-weighted mean pH varied from 5.8 to 6.2. Nitrogen levels in stream discharge were significantly lower ( $p < 0.05$ ) than in non-winter precipitation and significantly higher ( $p < 0.05$ ) than in winter snow. Annual VWM ammonium levels were ca. 0.5  $\mu\text{Eq L}^{-1}$  and nitrate ranged from 3.6 to 6.8  $\mu\text{Eq L}^{-1}$ . It is noteworthy that the VWM nitrate concentrations for 1993 and 1994, the two years with the most outflow chemistry samples (and perhaps the most accurate VWM chemistry), were nearly identical (4.6 and 4.8  $\mu\text{Eq L}^{-1}$  respectively) despite the fact that precipitation was nearly three times greater in 1993. A high degree of similarity between these years was also seen in the VWM concentrations of ANC, chloride, sulfate, base cations (calcium, magnesium, sodium and potassium) and silica (Table III-2).

For the 8 years with data, annual VWM sulfate concentrations varied from 5.3 to 7.0  $\mu\text{Eq L}^{-1}$  in outflow from the Emerald Lake watershed (Table III-4). Calcium and silicate levels were also fairly consistent, ranging from 17.2 to 24.9  $\mu\text{Eq L}^{-1}$  and 26.3 to 36.2  $\mu\text{M}$ , respectively. For the other cations, annual VWM concentrations were about 3  $\mu\text{Eq L}^{-1}$  for magnesium and potassium and ca. 11  $\mu\text{Eq L}^{-1}$  for sodium. Acid neutralizing capacity (ANC) of the outflow from the watershed was in the range of 20 to 30  $\mu\text{Eq L}^{-1}$  on an annual basis.

### 3.3.1.2. Pear Lake Watershed

Winter snowfall at Pear Lake had pH in the range of 5.4 to 5.5 (Table III-7) and hydrogen-ion was usually the dominant ion in solution. VWM ammonium in winter

precipitation varied from 1.9 to 4.1  $\mu\text{Eq L}^{-1}$  during water years 1990 through 1993 and nitrate concentrations ranged from 1.6 to 2.9  $\mu\text{Eq L}^{-1}$ . Sulfate levels were similar to nitrate and varied from 1.7 to 2.7  $\mu\text{Eq L}^{-1}$ . The annual VWM concentration of most base cations was less than 1.0  $\mu\text{Eq L}^{-1}$ . Organic anions were found in low concentrations during all four winters. Non-winter precipitation chemistry at Pear Lake was from the Emerald Lake watershed.

The annual VWM pH of the Pear Lake outlet, 5.8 to 6.1, was the second lowest of the seven headwater catchments (Table III-7). The average of VWM ANC for the four years of study was 21.1  $\mu\text{Eq L}^{-1}$  and, overall, ANC in the Pear Lake outflow was significantly ( $p < 0.05$ ) lower than at Topaz Lake and the eastern Sierra catchments. Nitrate levels varied from 2.7 to 6.1  $\mu\text{Eq L}^{-1}$  and sulfate concentrations were in the range of 5.5 to 6.5  $\mu\text{Eq L}^{-1}$ . These values are similar to those measured at Emerald Lake which is not surprising given the close proximity and similarity between the two catchments. However, the Pear Lake outflow had significantly ( $p < 0.05$ ) lower sodium and silicate concentrations compared to the Emerald Lake outflow. The most abundant cation in solution at Pear Lake was calcium (ca. 17  $\mu\text{Eq L}^{-1}$ ) followed by sodium (ca. 9  $\mu\text{Eq L}^{-1}$ ); magnesium and potassium values were on the order of 3  $\mu\text{Eq L}^{-1}$ . The concentration of dissolved silica ranged from 15.4 to 23.0  $\mu\text{M}$  on an annual basis.

### **3.3.1.3. Topaz Lake Watershed**

Non-winter precipitation chemistry used at Topaz Lake was also assumed to be the same as at Emerald Lake, although the rainfall quantity used for solute balance calculations was derived from a tipping bucket raingauge located at Topaz Lake. Winter precipitation chemistry was measured in snowpits dug in the Topaz catchment (Table III-8). For the period of 1990 through 1993 the annual VWM pH of winter snowfall at Topaz Lake ranged from 5.4 to 5.5. The next most abundant ion in snowfall at Topaz was ammonium (range: 2.0 to 3.2  $\mu\text{Eq L}^{-1}$ ) followed by nitrate and sulfate (ca. 1.5 to 2.5  $\mu\text{Eq L}^{-1}$ ). With the exception of calcium, base cation and organic anion levels were typically near the detection limit during most years. Overall, snow chemistry in the Topaz Lake basin was similar to most high elevation areas of the Sierra Nevada (Melack et al. 1997).

Annual VWM chemistry in the outlet of Topaz Lake was different from other sites in the Tokopah Valley (Table III-8). Annual pH was slightly higher (in the range of 6.1 to 6.2) for the four years of study and ANC was significantly ( $p < 0.05$ ) greater (ca. 50%) than at Emerald and Pear lakes (four year average, 37.9  $\mu\text{Eq L}^{-1}$ ). Most of the base cations and silicate were also significantly ( $p < 0.05$ ) higher at Topaz than at Emerald or Pear lakes (Table III-4). In contrast, sulfate levels were similar among these catchments, ranging from 4.6 to 6.0  $\mu\text{Eq L}^{-1}$ . Dissolved silica levels in the outlet stream to Topaz Lake were in the range of 25 to 30  $\mu\text{M}$  on an annual basis except during water year 1990 when the VWM concentration was 42.1  $\mu\text{M}$ . VWM nitrate concentration in the outlet of Topaz Lake was significantly lower ( $p < 0.05$ ) than in Emerald and Pear lake outflows; lower nitrate in Topaz outflow is probably caused by higher uptake of nitrogen in Topaz Lake where phytoplankton productivity has been found to be limited by the availability of nitrogen (Sickman and Melack unpublished). In contrast, nitrogen limitation in Emerald Lake is much less common than phosphorus limitation (Sickman 1991) resulting in higher nitrate concentrations in the outflow. It should be noted, however, that transient episodes

with high nitrate concentrations (i.e.,  $> 20 \mu\text{Eq L}^{-1}$ ) have been observed in Topaz Lake and its outflow under low-flow conditions in late summer and autumn (Figure I-106).

#### **3.3.1.4. Marble Fork of the Kaweah**

The VWM chemistry of winter and non-winter precipitation in the Marble Fork drainage was assumed to equal that measured at Emerald Lake. During snowmelt, outflow chemistry was determined from samples collected on a weekly to biweekly basis in 1993 and every 24 to 48 hours using an automated sampler in 1994.. Annual VWM pH in the Marble Fork during the two years of study ranged from 6.1 to 6.4 with an ANC of ca.  $32 \mu\text{Eq L}^{-1}$ . Nitrate varied from 2.1 to  $2.7 \mu\text{Eq L}^{-1}$  and sulfate concentrations were between 7 and  $9 \mu\text{Eq L}^{-1}$ . Base cation and dissolved silica concentrations in the Marble Fork were similar to those in the outlets to the other Tokopah Valley catchments: calcium, 22.6 to  $25.3 \mu\text{Eq L}^{-1}$ ; sodium, 10.4 to  $12.3 \mu\text{Eq L}^{-1}$ ; magnesium and potassium, 3.1 to  $3.6 \mu\text{Eq L}^{-1}$ ; silicate, 30.8 to  $37.1 \mu\text{M}$ .

VWM stream chemistry of the Marble Fork river was fairly similar to that of the Topaz Lake outflow, but had slightly higher solute concentrations than the Emerald and Pear Lake outflows. Together these three subcatchments comprise less than 25% of the Marble Fork drainage. This suggests that stream chemistry is relatively heterogeneous in the Tokopah Valley and that the biogeochemical controls on surface water chemistry may not act uniformly over the area. This result is surprising given the relatively simple granodiorite geology of the Marble Fork basin and the similarity and uniformity of its soils and vegetation (Moore and Sisson 1987, Appendix One). As discussed in Chapter One, stream chemistry in the Marble Fork diverges from that of the three headwater basins mainly during baseflow periods in the late summer and autumn when river-flow is being supplied by groundwater and not melting snow.

#### **3.3.1.5. Crystal Lake Watershed**

In contrast to the Tokopah Valley, the geology and soils of the eastern Sierra Nevada catchments are diverse and largely responsible for the wide range in stream chemistry observed in the outflows from these basins. At the Crystal Lake watershed, bedrock geology ranges from granodiorite to andesitic lava flows (Huber and Rinehart 1965). The basin is largely covered in deep soils of volcanic origin and ash from volcanic eruptions which have occurred as recently as 500 years ago. Thus, it is not surprising that stream chemistry from Crystal Lake is distinctive among the catchments in our study (Table III-4). Outflow pH ranged from 6.0 to 6.3 during the four years of study (Table III-10). The VWM ANC of the outlet stream ranged from 61.4 to  $73.1 \mu\text{Eq L}^{-1}$ , and was significantly higher ( $p < 0.05$ ) than at any of the other study catchments. Silicate concentrations (ca.  $60\text{-}70 \mu\text{Eq L}^{-1}$ ) in outflow from Crystal Lake were also significantly greater ( $p < 0.05$ ) than at all other sites.

Despite higher concentrations of ANC and silicate in the Crystal Lake outflow, sulfate levels were similar to or significantly ( $p < 0.05$ ) lower than concentrations measured at other catchments (ca.  $6\text{-}7 \mu\text{Eq L}^{-1}$ , Table III-10). In contrast, concentrations of magnesium and potassium were significantly ( $p < 0.05$ ) greater in the Crystal outflow than at all other catchments. With the exception of Ruby and Spuller lakes, calcium in outflow from Crystal Lake was also significantly ( $p < 0.05$ ) greater than at other sites. In contrast

to other sites, outflow from Crystal Lake was enriched with sodium in relation to calcium; mean VWM concentrations of calcium and sodium for the four years of study were 35.2 and 21.1  $\mu\text{Eq L}^{-1}$ , respectively, and showed little difference from year to year (Table III-10). As an indication of the nitrogen-limited conditions of phytoplankton in the lake, VWM nitrate concentrations, in Crystal Lake and its outlet, were near the detection limit even though nitrate was found in concentrations up to 10  $\mu\text{Eq L}^{-1}$  in inflowing waters to the lake during snowmelt.

Snow chemistry and quantity were determined from catchment snow surveys. Winter snowfall collected during these surveys had, with two exceptions, VWM chemistry similar to snowfall at the other basins (Table III-10). VWM pH of snow ranged from 5.3 to 5.5. During most years, ammonium was the next most abundant solute (after hydrogen-ion) in winter snowfall with levels from 1.7 to 5.5  $\mu\text{Eq L}^{-1}$ . VWM nitrate and sulfate ranged from about 1.5 to 3.5  $\mu\text{Eq L}^{-1}$ . Other cations and organic anions were found in concentrations of less than 1 or 2  $\mu\text{Eq L}^{-1}$ .

Compared with the other catchments, snow at the Crystal Lake watershed had significantly ( $p < 0.05$ ) higher concentrations of sulfate and magnesium ( $p < 0.1$  and  $p < 0.05$ , respectively) than at the other lake basins (Table III-5). This is consistent with findings in Melack et al. (1997), that sulfate levels in snow at Mammoth Mountain were significantly ( $p < 0.05$ ) higher than at other stations in the Sierra Nevada. At Mammoth Mountain we attributed higher sulfate concentrations to anthropogenic sources, but the results from Crystal Lake suggest there may be a source of wind-blown gypsum (either natural or man-made) in the Mammoth Lakes area.

Non-winter precipitation chemistry for the Crystal Lake basin was extrapolated from the Mammoth Mountain wet-deposition station operated by UCSB. This station is located about 5 km north of the lake at the Mid-Chalet complex in the Mammoth ski-area. Precipitation quantity during June through October, was measured with a tipping bucket raingauge located in the Crystal Lake watershed. Ammonium, nitrate and sulfate concentrations were, on an annual basis, 5 to 10 times greater in non-winter precipitation at Crystal Lake compared to winter snowfall (Table III-10). In non-winter precipitation, VWM concentrations of the nitrogen species ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) ranged from 11.0 to 29.0  $\mu\text{Eq L}^{-1}$  and sulfate averaged about 15.5  $\mu\text{Eq L}^{-1}$ . Base cation concentrations in non-winter precipitation ranged as follows: calcium, 3.1 to 11.6  $\mu\text{Eq L}^{-1}$ ; sodium, 1.3 to 9.1  $\mu\text{Eq L}^{-1}$ ; magnesium 0.8 to 2.2  $\mu\text{Eq L}^{-1}$ ; potassium, 0.6 to 2.0  $\mu\text{Eq L}^{-1}$ . VWM acetate and formate concentrations varied from year to year and ranged in concentration from 2.0 to 15.4  $\mu\text{Eq L}^{-1}$ .

#### **3.3.1.6. Ruby Lake Watershed**

Snow chemistry in the Ruby Lake basin was found to be similar to other sites in the Sierra Nevada (Table III-11). VWM pH varied from 5.3 to 5.6. Ammonium values ranged from a low of 1.2  $\mu\text{M}$  in 1993 to a high of 4.0  $\mu\text{M}$  in water year 1994. Nitrate and sulfate had mean concentrations of 2.4 and 1.9  $\mu\text{Eq L}^{-1}$  respectively. VWM nitrate concentrations in winter snowfall exceeded sulfate levels in all but one year (1993). Base cation concentrations ranged from 0.5 to 2.0  $\mu\text{Eq L}^{-1}$  with calcium and sodium the dominant ions. Organic anion levels were usually at or near the detection limit (i.e., less than 0.5  $\mu\text{Eq L}^{-1}$ ).

Non-winter chemistry for the Ruby Lake watershed was obtained from Eastern Brook Lake, a station in the wet deposition monitoring network operated by UCSB (Melack et al. 1997), located four kilometers down-canyon from Ruby Lake (collector elevation: 3,170 m). The collector was mounted on a platform, approximately 7 meters above the ground in a small forest clearing. Because of logistics, few late season (generally more dilute) storms were sampled. Consequently, the non-winter precipitation had higher solute concentrations than stations with more complete seasons (i.e., Tokopah Valley sites, Crystal Lake). Water year 1993, when a paucity of summer rain caused VWM chemistry of non-winter precipitation to be more dilute, was an exception.

The VWM pH of non-winter precipitation at Ruby Lake varied from 4.7 to 5.2 (Table III-11). Ammonium and nitrate were found in concentrations from about 8  $\mu\text{Eq L}^{-1}$  (1993) up to 25 or 35  $\mu\text{Eq L}^{-1}$ . VWM sulfate varied from 8.3 to 23.0  $\mu\text{Eq L}^{-1}$ . Cation concentrations were similar to those at other stations. Average VWM concentrations for calcium, magnesium, sodium and potassium were: 12.3  $\mu\text{Eq L}^{-1}$ , 2.1  $\mu\text{Eq L}^{-1}$ , 3.2  $\mu\text{Eq L}^{-1}$ , and 1.3  $\mu\text{Eq L}^{-1}$  respectively. Organic anions (acetate and formate) had modest concentrations, on an annual basis, which varied from about 2 to over 13  $\mu\text{Eq L}^{-1}$ .

The outflow from Ruby Lake had significantly ( $p < 0.05$ ) higher ANC, calcium and sulfate than outflow from catchments in Sequoia N.P. (Table III-4). VWM sulfate concentrations (range, 9.3 to 12.1  $\mu\text{Eq L}^{-1}$ ) were significantly ( $p < 0.05$ ) higher at Ruby Lake than at all other catchments except Spuller Lake. In addition, a clear upward trend in sulfate levels, in both the lake and outflow, were observed during 1986 through 1994. This increase, over a period of 8 years, amounted to an approximate doubling of sulfate concentrations in the outflow stream. In 1987 levels of ca. 6.0  $\mu\text{Eq L}^{-1}$  were typical, but by 1994 concentrations had risen to 12 to 14  $\mu\text{Eq L}^{-1}$ . This finding is discussed in more detail in Chapter One.

At Ruby outflow, VWM ANC was second only to Crystal Lake (Table III-4) and varied from 49.4 to 56.9  $\mu\text{Eq L}^{-1}$ . Calcium was significantly greater ( $p < 0.05$ ) than at all other catchments including Crystal Lake. Calcium concentrations in the Ruby Lake outflow were similar to ANC, ranging from 45 to 50  $\mu\text{Eq L}^{-1}$ . Sodium concentrations were one quarter as large as calcium. Magnesium and potassium were measured at similarly low levels (ca.  $\leq 5 \mu\text{Eq L}^{-1}$ ). VWM silicate varied from 34.9 to 42.1  $\mu\text{M}$  during water years 1990 through 1994. Nitrogen limitation of phytoplankton does not appear to be as severe in Ruby Lake as compared to other lakes as evidenced by the modest to high levels (i.e., 3 to 5  $\mu\text{Eq L}^{-1}$ ) of nitrate in outflowing waters during most years. The annual VWM pH of the outflow ranged from 6.0 to 6.7.

### 3.3.1.7. Spuller Lake

Spuller Lake was another catchment where relatively high concentrations of sulfate were observed (Table III-12). VWM sulfate ranged from 8.3 to 12.0  $\mu\text{Eq L}^{-1}$  and sulfate levels at Spuller Lake were significantly ( $p < 0.05$ ) greater than at all but Ruby Lake (Table III-4). Similarly, ANC and calcium concentrations were significantly ( $p < 0.05$ ) higher at Spuller Lake than at all sites other than Crystal and Ruby. There was a congruence between calcium and ANC in the outflow to Spuller Lake: means for both constituents were in the range of ca. 35 to 45  $\mu\text{Eq L}^{-1}$ . VWM sodium, magnesium and potassium ranged from 9.7 to 12.3  $\mu\text{Eq L}^{-1}$ , 3.8 to 5.1  $\mu\text{Eq L}^{-1}$  and 2.8 to 3.7  $\mu\text{Eq L}^{-1}$  respectively.

VWM nitrate levels were modest to high (2.6 to 5.5  $\mu\text{Eq L}^{-1}$ ) during the five years of record and the VWM pH varied from 6.0 to 6.7.

There was little to distinguish winter precipitation chemistry at Spuller Lake watershed from the other catchments (Table III-12). Volume-weighted mean pH varied from 5.3 to 5.5 during the five years of record. Levels of ammonium, nitrate and sulfate were in the range of 1 to 3  $\mu\text{Eq L}^{-1}$ . Calcium and sodium were the most abundant base cations in solution with VWM concentrations typically in the range of 1 to 2  $\mu\text{Eq L}^{-1}$ . Mean magnesium and potassium levels were ca. 0.3 to 1.0  $\mu\text{Eq L}^{-1}$ . Acetate and formate were found in concentrations at or near the detection limit.

Non-winter precipitation chemistry at Spuller Lake was extrapolated from Tioga Pass. This station, part of the deposition monitoring network operated by UCSB and CARB, was located 1.5 km north-northwest of and 138 meters lower than Spuller Lake. VWM pH varied from 4.4 to 4.7 (Table III-12). VWM ammonium and nitrate levels in non-winter precipitation were high with values typically greater than 20  $\mu\text{Eq L}^{-1}$ . Ammonium concentrations exceeded nitrate levels in three of the five years. Sulfate concentrations were nearly as high as nitrate and ammonium with an average VWM concentration of 18.6  $\mu\text{Eq L}^{-1}$ . As was typical of non-winter precipitation during the study, calcium and sodium were the dominant base cations with VWM values of 3 to 13  $\mu\text{Eq L}^{-1}$ . VWM potassium and magnesium concentrations were ca. 2 to 3  $\mu\text{Eq L}^{-1}$ . Acetate and formate were found in modest to high concentrations in non-winter precipitation at Spuller Lake; VWM acetate ranged from 8.3 to 20.6  $\mu\text{Eq L}^{-1}$  and typically exceeded formate levels (VWM concentration range, 4.8 to 13.2  $\mu\text{Eq L}^{-1}$ ).

#### **3.3.1.8. Lost Lake Watershed**

On the basis of VWM pH and ANC, Lost Lake may have the greatest sensitivity to acid deposition among the eight study sites (Table III-13). VWM pH was less than 6.0 during all four years and was only 5.6 in water year 1992. Similarly, VWM ANC was quite low, ranging from a high of only 26.0  $\mu\text{Eq L}^{-1}$  in 1990 to a low of 19.6  $\mu\text{Eq L}^{-1}$  during 1993. These ANC levels were the second lowest among the eight catchments; only Pear Lake watershed had lower VWM ANC. ANC at Lost Lake was significantly ( $p < 0.05$ ) lower than at the eastern Sierra catchments and at Topaz Lake (Table III-4). Most other chemical constituents were present in concentrations similar to catchments in Sequoia National Park. VWM sulfate levels in the outflow to Lost Lake varied from 5.3 to 6.9  $\mu\text{Eq L}^{-1}$ , similar to those found in the other watersheds, with the exception of Ruby and Spuller lakes. Nitrate concentrations were similar to those found in other nitrogen limited systems (i.e., Crystal and Topaz lakes) and ranged from 0.5 to 0.7  $\mu\text{Eq L}^{-1}$ . Calcium was the major cation in solution (mean concentration, 17.3  $\mu\text{Eq L}^{-1}$ ) followed by sodium (mean, 8.7  $\mu\text{Eq L}^{-1}$ ) and then magnesium and potassium (range ca. 2 to 4  $\mu\text{Eq L}^{-1}$ ). Silicate concentrations were similar to ANC, ranging from 18.9 to 31.7  $\mu\text{M}$ .

Non-winter precipitation chemistry was extrapolated from Angora Lake, site of a deposition monitoring station operated by UCSB and CARB. Angora Lake is located about 3 km west and 189 meters lower than Lost Lake. The VWM pH of non-winter precipitation at Lost Lake ranged from 4.8 to 5.7 (Table III-13). The wide range in pH was caused by the variable mix of storms received in any year. Years with frequent, solute rich summer rain, had lower pH. Volume-weighted mean concentrations of nitrate and

ammonium were high in non-winter precipitation at Lost Lake (Table III-13). Values ranged from 10.1 to 26.5  $\mu\text{Eq L}^{-1}$ , with nitrate exceeding ammonium in three out of four years. VWM sulfate ranged from 13.2 to 18.2  $\mu\text{Eq L}^{-1}$ . Calcium and sodium were the major base cations in non-winter precipitation at this site with values of 7.1 to 13.2  $\mu\text{Eq L}^{-1}$  and 3.3 to 7.0  $\mu\text{Eq L}^{-1}$  respectively. VWM potassium and magnesium concentrations were between 1 to 4  $\mu\text{Eq L}^{-1}$ . Organic anion were an important component of non-winter precipitation at Lost Lake; mean ranged from about 4 to 20  $\mu\text{Eq L}^{-1}$ .

### 3.3.2. Average Precipitation and Outflow Chemistry

In previous sections, winter and non-winter precipitation and outflow chemistry were discussed on a site-by-site basis. However, it is useful to combine the data from all the study sites in order to characterize precipitation and surface water conditions in the Sierra Nevada. Therefore, the annual VWM chemistry of snow, non-winter precipitation and outflow from all catchments (presented Tables III-6 through III-13) were averaged and presented in Tables III-14 through III-17. Included in the tables are the range of measured volume-weighted means and coefficient of variation (CV) for the volume-weighted means for each solute.

#### 3.3.2.1. Winter Snow

Snow in the Sierra Nevada is a dilute solution of hydrogen-ion, ammonium, nitrate and sulfate (Table III-14). Cations in solution total 10.5  $\mu\text{Eq L}^{-1}$  and are only partially balanced by measured anions of 7.2  $\mu\text{Eq L}^{-1}$ . We attribute this imbalance to an unmeasured anion, most likely bicarbonate (see Melack et al. 1997). Potassium and the organic anions were the most variable solutes in snow (using CV as an index), probably because of concentrations near the detection limits. The least variable solute was hydrogen-ion and, for the 5 calendar-years of record, mean pH of snow was 5.42 (range, 5.57-5.25). Average nitrate concentrations in snow (2.4  $\mu\text{Eq L}^{-1}$ ) exceeded sulfate (2.0  $\mu\text{Eq L}^{-1}$ ) by 20%. After hydrogen-ion and ammonium, the next most abundant cations were calcium and sodium; the average calcium concentration in Sierran snow was about 30% greater than the average sodium level. The average winter snowfall for the 36 water years of record (i.e., 1985 through 1994) was 1027 mm.

Using data from the seven lake-basins we tested for year-to-year differences in annual VWM snow chemistry using the approach described in Section 3.3.1. Only a few statistically significant differences in snow chemistry were detected between water years from 1990 through 1993 (Table III-18). Hydrogen-ion was significantly ( $p < 0.05$ ) greater during 1990 than in all other years, however, we have attributed this difference to HCl contamination of sampling equipment during 1990 (Melack et al. 1997). Acetate was significantly ( $p < 0.05$ ) greater during 1991 and formate was higher in 1990, but these findings should be viewed cautiously since organic anion levels were near the detection limit during most years. While few significant differences in chemistry were found, it should be noted that, for nearly all solutes, average concentrations were slightly lower in 1993 than in other years.

### 3.3.2.2. Non-winter Precipitation

In contrast to snow, non-winter precipitation in the Sierran Nevada, particularly rain, is relatively rich in solutes (Table III-15). It has similar primary solutes, ammonium, nitrate, sulfate and hydrogen-ion, but the concentrations of these solute is many times greater than in winter snow. Total cations and anions in solution were, respectively, 54.8 and 56.4  $\mu\text{Eq L}^{-1}$ , about 5 times greater than concentrations in snow. As a whole, the chemistry of non-winter precipitation exhibited greater variability than snow chemistry, and the solutes with the greatest coefficients of variation were ammonium, potassium and sodium. Mean pH of non-winter precipitation, from 1990 through 1994 was 4.93, and ranged from 4.59 to 5.66. The large range of non-winter precipitation chemistry is due, primarily, to the mix of storms occurring in any year, i.e., summer rains have the highest solute concentrations, autumn and spring precipitation is more dilute. These storms were small in relation to winter precipitation (Melack et al. 1997) and in total, mean non-winter precipitation represented only ~10% (117 mm) of mean annual winter deposition.

### 3.3.2.3. Annual Precipitation

Despite considerable interannual variability in precipitation chemistry and quantity, annual wet-deposition chemistry was fairly consistent from year to year and among the catchments (labeled as Loading in Tables III-6 through III-13). (The chemistry of annual wet-deposition was computed by volume-weighting chemistry from winter and non-winter periods. This is the same method used to volume-weight precipitation in the previous section). The volume-weighted mean chemistry of annual wet-deposition is summarized in Table III-16. Overall, the chemistry of annual wet-deposition is more similar to winter snowfall than non-winter precipitation because winter snowfall greatly exceeds non-winter precipitation in the Sierra Nevada. Solutes consist primarily of hydrogen-ion, compounds of nitrogen (ammonium and nitrate) and sulfate with some chloride and calcium. Together these solutes comprise 63% of all ions in solution. Other constituents like potassium, sodium, magnesium and the organic anions were found at lower concentrations. The mean annual pH for wet deposition in the study was 5.3 and ranged from 5.1 to 5.5. Ammonium and nitrate were the most abundant cation and anion in solution with mean concentrations of 5.1  $\mu\text{M}$  and 4.6  $\mu\text{Eq L}^{-1}$ , respectively. The average sulfate concentration in wet deposition was slightly lower, 3.6  $\mu\text{Eq L}^{-1}$ , and ranged from 1.8 to 9.9  $\mu\text{Eq L}^{-1}$ . The order of base cations based on concentration was calcium > sodium > potassium · magnesium. The mean concentration of acetate and formate in wet deposition was ca. 1.4  $\mu\text{Eq L}^{-1}$ . Mean annual precipitation for the study was slightly over one meter (1144 mm) of water equivalence and varied by nearly a factor of five. Using the coefficient of variation as an index, the most variable solutes (variability from year to year and site to site) in annual precipitation during the study were formate, potassium, acetate and ammonium (Table III-14); concentrations of hydrogen-ion and sulfate varied the least.

One final observation regarding precipitation chemistry should be noted. Water year 1987 at the Emerald Lake watershed had some of the highest solute concentrations and loading rates measured during our study. This is especially true for constituents such as ammonium, nitrate, sulfate, magnesium, sodium and acetate. High VWM chemistry and chemical loading during water year 1987 were caused by a series of rain events during the spring. These storms were relatively large in size and had high solute concentrations.

Typically, chemical concentrations in Sierra Nevada precipitation are inversely related to storm size (Melack et al. 1997), but during this particular spring, storms were both large and solute-rich. A comparison of solute loading per cm of non-winter precipitation illustrates the uniqueness of 1987. At Emerald Lake in 1987, the rate of ammonium deposition was  $1.47 \text{ Eq ha}^{-1} \text{ cm}^{-1}$ , three-times the mean of  $0.46 \text{ Eq ha}^{-1} \text{ cm}^{-1}$  for the period of 1990 through 1994. Large differences were also observed for nitrate ( $1.21$  vs.  $0.52 \text{ Eq ha}^{-1} \text{ cm}^{-1}$ ) and sulfate ( $0.99$  vs.  $0.37 \text{ Eq ha}^{-1} \text{ cm}^{-1}$ ). The depositional rates for rain in 1987 were, by far, the highest ever measured at Emerald Lake.

Based on 1987 it was believed that a likely scenario for acute acidification of surface waters would involve a large, dirty storm during the spring snowmelt period. The acidifying capacity of these storms would be relatively large owing to high deposition of acidulating compounds, coupled with the dilute, and relatively unbuffered condition of streams and lakes during snowmelt. However, further study of deposition patterns in the Sierra Nevada (Melack et al. 1997) has shown that large, solute rich storms during the snowmelt runoff season are uncommon. Furthermore, the ANC minimum for 1987 (ca.  $16 \mu\text{Eq L}^{-1}$ ) was similar to the minima for most other years at Emerald Lake. Thus, we believe that large, solute-rich, rain on snowmelt events are a rare phenomenon and probably pose little threat to aquatic ecosystems in the Sierra Nevada.

#### **3.3.2.4. Outflow**

The average VWM pH for outflow during the study was 6.05 and ranged from 5.6 to 6.7 (Table III-17). The pH of outflow from the Lost Lake catchments was significantly ( $p < 0.05$ ) lower than the pH at Crystal, Ruby and Spuller lakes. With respect to VWM ANC, the catchments fell into three categories: low, modest and high. Catchments in the lowest ANC category, i.e.,  $15$  to  $30 \mu\text{Eq L}^{-1}$ , were Lost Lake, Pear Lake and Emerald Lake. Watersheds with ANC in the range of  $30$  to  $50 \mu\text{Eq L}^{-1}$  would be classified as having modest ANC and would include the Topaz Lake, Spuller Lake and Marble Fork. In the high category, with greater than  $50 \mu\text{Eq L}^{-1}$  of ANC were Crystal Lake and Ruby Lake. The average VWM ANC measured in the study was  $36.2 \mu\text{Eq L}^{-1}$ .

Sulfate was the most consistent solute among the catchments and water years studied. The average VWM sulfate concentration for the eight catchments was  $7.4 \mu\text{Eq L}^{-1}$  (Table III-17). With the exception of Ruby and Spuller lakes, VWM sulfate concentrations ranged from  $\sim 5$  to  $7 \mu\text{Eq L}^{-1}$ ; Ruby and Spuller outflow had sulfate levels from  $8$  to  $10 \mu\text{Eq L}^{-1}$ . Higher sulfate concentrations at these catchments may be the result of storage and release of groundwaters and/or weathering of sulfide minerals, e.g.,  $\text{FeS}_2$ .

Nitrogen transformations within the study catchments had a large effect on the levels of ammonium and nitrate in outflowing waters. The average VWM ammonium concentration was  $0.2 \mu\text{M}$  and ranged from  $0.0$  to  $0.8 \mu\text{M}$  (Table III-17). Lake basins with predominantly nitrogen-limited phytoplankton populations, such as Crystal, Lost and to some extent Topaz, also had low levels of nitrate in outflow streams (ca.  $< 1 \mu\text{Eq L}^{-1}$ ). Other catchments had VWM nitrate concentrations of  $3$  to  $8 \mu\text{Eq L}^{-1}$  and may have phytoplankton that are limited by phosphorus or some other trace constituents during some portions of the year (Sickman and Melack unpublished, Stoddard 1987).

Base cations in surface waters of the Sierra Nevada are primarily the result of weathering of granitic minerals (Melack and Stoddard 1991). In addition, a strong

relationship between ANC and base cations in these waters demonstrates that mineral weathering is the dominant pathway for neutralization of acids in these catchments. At all eight watersheds the predominant cations in outflows were calcium and sodium (Table III-17). VWM calcium ranged from 20 to 50  $\mu\text{Eq L}^{-1}$ , with the highest levels measured in catchments in the eastern Sierra Nevada. The average VWM sodium in outflow waters was less than half that of calcium: 11.9  $\mu\text{Eq L}^{-1}$ . An exception was the Crystal outflow which was enriched with sodium and magnesium relative to calcium. The VWM concentrations in this catchment ranged from 19.4 to 22.3  $\mu\text{Eq L}^{-1}$  for sodium and were near 12  $\mu\text{Eq L}^{-1}$  for magnesium. A plot of annual VWM calcium vs VWM ANC in outflow waters (Figure III-1) shows a strong linear relationship ( $r^2$ , 0.92 without Crystal Lake data) amongst the catchments. However, when the sum of base cations (SBC) is plotted against VWM ANC, data from Crystal Lake fall close to the line defined by the other basins ( $r^2$ , 0.95;  $\text{SBC} = 1.06(\text{ANC}) + 10.4$ ) owing to greater amounts of sodium and magnesium in surface waters of the Crystal Lake basin (Figure III-1). Thus, even at Crystal Lake, VWM ANC is strongly related to the annual production of base cations from weathering reactions and suggests that, on an annual basis, weathering is the dominant neutralizing pathway in Sierran catchments.

Average VWM concentrations for magnesium and potassium were relatively low in outflow in this study. Averages mean levels were 3.7 and 4.7  $\mu\text{Eq L}^{-1}$ , respectively. Silicate is also produced from weathering of granite and VWM concentrations ranged from 15.4 to 72.9  $\mu\text{M}$  with a mean value of 34.7. Overall, the fit of a regression between ANC and silicate ( $r^2 = 0.65$ ) was not as good as for base cations which may indicate biological cycling of silicon by aquatic diatoms.

As was seen with snow chemistry, interannual differences in average VWM outflow chemistry were small (Table III-19). The only significant differences detected were lower pH during 1991 and lower chloride during 1993. However, as with snow chemistry, mean outflow solute concentrations tended to be lower during 1993 than in other years.

### 3.3.3. Solute Loadings, Exports and Yields

Fluxes of solutes into and out of the study catchments were calculated as described in Section 3.2. and presented in Tables III-20 through III-27. We will not discuss the solute fluxes from individual catchments separately, but will compare and contrast the solute balances, and describe (qualitatively and quantitatively) the chemical alterations (e.g., hydrogen-ion and nitrogen consumption, mineral weathering etc..) that occur in Sierran catchments. In the discussion, data from the complete set of catchments will be used, but we will emphasize the Emerald Lake watershed because of the larger quantity and higher quality of data from this site. Using this approach, we will attempt to describe the major biogeochemical processes controlling surface water chemistry in the Sierra Nevada and assess the relative sensitivity of the study catchments to acid deposition.

Statistical comparisons identified significant differences ( $p < 0.05$ ) in solute loadings, exports and yields among catchments and among years (Tables III-28 through III-30). These analyses were identical to those used to detect differences in VWM chemistry (described in Section 3.3.1.) with the exception that data from 1993 were not included in some of the tests because abundant snowfall during this extremely wet year

caused relatively high solute loadings and large amounts of runoff. (For the aggregate of the catchments, loading, exports and yields in 1993 were significantly greater ( $p < 0.05$ ) than during 1990 through 1992 for nearly all ions). High runoff in turn caused yields and exports for most solutes to be 2-4 times greater in 1993 than during the period of 1990 to 1992. The large differences in solute loading, exports and yields between 1993 and other years, increased the variance of the average catchment values, reducing the power of the ANOVA to identify catchment differences. By using the three years with similar snowfall and runoff, we have tried to control for the effect of precipitation which enabled us to isolate inter-catchment differences in biogeochemistry. However, we would note that the inter-catchment differences in solute exports and yield detected in the 1990-1992 data hold true, in nearly all cases, for water year 1993 as well.

### 3.3.3.1. Hydrogen-ion

The eight watersheds in this study effectively neutralized acid deposition from winter and non-winter precipitation (Figure III-2). In Figure III-2 the areal yield of hydrogen-ion is plotted as a function of areal loading. Most points fall along a line that describes total retention (i.e., neutralization) of hydrogen-ion in the basins. The average hydrogen-ion yield for 1990 through 1994 was  $-45.2 \text{ Eq ha}^{-1}$  (range:  $-18.9$  to  $-111 \text{ Eq ha}^{-1}$ , Table III-31). Annual deposition of hydrogen-ion during the study ranged from  $22.5$  to  $128 \text{ Eq ha}^{-1}$  (Table III-32). Both the upper and lower extremes of deposition were measured in the Emerald Lake catchment (Figure III-3). The greatest deposition of hydrogen-ion occurred during water year 1986 ( $128 \text{ Eq ha}^{-1}$ ) at Emerald Lake and in water year 1993 at all other catchments (1993 mean loading:  $76 \text{ Eq ha}^{-1}$ ). Overall, hydrogen-ion deposition at Emerald Lake varied by a factor of 6 during the period of 1985 through 1994 and the average annual deposition of hydrogen-ion during the study (all years and catchments) was  $51.9 \text{ Eq ha}^{-1}$  (Table III-31).

Most of the hydrogen-ion deposition in high elevation catchments of the Sierra Nevada occurs during winter months. A comparison of winter and non-winter loading of  $\text{H}^+$  during 1990 through 1993 showed that 67% to 92% of the annual deposition is from winter snowfall (Table III-33). The data in this table are from the seven headwater catchments in the present study along with stations from the UCSB wet-deposition monitoring network (Melack et al. 1997). The percentage of hydrogen-ion deposition from winter loading (including dryfall onto snow) is directly related to the quantity of snowfall, thus, hydrogen-ion deposition from non-winter periods comprised a higher percentage of annual loading during years with low winter snowfall.

Based on input-output budgets of  $\text{H}^+$ , the catchments best able to neutralize acidic inputs were Spuller, Ruby and Crystal. The mean percentage of hydrogen consumed in these catchments during water years 1990 through 1994 was 94%. With the exception of Lost Lake, the remaining catchments neutralized from 80 to 90 percent of annual hydrogen-ion deposition. In addition, Spuller, Ruby and Crystal lakes had significantly ( $p < 0.05$ ) lower hydrogen-ion yield than Lost Lake or the lakes in Sequoia N.P. (Table III-19). The Lost Lake watershed was not as efficient in neutralizing acidic inputs and had efficiencies for water years 1990 through 1993 of 82%, 57%, 62%, and 61%, respectively. The low VWM pH and ANC in outflow and low percentages of acid neutralization within

the catchment suggests that the Lost Lake watershed is perhaps the most sensitive to alteration from acid deposition of the catchments in our study.

### 3.3.3.2. Acid Neutralizing Capacity (ANC)

The eight watersheds in this study exported from about 100 to 500 Eq ha<sup>-1</sup> of ANC annually (mean, 250 Eq ha<sup>-1</sup>; Table III-27). Since no ANC was measurable in precipitation, all (or the vast majority) of the ANC exported from the catchments originated within the basins. Pear Lake watershed had significantly ( $p < 0.05$ ) lower ANC yield (1990-1993 mean: 138 Eq ha<sup>-1</sup>) than any other catchment (Table III-28). During 1990 through 1992, ANC yields at Spuller and Ruby were significantly ( $p < 0.05$ ) higher than at all other catchments (Table III-28), and the basin with the largest ANC export was Spuller Lake (1990-1994 mean: 304 Eq ha<sup>-1</sup>). Average ANC yields for the remaining catchments were in the range of 200 to 280 Eq ha<sup>-1</sup>. At all sites the export of ANC was positively related to the quantity of runoff and was significantly ( $p < 0.05$ ) greater in years with large snowpacks, i.e., 1993. The relationship between solute export and runoff is discussed further in Section 3.3.5.

### 3.3.3.3. Chloride

As with hydrogen-ion, the majority of chloride deposition occurred during the winter. Non-winter precipitation contributed less than 36% of annual chloride loading (Table III-33) during 1990 through 1993. In wet water years, such as 1993, the annual contribution from winter snowfall represented an average of 94% of annual loading at 15 stations in the Sierra Nevada (Table III-33). The mean annual loading of chloride at the eight study sites was 22.5 Eq ha<sup>-1</sup> (Table III-32).

In contrast to hydrogen-ion and ANC, chloride was neither strongly retained nor exported from the catchments; in about half of the solute balances yields for chloride were positive (Figure III-4). In addition, statistical analyses indicated there were no significant inter-annual differences in chloride yield for the period of 1990 through 1993 (Table III-30). With few exceptions yields were in the range of  $\pm 10$  Eq ha<sup>-1</sup> with the mean yield being -0.6 Eq ha<sup>-1</sup> (Table III-27). In the 1993 and 1994 solute budgets for Emerald Lake (two our most precise solute balances, see Section 3.3.4.), there was a modest retention of chloride during both years (Table III-20).

Four outliers were noted in regards to the chloride solute balance: water years 1985 and 1986 at Emerald Lake, water year 1992 at Lost Lake and water year 1993 at the Marble Fork (Figures III-4 and III-5). For these years, there was a large retention of chloride at the Emerald Lake basin (yields, -35 and -27 Eq ha<sup>-1</sup>, respectively) and large exports from the Lost Lake and Marble Fork catchments (18 and 23 Eq ha<sup>-1</sup> respectively), results which cast doubt on either the accuracy of the water balances or the quality of chloride chemistry for these years. It is likely that the large retention of chloride at Emerald Lake was due to chloride contamination of snow samples during 1985 and 1986. During this period, bags used for snow samples were routinely soaked with HCl prior to rinsing with DI water. In Melack et al. (1997), we reported that HCl washed bags resulted in chloride contamination of snow samples and snow from these years had the second and third highest VWM chloride concentration measured at Emerald Lake (1989 was highest, see Table III-6). HCl contamination would produce an overestimate of

chloride loading, resulting in an apparent retention of Cl<sup>-</sup> in the catchment. If a more typical chloride value (i.e., 1.7  $\mu\text{Eq L}^{-1}$ , see Table III-14) is used for snow chemistry in 1985 and 1986 then the yields become -11  $\text{Eq ha}^{-1}$  and -6  $\text{Eq ha}^{-1}$ , respectively, which are more in line with data from other sites.

The large positive yields at Lost Lake and Marble Fork are more difficult to explain. At both sites, chloride loading during 1992 and 1993 appears to be reasonable when compared with the other catchments. Therefore, the problem may lie in measurement of the outflow fluxes. Discharge at the Marble Fork was not directly measured during water year 1993 but was computed based on Emerald discharge (see Chapter Two) and the relatively large chloride yield may be caused by overestimated discharge. Further evidence for this is the apparent lack of snow carry-over in Marble Fork water balances from water years 1993 into 1994 despite the fact that unmelted snow from the winter of 1993 persisted into 1994 (see Figure II-46).

The water balance for Lost Lake had a relatively large and negative residual in 1992 indicating that outflow was overestimated by about 20%. In this case the explanation may lie in the timing of samples during snowmelt; at Lost Lake, only one sample was collected from the outlet during the month of April and this sample had a relatively high chloride concentration (ca. 7  $\mu\text{Eq L}^{-1}$ ). The chemistry from this sample was extrapolated over a considerable period of time (and hence discharge) resulting in an overestimate of export for the month of April. Thus, the inaccuracy in the chloride balance at Lost Lake may be the result of two complementary errors: error in water quantity and error in solute concentration.

#### 3.3.3.4. Sulfate

Deposition of sulfate during non-winter periods accounted for the majority of annual loading in water years 1990 through 1992 (mean for three years, 59%; Table III-33). During water year 1993, non-winter precipitation comprised, on average, 3.6% of water deposition but contributed ~16% of annual sulfate loading. Non-winter sulfate deposition is relatively large because of high concentrations of sulfate in precipitation (mean, 15.1  $\mu\text{Eq L}^{-1}$ ). Mean sulfate loading for the study was 37.4  $\text{Eq ha}^{-1}$  and ranged from a high of 95  $\text{Eq ha}^{-1}$  (Emerald Lake, water year 1987) to a low of 16  $\text{Eq ha}^{-1}$  (Marble Fork basin, water year 1994, Table III-28). At Emerald Lake, high sulfate deposition in 1987 resulted from frequent, high-solute storms during spring snowmelt.

The sulfate budgets showed that the catchments tended to be a net source for this ion, however, the data revealed two distinct classes of watersheds. In 24 of 36 catchment-water years, sulfate yields were positive (Figure III-4) and where the yield was negative, few values were less than -15  $\text{Eq ha}^{-1}$ . Certain watersheds always exhibited positive yields, Ruby, Spuller, Marble Fork and Lost, while others had negative yields in all but wet years, Pear, Topaz and Crystal. In addition, during 1990 through 1992, sulfate yield at Ruby, Spuller and Lost lakes was significantly ( $p < 0.05$ ) greater than at Crystal, Pear and Topaz lakes. The mean sulfate yield during the study was 17.0  $\text{Eq ha}^{-1}$  (Table III-33). At Emerald Lake, four years had large positive yields (1986, 1991, 1993 and 1994), two had near zero yields (1990 and 1992) and two had negative yield (1985 and 1987 Figure III-5). In 1993 and 1994, sulfate yields at Emerald Lake were 37  $\text{Eq ha}^{-1}$  and 21  $\text{Eq ha}^{-1}$  respectively. The sulfate budgets suggest there is a net export of sulfate from most

watersheds in the Sierra Nevada during most years and in wet years all Sierran catchments have positive yields of sulfate. The most likely source of sulfate in these basins is mineral weathering of sulfur bearing rocks. Dry deposition of sulfate may also play some role in the sulfate budgets in Sierran watersheds but it is unlikely that it accounts for the relatively large sulfate yield from catchments like Ruby Lake, Spuller Lake and Lost Lake. On the other hand, dry deposition may explain some of the positive sulfate yield in the Tokopah Valley catchments.

### **3.3.3.5. Base Cations**

Calcium and sodium comprised the majority of base cation deposition to the catchments in this study. For calcium, annual deposition rates ranged from 16 to 67 Eq ha<sup>-1</sup> and the mean for the study period was 28.0 Eq ha<sup>-1</sup> (Table III-32). Mean deposition for magnesium and potassium were: 7.4 Eq ha<sup>-1</sup> and 7.7 Eq ha<sup>-1</sup>, respectively. In dry to normal years (i.e., 1990 through 1992), non-winter precipitation comprised from 40 to 50% of the annual loading of base cations (Table III-33). This percentage dropped to 7 to 12% in 1993.

High rates of base cation export were a conspicuous feature of the solute balances for the study catchments (Figures III-6 and III-7). With the exception of potassium at Crystal Lake during 1992, yields for base cations were always positive. The negative yield at Crystal is an artifact introduced by the large positive residual (i.e., underestimated outflow) in the water balance for this year. Calcium and sodium were the major cations exported from all the catchments; the mean and range of yields for calcium were 171 Eq h<sup>-1</sup> and 42.7 to 407 Eq ha<sup>-1</sup>, respectively, and for sodium: 66.4 Eq ha<sup>-1</sup> and 24.5 to 154 Eq ha<sup>-1</sup>, respectively (Table III-31). Annual yields for magnesium and potassium ranged from -2.9 to 99.5 Eq ha<sup>-1</sup> (means, 25.6 and 18.2 Eq ha<sup>-1</sup> respectively). Similar values for base cation yield was measured in the Emerald Lake watershed (Figures III-8 and III-9).

Calcium yield and exports at the Ruby and Spuller lake catchments were significantly greater ( $p < 0.05$ ) than at all other catchments (Tables III-28 and III-29). In addition, the Pear Lake and Crystal Lake basins had significantly ( $p < 0.05$ ) lower calcium yield than Emerald and Lost, which is partially explained in the case of Crystal Lake by errors in the water balance (i.e., underestimation of outflow discharge and hence calcium yield). For yields of the remaining base cations, few significant differences were identified and are worth noting other than the fact that magnesium and sodium yield from the Pear Lake watershed was lower than at Emerald.

### **3.3.3.6. Nitrogen**

High rates of nitrogen deposition were measured in the study catchments. Average annual ammonium-deposition was significantly greater ( $p < 0.05$ ) than nitrate deposition and ranged from 20.8 to 141 Eq ha<sup>-1</sup> with a mean value of 50.8 Eq ha<sup>-1</sup> (Figure III-10 and Table III-32). Mean annual nitrate-loading varied from 26.8 to 116 Eq ha<sup>-1</sup> and had a mean of 44.8 Eq ha<sup>-1</sup> per year during the study. For both ions the highest loading rate was measured at Emerald Lake during water year 1987 (Figure III-11).

Non-winter precipitation is the major contributor of nitrogen during drought years. For the period of 1990 through 1992, well over half of the annual deposition of ammonium and nitrate took place during the months of ca. April through November

(Table III-33). Similar patterns of nitrogen deposition were also seen in water years 1985 through 1987 at Emerald Lake (Table III-20). Moreover, even in relatively wet years such as 1993, deposition from non-winter precipitation was ca. 22% of annual loading.

Most of the nitrogen intercepted by high elevation catchments in the Sierra Nevada is utilized by terrestrial and aquatic ecosystems. Based on the input-output budgets for ammonium and nitrate, biological demand for nitrogen is high. During the study, utilization of ammonium from wet deposition averaged greater than 99% on an annual basis (Tables III-31 and III-32, Figure III-10) and it was one of the few solutes where yields were not significantly ( $p < 0.05$ ) higher during 1993 (Table III-30). Negative yields for nitrate were measured in 32 of the 36 cases (Figure III-10) indicating that the watersheds are, predominantly, a sink for nitrate as well. If dry deposition of nitrate during non-winter periods were included in the budgets it is likely that all of the nitrate balances would have negative yield since the apparent yield of nitrate could be accounted for by additional loading (see Section 3.3.5.1.). At Crystal and Lost, nitrate utilization was in the range of 85% to 95%, but for the remaining catchments, uptake was typically on the order of 20 to 60%.

Nitrate yields, while predominantly negative, varied considerably both among catchments and from year to year (Figure III-10). For example, nitrate yields at Emerald Lake varied from a low of  $-62 \text{ Eq ha}^{-1}$  during water year 1987 to a high of  $25 \text{ Eq ha}^{-1}$  in 1993. Positive yield of nitrate (indicating a net source of nitrate in the catchment) was measured in only 4 out of the 36 cases and these years include 1986 and 1993 at the Emerald Lake watershed and 1993 at the Ruby and Spuller lakes' basins (Figures III-10 and III-11). However, no net export of dissolved inorganic nitrogen (DIN, i.e., nitrate plus ammonium) was measured at these four catchment during the study (Figure III-12) despite the fact that mean nitrate yield during 1993 ( $-11 \text{ Eq ha}^{-1}$ ) was significantly ( $p < 0.05$ ) higher (2-3 times) than in all other years (Table III-30).

### 3.3.4. Sources of Error in Solute Balances

The solutes balances presented in this report are the end result of thousands of individual measurements of water chemistry and water quantity. Inherent in these measurements is some degree of error which carries through the calculations of solute flux. Since solute flux is largely a function of water flux, solute balance errors will be of the same magnitude and in the same direction (i.e., over- or under- estimates) as the errors in the water balance. Uncertainties in solute fluxes are also introduced through bias and imprecision in chemical analyses and in the manner (e.g., frequency) in which samples were obtained. Thus, the interactions of these errors must be examined to determine the accuracy and precision of the solute balance calculations.

Three types of error were identified in the solute balance estimates: (1) volume errors, (2) analytical errors and (3) sampling errors. Volume errors are the uncertainty in estimates of winter and non-winter precipitation volume and outflow discharge. Since solute fluxes are the product of water volumes ( $\text{m}^3 \text{ yr}^{-1}$ ) and VWM concentrations ( $\text{Eq m}^{-3}$ ), errors in measuring precipitation or streamflow will affect the uncertainty of the fluxes and must be accounted for in the error analysis. Another source of error is introduced during chemical analyses of precipitation and stream samples. Lastly, missed precipitation and low-frequency stream sampling will introduce errors into VWM

above the analytical error. In the following sections we will examine each type of error individually and describe how it was estimated. Next, individual errors will be combined and propagated to estimate the uncertainty in VWM chemistry, flux estimates (i.e., solute loading and export) and solute yields.

#### **3.3.4.1. Volume Errors**

Derivation of volume errors was addressed in Chapter Two (see Sections 2.2.1 and 2.2.2. and Tables II-3 and II-7) and we will only summarize the results here. Errors in estimating precipitation depended on the timing of storms and whether precipitation fell as snow or rain. We estimated that the measurements of winter snowfall had an uncertainty of  $\pm 5\%$ . Errors in non-winter precipitation volume depended on the timing and form of the precipitation and, because of logistical factors, some catchments had greater error than others. At Crystal, Emerald, Marble Fork, Pear and Topaz watersheds, non-winter precipitation volume had an error of  $\pm 9\%$ ; uncertainty in non-winter precipitation at the Lost, Ruby and Spuller watersheds was  $\pm 14\%$ .

Errors in discharge measurements varied from site to site and from year to year. On an annual basis, uncertainty in outflow ranged from  $\pm 5\%$  to  $\pm 25\%$ . Stream gauging was most accurate in catchments with weirs (i.e., water years 1991 through 1994 at Emerald and Spuller lakes) and in years where rating curves were based on constant-injection discharge measurements (i.e., basins other than Emerald and Spuller in water years 1993 and 1994). Discharge calculated with rating curves based on slug-injection discharge measurements were less accurate and tended to overestimate true flows. Therefore, during 1990 through 1992 uncertainty of  $\pm 15\text{-}25\%$  was the rule. After 1992 discharge errors decreased and the systematic bias was reduced, although, because of problematic stream morphology, discharge errors at Lost, Pear and Topaz lakes remained higher than at other catchments.

#### **3.3.4.2. Analytical Errors**

Results from the Quality Assurance/ Quality Control (QA/QC) program for chemical analyses are summarized and discussed in Melack et al. (1997) and in Chapter One. For the error analysis, these data, summarized in Table III-34, represent the average analytical uncertainty over the period of 1990 through 1994 and were determined by spike recoveries and analyses of standard reference materials. In the QA/QC program, accuracy was determined at a 10% frequency within each analytical run. Melack et al. (1997) reported yearly averages of analytical precision and accuracy but for purposes of this error analysis we chose to average the yearly estimates in order to simplify calculations. We feel that this is a reasonable approach, since differences in analytical uncertainties between water years were small.

Errors introduced into the solute balances from analytical chemistry were smaller than errors from water quantity measurements (Table III-34). For snow samples uncertainties of  $\pm 2\text{-}7\%$  were measured for most solutes; organic anions, because of their low concentrations had error of  $\pm 10\%$ . Solute concentrations were higher in non-winter precipitation and uncertainties in chemical concentrations were usually less than in snow. For most solutes analytical errors were in the range of  $\pm 1$  to  $5\%$ , exceptions being sodium ( $\pm 10.4\%$ ), organic anions ( $\pm 7.0\%$ ) and sulfate ( $\pm 5.8\%$ ). In lake and stream samples,

analytical errors were typically  $\pm 2\text{-}6\%$ , but were  $\pm 10\%$  for ammonium owing to low or undetectable concentrations (Table III-34). Note that organic anions were undetectable in outflow samples as was ANC in precipitation.

#### 3.3.4.3. Sampling Errors

Collecting stream and precipitation samples from remote watersheds in the Sierra Nevada is difficult and subject to logistical constraints. During the transitions between spring snow-surveys and operation of the rain collectors in the summer some precipitation events were not sampled. Likewise, during late autumn, storms were occasionally unsampled because the rain collectors were dismantled prior to the start of the snow-season. By using data from nearby stations to fill in these gaps, we accounted for most precipitation, but at the same time, we introduced a new source of error into estimates of VWM chemistry and, hence, solute loading. Thus, to accurately assess the uncertainty of precipitation chemistry and loading, this sampling error must be considered.

In a similar fashion, the number and timing of outflow chemistry samples had a direct effect on the uncertainty of VWM stream chemistry and solute exports. Since snowmelt is the period of maximum discharge of both water and solutes, frequent stream sampling is necessary during this period to account for changing solute concentrations and to accurately measure exports. Depending on the timing of the samples, the effect of low sampling frequency could be either to over- or under-estimate annual VWM chemistry and solute export. For example, if few samples are collected during the annual nitrate pulse, VWM chemistry, export and yield of nitrate will be underestimated. Conversely, if chemical samples are missing from the period of peak discharge, when most solutes are at their minimum concentrations, then these same parameters will be overestimated.

In the case of winter and non-winter precipitation, sampling error was a function of the quantity of unsampled precipitation and the probable error in the chemistry of this unsampled fraction. In these calculations we assumed that extrapolation of VWM chemistry caused a 50% error in the chemistry of unsampled non-winter precipitation and 20% error in unsampled snow. These errors were estimated by inter-station comparisons of rain and snowpack chemistry. To estimate the contribution of sampling error to the uncertainty of VWM chemistry, the uncertainty in unsampled winter or non-winter precipitation (20% and 50% respectively) was multiplied by the ratio of unsampled precipitation to total precipitation (sampled + unsampled precipitation). These estimates are presented in Table III-35. In most cases the sampling errors for non-winter precipitation were zero since all precipitation was sampled; in other cases the sampling error ranged from  $\pm 3\text{-}35\%$  (Table III-35). High sampling errors in water year 1990 are due to unsampled rain from the autumn of 1989 since the rain collection network was not installed until the summer of 1990. Sampling errors for VWM snow chemistry are low since (1) relatively little snow fell after the spring snow surveys and (2) if a sizable event did occur we sampled it using snowboards or snowpits. During most years, sampling errors for snow were less than  $\pm 2\%$  but increased to  $\pm 4$  at Emerald Lake and Marble Fork during 1994 because of appreciable spring snowfall.

The sampling error for VWM outflow chemistry was estimated using Tukey's jackknife method (Sokal and Rohlf 1981). The jackknife procedure provides a measure of the variability of VWM outflow chemistry by iteratively computing the means with a

different one of the observations (i.e., stream samples) omitted each time. The variability among the means is then used to calculate an approximate standard error for the VWM chemistry of each solute and are presented in Table III-36. Outflow sampling-error is inversely related to the number of samples collected during snowmelt and directly related to the variability of stream chemistry during this period. As such, each solute will have a unique error that will vary among catchments and years. Catchments and years with high sampling error (e.g., Spuller Lake in 1994) had infrequent chemical sampling during snowmelt and relatively large annual variations in solute chemistry. Solutes that had less concentration variability during snowmelt, i.e., sulfate, had lower sampling error than did base cations or silicate which declined markedly during snowmelt or solutes such as ammonium or nitrate which frequently fell to undetectable levels (Table III-36).

#### 3.3.4.4. Uncertainty of VWM Chemistry

The uncertainty of VWM chemistry ( $S_{\text{vwm}}$ ) was computed as the square-root of the quadratic sum of the component errors (root-sum-square method, Sokal and Rohlf 1981):

$$S_{\text{vwm}} = (S_{\text{analytical}}^2 + S_{\text{sampling}}^2)^{1/2} \quad (5)$$

where:

$S_{\text{analytical}}$  = analytical error for precipitation or outflow chemistry, and

$S_{\text{sampling}}$  = sampling error for precipitation or outflow.

The estimated errors in VWM chemistry for each solute, from every year and at all catchments are presented in Tables III-37 through III-39 and are expressed as percentages for ease of comparison. In addition, absolute standard errors for VWM chemistry were computed and are presented along with the volume-weighted means in Tables III-6 through III-13.

With the exception of 1990, errors in VWM rain chemistry were low and were mainly caused by analytical uncertainty (Table III-37). Standard errors for VWM snow chemistry were also small and primarily due to analytical errors (Table III-38). In most cases, there was no sampling-error since all precipitation was collected and the uncertainty in VWM chemistry was equal to the analytical error for each solute. In the case of water year 1990, however, VWM rain chemistries have standard errors of 15 to 30% owing to relatively large sampling error (rain was not sampled in the autumn of 1989).

Small analytical and sampling errors resulted in modest to large uncertainties in VWM outflow chemistry (Table III-39). Solutes with concentrations at or below detection limits, such as ammonium and nitrate, had the greatest uncertainty while relatively invariant solutes, like sulfate, had the lowest error. With few exceptions, standard errors for most other solutes were in the range of 1 to 25%. Large errors at Spuller Lake during 1994 and, to a lesser extent at Ruby Lake during the same year, are primarily due to a paucity of samples during peak runoff.

#### 3.3.4.5. Uncertainty of Flux and Yield Estimates

Since solute fluxes were computed as the product of water volumes and VWM chemistry, the uncertainty in solute flux will derive from errors in both. Using the root-sum-square method we computed the flux uncertainty ( $S_{\text{flux}}$ ) as:

$$S_{\text{flux}} = (S_{\text{vwm}}^2 + S_{\text{volume}}^2)^{1/2} \quad (6)$$

where:

$S_{\text{vwm}}$  = the uncertainty in VWM chemistry for precipitation or outflow, and  
 $S_{\text{volume}}$  = volume error for precipitation or outflow.

The estimated errors in loading (snow and non-winter) and exports for each solute, for all years and at all catchments are presented in Tables III-40 through III-42, expressed as percentages for ease of comparison. The absolute standard errors for the solute fluxes were computed and are presented in Tables III-20 through III-27.

The uncertainty in annual solute loading ( $S_{\text{A-flux}}$ ) and solute yield ( $S_{\text{yield}}$ ) were estimated by propagating the absolute errors in (1) solute loading from snow, (2) solute loading from non-winter precipitation and, in the case of yield, (3) solute exports in outflow. The following equations were used:

$$S_{\text{A-flux}} = (S_{\text{S-flux}}^2 + S_{\text{R-flux}}^2)^{1/2} \quad (7)$$

$$S_{\text{yield}} = (S_{\text{S-flux}}^2 + S_{\text{R-flux}}^2 + S_{\text{O-flux}}^2)^{1/2} \quad (8)$$

where:

$S_{\text{S-flux}}$  = the absolute uncertainty in solute loading from snow,  
 $S_{\text{R-flux}}$  = the absolute uncertainty in non-winter solute loading, and  
 $S_{\text{O-flux}}$  = the absolute uncertainty in solute export in the outflow.

Absolute uncertainties in annual solute loading and yield were converted to percentages and presented in Tables III-43 and III-44. Uncertainties are also included, along with yields, in Tables III-20 through III-27.

The solute balance component with the greatest degree of uncertainty was export. In most cases, errors were on the order of  $\pm 20$  to 30%, but in the case of ammonium and nitrate, much larger errors were computed. Solute exports had higher error for two reasons: (1) sampling errors were relatively high and (2) volume errors for discharge were generally greater than for snow or rain. The two years with the lowest export error were at Emerald Lake in 1993 and 1994. Accurate discharge measurements from the weir and daily chemistry samples during runoff were responsible for export uncertainties of less than  $\pm 10\%$  for most solutes. For non-winter precipitation, errors were typically  $\pm 10$  to 25%. Uncertainty was even lower in snow loadings since volumes were more accurately measured and spring snow storms are comparatively rare in the Sierra Nevada. The uncertainties in solute yield were typically  $\pm 5$  to 20%.

#### 3.3.4.6. Systematic Errors

The random errors, discussed in previous sections, are the most important components in evaluating uncertainties in the solute balances. However, several systematic errors (i.e., bias) were also identified, the most important of which were (1) overestimates of outflow discharge at catchments without weirs, (2) underestimates of precipitation at catchments without nearby weather stations (e.g., Lost Lake) and (3) lack of non-winter dry deposition measurements (all stations). The combined effect of these systematic errors varies because some errors cancel while other combine. It is also difficult to estimate the magnitude of the biases. Overestimates of outflow discharge resulted in overestimates in solute export at stations where dilution gauging techniques were used. Bias was greater in 1990 and 1991 when slug-injections were the primary

method for measuring discharge. In later years, more accurate gauging techniques decreased the bias.

Considerable effort went into measuring rain and snowfall into the catchments, but undoubtedly some precipitation was missed. The bias for snow-volumes is small since missed spring-snowfall is balanced, to some extent, by positive bias introduced in the spring snow surveys: areas where snow-cover was thin were undersampled, thereby overestimating average depth and hence SWE. Nevertheless, on an annual basis, we believe that precipitation, and hence solute loading from wet deposition, may be slightly underestimated. In combination, overestimates of outflow and underestimates of precipitation most likely resulted in some overestimation of solute yields from the catchments; this effect is lessened in the case of ANC and silicate since these solutes were not present in precipitation. This problem is exacerbated (to an unknown extent) by the fact that no determinations of dry-deposition are included for non-winter periods; dry deposition during the winter is captured in the snowpack. However, underestimates in solute deposition are somewhat counter-balanced (more so in a wet year like 1993) for solutes like organic anions, sulfate, sodium and potassium because of the positive bias introduced from chemical analyses (Melack et al. 1997).

We also investigated the possibility that sampling errors caused systematic errors in solute exports. Utilizing sampling errors computed with the jackknife procedure and propagated with errors from VWM chemistry, we were able to estimate the uncertainty in solute export from the study catchments. However, these calculations do not address the issue of systematic errors introduced by variations in sampling frequency. Using data from 1993 and 1994 from Emerald Lake, we investigated the relationship between sampling frequency and solute exports by examining changes in annual exports as the number of chemistry samples was incrementally decreased. During these years, samples were collected on approximately a daily basis during snowmelt. In the analysis the daily chemistry record was degraded to simulate weekly (every 7 days), biweekly (14 days), monthly (28 days) and bimonthly (56 days) sampling regimes. Next, the cumulative and annual solute export was calculated for each constituent using the degraded chemistry records, the results of which are summarized in Table III-45 and Figures III-13 through III-16.

Differences in annual solute export increased as a function of the time period between samples. For weekly samples, annual solute exports differed by an average of 2.9% in 1993 and 3.5% in 1994 from exports computed from the daily sample record (Table III-25). With biweekly samples, annual exports differed by an average of 5.9% in 1993 and 3.8% in 1994. When the sampling interval was increased to monthly, the difference in annual solute export increased to an average of 13.2% in 1993 and 8.9% in 1994. Not surprisingly the largest uncertainty in annual solute export were measured for bimonthly sampling with average differences of 20.3% in 1993 and 11.9% in 1994.

Low sampling-frequency not only increased the uncertainty in estimates of annual solute export, it also introduced a systematic bias in export for most solutes. For base cations, silicate, and chloride a lower sampling frequency resulted in overestimated exports for both years (Figure III-13). A smaller overestimate was produced in sulfate export because sulfate concentrations varied little during snowmelt. For nitrate and chloride, positive bias occurred in both years at most sampling frequencies (Figure III-14).

Other solutes such as ANC and hydrogen-ion showed no systematic bias in either annual solute export or cumulative export (Figures III-13 through III-16). For most solutes, overestimates occurred because coarse sampling regimes failed to capture stream chemistry when discharge was highest and solute concentrations were lowest (i.e., the dilution pattern described in Chapter One). We therefore conclude that annual solute exports based on less than biweekly to monthly stream sampling, will overestimate exports for most solutes. In addition, overestimates will be greatest in catchments where solute concentrations show more variability during snowmelt, and during wet years like 1993 because of greater snow-melt dilution of surface waters.

#### **3.3.4.7. Chloride Balances**

Chloride yield can be used as an internal check on the accuracy of the solute balances because, with the exception of evapo-concentration, there are few biogeochemical or physical processes within the catchments that affect chloride concentration and none which would be expected to alter the yield. Thus, the ratio of chloride input to chloride export should be one and chloride yield should approach zero. Excluding known outliers (i.e., Crystal Lake, Emerald Lake 1985-86, Lost Lake 1992), most chloride yields were in the range of  $\pm 10 \text{ Eq ha}^{-1}$  (1990-1993 mean yield:  $-0.13 \text{ Eq ha}^{-1}$ ). The average ratio of inputs to exports for this subset of water years (29) was 0.96. In over half of these years chloride inputs and exports agreed within 10% and in two-thirds of the cases the agreement was better than 20%. These findings suggest that chloride behaves as a conservative ion in Sierran catchments and the chloride yields are consistent with the solute balance errors presented in Sections 3.3.4.1. through 3.3.4.5..

#### **3.3.5. Relationship Between Solute and Water Flux**

The amount of solute entering a catchment in precipitation or leaving a catchment in streamflow is a product of solute concentration and the quantity of water transported. If either the concentration or quantity of water increases, so will the amount of solute transported. However, the relative importance of these factors with respect to the total solute flux varies. For example, most of the deposition of hydrogen-ion, chloride and base cations in the Sierra Nevada occurs during the winter because snowfall greatly exceeds non-winter precipitation and winter snow and non-winter precipitation have similar concentrations of these ions. In contrast, most deposition of nitrogen, sulfate and organic acids occurs during non-winter periods owing to high concentrations of these constituents in non-winter precipitation. In a similar way, solute export depends on outflow volume and chemistry, however, because of its relatively large variability (i.e., orders of magnitude), water volume is the major factor affecting solute exports. For example, VWM concentrations of solutes in outflow streams are higher in December than in May, but the flux of solutes is 1 to 2 orders of magnitude higher in May owing to higher discharge.

To investigate the relationships between runoff and solute flux, we tested the assumption that solute exports increased in direct proportion to catchment runoff. By observing the discharge-solute export relationship over a wide range of flows and from a variety of watersheds we attempted to determine if rates of biogeochemical reactions within the catchments are affected by annual precipitation or solute loading.

In this section we will discuss the relationship between solute flux and water quantity as they relate to solute exports in outflow and solute inputs from winter snowfall. Because of a weak relationship between non-winter solute loading and non-winter precipitation quantity, annual solute deposition (the sum of winter and non-winter loading) is hard to associate with annual precipitation quantity. Thus, our discussion will deal only with the outflow-export and snowfall-loading relationships.

### 3.3.5.1. Winter Snowfall vs. Solute Loading

There is a high correlation between winter snowfall and winter solute deposition in the Sierra Nevada. For the 36 catchment-years, there were significant ( $p < 0.01$ , Pearson product moment correlation), positive correlations between all measured constituents and snow-water equivalence (SWE) measured in the spring snowpacks. Linear functions were fit to these relationships and are presented in Figures III-17 through III-22.

Strong correlations were found between SWE and the deposition of ammonium and nitrate (Figure III-17). Snowfall explained 59% of the variability in ammonium loading and 71% of the variation in nitrate deposition. Linear functions fit to these relationships have y-intercepts (4.95 and 6.08 Eq ha<sup>-1</sup>, respectively) that were significantly ( $p < 0.05$ ) greater than zero. We submit that dry deposition onto the snowpack may be one possible explanation for this finding. In Melack et al. (1997) similar equations were fit for a larger set of Sierran stations (including the sites in this report) and the y-intercepts for ammonium and nitrate were 8.72 Eq ha<sup>-1</sup> and 8.8 Eq ha<sup>-1</sup>, respectively.

If the y-intercepts for the relationships between SWE and N deposition represent dry deposition then they are in agreement with previous measurement of dry deposition at Emerald Lake. For example, during water year 1987, N-loading from dry deposition in the Emerald Lake basin was estimated by Williams et al. (1995) to be 5.2 moles ha<sup>-1</sup> during the winter (ca. mid-November through March) and 39.5 moles ha<sup>-1</sup> on an annual basis. Nitrogen loading reported in their study was based on measurements of nitrate deposition-velocities determined at a NOAA dry deposition monitoring station in a forest clearing 7 km west of Emerald Lake (elevation 2250 meters); ammonium deposition was assumed to be 91% of nitrate loading. Winter and annual dry-deposition of N-NO<sub>3</sub> at the NOAA station were 6.3 moles ha<sup>-1</sup> and 48 moles ha<sup>-1</sup>, respectively and if we assume that ammonium deposition equals 91% of nitrate loading, winter and annual DIN loading (ammonium + nitrate) would equal 12 moles ha<sup>-1</sup> and 92 moles ha<sup>-1</sup>, respectively. In comparison, the average annual loading of DIN to the eight study sites, during the period of 1990-1994, was 96 moles ha<sup>-1</sup> and on average about half is contributed by winter snowfall (which includes dry deposition). Based on these estimates, non-winter, dry deposition of N along the western slope of the Sierra could be on the order of 30 to 80 moles ha<sup>-1</sup> yr<sup>-1</sup>. Thus, our estimates of annual N loading may be underestimated by 30 to 80%; the underestimate is probably less in catchments along the eastern slope because of better air quality and hence lower dry deposition.

Snowfall quantity explained over 80% of the variability in winter deposition of hydrogen-ion and sulfate (Figure III-18). The equations for the relationships between these solutes and SWE had y-intercepts not significantly ( $p < 0.05$ ) different from zero Eq ha<sup>-1</sup>. The slopes, intercepts and coefficient of determination for these relationships are similar to those presented in Melack et al. (1997). The high degree of correlation between

SWE and these solutes indicates a common source for hydrogen-ion and sulfate in winter deposition, and also implies that there is little regional effect on the loading of these solutes in the Sierra Nevada.

Good correlations were observed between SWE and winter deposition of some of the other major ions. For chloride and sodium  $r^2$  values were 0.75 and 0.84, respectively with y-intercepts less than zero (-7.99 and -2.84 Eq ha<sup>-1</sup> respectively; Figure III-19). In the case of chloride, the intercept was significantly ( $p < 0.05$ ) different from zero which is probably explained by relatively high analytical error for this ion in snow. In the larger data-set from Melack et al. (1997), the coefficients of determination ( $r^2$ ) between SWE and these solutes were lower, but y-intercepts for both were not significantly ( $p < 0.05$ ) different from zero (-1.71 Eq ha<sup>-1</sup> for chloride, +0.006 Eq ha<sup>-1</sup> for sodium).

SWE explained a relatively low percentage of the variation in winter loading of calcium, magnesium and potassium: 44%, 54% and 23%, respectively (Figures III-20 and III-21). Acetate and formate, typically found in low concentrations in snow, had very different coefficients of determination (Figure III-22). Snowfall quantity explained a relatively high percentage of the variability of acetate loading, 77%, but SWE had little predictive power for formate ( $r^2 = 0.14$ ). The y-intercept for acetate was indistinguishable from zero while for formate it fell significantly ( $p < 0.05$ ) above the origin.

### 3.3.5.2. Runoff vs. Solute Export

With the exception of nitrate and ammonium, there were significant ( $p < 0.01$ , Pearson product moment correlation), linear relationships between the export of all other measured solutes and runoff (Figures III-23 through III-31). Linear correlations were developed for the aggregate of the 36 catchment-years and separately for the Emerald Lake watershed (8 water years). We have also included regressions for other catchments, but the equations and correlation statistics must be viewed cautiously since they are based on only 4 to 5 years of data.

The variability of ANC yield among the catchments is seen in a plot of runoff vs ANC export (Figure III-23). Runoff explained only 51% of the variability in annual ANC export (for ANC, export = yield since there is no ANC in precipitation). Differences in watershed geology, hydrologic flow-paths, soils and perhaps vegetation account for the low predictive value of runoff in the aggregated data-set. Given this variability, it is difficult to assess the impact of factors such as annual precipitation on the export of ANC from Sierran catchments. However, the relationship between runoff and ANC export (yield) is clearer using data from individual catchments.

The plot of runoff versus ANC export (Figure III-24) shows a strong, linear relationship between these parameters at Emerald Lake. Runoff explained 98% of the variability in the annual ANC yield. The equation for the regression is:

$$\text{ANC Yield} = 0.18 (\text{Runoff}) + 42 \quad (9)$$

The relationship between runoff and ANC yield remained constant over a nearly fourfold range in runoff. Equation (9) was also calculated with data from water years 1995 (runoff = 2019 mm) and 1996 (runoff = 1404 mm) (Sickman, Leydecker and Melack unpublished). With these additional points,  $r^2$  was 0.96 and the slope increased to 0.19. Also shown in the figure are statistics computed for regressions between ANC yield and

runoff at all other lake basins as well. The square of the correlation coefficients for these regressions ranged from 0.97 to 0.99 and in no case did ANC yield per unit runoff decline in 1993. Please note, however, that in these catchments there was only one high-runoff year (1993) compared to three at the Emerald Lake catchment (1986, 1993 and 1995); high correlation is partly an artifact of the paucity of data. Assuming runoff more accurately approximates the relative input of acid to the catchment-systems (from year to year) than does winter hydrogen deposition, the linearity of the runoff-export relationships indicates that all of the catchments produce ample ANC and are probably not at risk of acidification under present-day acid loadings. If the acid-neutralizing capacity of the watersheds were being approached, then we would expect to see some diminishment of ANC export at high runoff; that is, a decline in the rate of ANC yield per unit discharge. Using ANC export per unit runoff (i.e., slope) as an index of catchment sensitivity to acid deposition, Crystal and Ruby would be the least sensitive (slope: 0.61 and 0.43, respectively) and Pear and Lost would be the most sensitive (slope: 0.15 and 0.17, respectively).

Our assumption that runoff is a better approximation of relative acid loading from year to year compared to winter hydrogen loading is based on two findings: (1) most of the inter-annual variation in snowpack pH is probably due to analytical error and (2) snow can carry-over from one water year into the next (e.g., 1993). When snow carries over, winter loading overestimates the actual input of hydrogen-ion or other solutes that enter the catchment biogeochemical system. By using runoff, we corrected for this carryover. No significant difference ( $p < 0.05$ ) in snowpack pH occurred during the period of 1991-1993 (Table III-18); 1990 was excluded because of probable HCl contamination of bags used to hold snow samples. Owing to the dilute nature of snow, accurate pH measurements are difficult to obtain. Samples are easily contaminated (see Melack et al. 1997) and most of the year to year variability in the pH is probably caused by variability in sample handling, laboratory techniques (e.g., pH measurements made under argon vs air atmospheres, Melack et al. 1997) and instrument performance. Since winter snow accounts for the majority of water and hydrogen-ion deposition to the catchments, errors in pH can have large effects on estimates of hydrogen-ion loading. By using runoff as a surrogate, we eliminated errors introduced by unmelted snow, errors in pH measurements and variability caused by non-winter precipitation. Given these problems, we suggest that runoff may be a truer measure of the relative acid loading from year to year.

Since water volume is the dominant factor affecting solute export (in comparison to water chemistry), a strong correlation between runoff and export for all solutes could be expected. Indeed,  $r^2$  values greater than 0.90 were found for sulfate, most of the base cations and silicate at for all of the catchments (Figures III-26 and III-30). At Emerald Lake, the high correlation held true when data from water years 1995 and 1996 were included (Sickman, Leydecker and Melack, unpublished). However,  $r^2$  values between runoff and the export of other solutes were not as good (i.e., chloride, 0.84; potassium, 0.75; hydrogen-ion, 0.75). Furthermore, the relationships between runoff and nitrate at Emerald Lake, Crystal Lake and Pear Lake were not linear but rather log-linear. These findings show that solute export is not solely a linear function of runoff and indicates that variations in outflow chemistry can affect the relationship between annual runoff and export.

The runoff-export relationship for nitrate was unique among the solutes measured in this study. For the aggregate of the data, a weak, positive association is seen (Figure III-25). Much of scatter is due to the variable nature of nitrate utilization in the catchments. Low exports of nitrate were measured at the Crystal Lake and Lost Lake basins, a probable result of nitrogen-limited phytoplankton in the lakes. A log-linear function fit the data better in many cases (Figure III-26). At Topaz Lake there was no relationship whatsoever between nitrate export and runoff. The inter-catchment variability in the runoff-export relationship suggests that watershed processes exert a large degree of control on the export of nitrate and nitrogen dynamics vary considerably from catchment to catchment.

A significant ( $p < 0.01$ ) ln-linear fit was obtained for the relationship between runoff and nitrate export at Emerald Lake (Figure III-26). The  $r^2$  statistic for the best fit line was 0.88 and the equation for the function was:

$$\text{Nitrate Export} = 47.2 (\ln \text{Runoff}) - 269 \quad (10)$$

Equation (10) shows that nitrate export per unit discharge declines as runoff increases. Data from 1995 and 1996 closely match this regression and in fact increase  $r^2$  to 0.90.

One cause of the ln-linear association between nitrate export and runoff could be that nitrate utilization is highest during wet years. Following a wet winter, more water (and snowpack DIN) is available throughout the long, warm days of summer, for plant and microbe growth. It is likely that soil moisture becomes limiting to plant growth during the late summer and early autumn in drought years (Rundell et al. 1988). During droughts, water and snowpack DIN enter the catchments soils earlier in the year when temperatures are cold, days are shorter and vegetation is not actively growing. Under these conditions, nitrate from snowmelt would be more likely to pass through the catchments without being utilized. During wet years, warm temperatures, greater insolation, adequate soil moisture and high snowmelt inputs of N are contemporaneous and nitrate utilization is relatively high.

Other interpretations of the relationship between nitrate export and runoff depend on whether the nitrate exported from the catchments is primarily derived from the seasonal snowpack (i.e., atmospherically-derived) or is derived from catchments reservoirs e.g., soils, talus or groundwater (i.e., watershed-derived). If the snowpack is the primary source of exported nitrate then solute balances suggest that some of this nitrate must be produced by nitrification of snowpack ammonium. Nitrification of snowpack-ammonium could occur in the pack or, more likely, in catchment soils. If this is so, then lower nitrate export during wet years may be explained by depressed rates of nitrification in soils following wet-winters; in the spring and summer snow-covered soils are colder temperatures than snow-free soils. Lower temperatures could depress a biologically mediated process like nitrification and produce the export-runoff relationship modeled in Equation (10). However, given the fact that little or no ammonium is measured in stream waters during the snowmelt period, this hypothesis is unlikely. If biologically-mediated transformations of N are depressed by colder temperatures or snowcover, then un-utilized snowpack-ammonium should be found in surface runoff.

The log-linear relationship may, in itself, support the theory that most nitrate exported from the watersheds is derived from catchment sources. Decreased export of

nitrate at high runoff may be an indication that reservoirs of transportable nitrate were being depleted. A log-linear relationship would be expected from the dilution of, and export from, a finite pool of nitrate and, therefore, supports the inference that much of the exported nitrate was derived from catchment sources. In the next section nitrogen dynamics will be discussed and the source of the nitrate pulse examined in more detail.

### **3.3.6. Nitrogen Dynamics in High-elevation Watersheds**

Understanding the dynamics of nitrogen in Sierran catchments is fundamental to our understanding of how the chemistry of surface waters is influenced by watershed processes. Nitrogen supply not only substantially determines the productivity of terrestrial and aquatic ecosystems, it is also involved in the generation and consumption of hydrogen-ion and ANC in Sierran watersheds (Stoddard 1994, Williams et al. 1993). Atmospheric deposition of inorganic N to high elevations in the Sierra Nevada is usually less than 30% of nitrogen loading in the eastern United States or the Rocky Mountains (Melack et al. 1997; Williams et al. 1996a; Melack and Stoddard 1991), however, the oligotrophic nature of aquatic ecosystems in the Sierra Nevada makes them sensitive to nutrient inputs. Fertilization experiments conducted in mesocosms in Emerald Lake have shown that phytoplankton biomass and species composition are altered by varying inputs of N and P (Sickman 1991; Sickman and Melack 1992). In another Sierran lake, Lake Tahoe, atmospheric deposition of N has resulted in a shift from co-limitation of phytoplankton by N and P to persistent P limitation (Jassby et al. 1994). Nitrogen deposition in excess of uptake capacity has resulted in nitrogen saturation of terrestrial and aquatic ecosystems in forested watersheds in North America (Stoddard 1994, Sullivan et al. 1997, Aber et al. 1995), and evidence is growing that this process may be occurring in high elevation watersheds in the Colorado Front Range of the Rocky Mountains (Williams et al. 1996a). In light of these findings, we will discuss the nutrient status of Sierran lakes and provide information on how the watersheds interact with atmospheric deposition of nitrogen.

#### **3.3.6.1. Seasonal and Interannual Variations in Nitrate**

High nitrate concentrations at Topaz Lake during the period of late summer through the onset of snowmelt were not associated with nitrate-rich precipitation events or melting snow. The large annual range of nitrate concentrations at Topaz suggests that biological processes are largely responsible for the accumulation and release of nitrate during periods of low runoff, i.e., late autumn through onset of snowmelt. The shallow lake and extensive, seasonally flooded meadow at Topaz Lake likely accentuated the influence of biological processes. High nitrate concentrations during the autumn and winter seasons are probably the result of low N uptake by plants and relatively high rates of N mineralization and nitrification. While we have no direct measurements of these processes, studies in the Colorado Rockies have found that N mineralization and nitrification occur in snow-covered soils (Williams et al. 1996b; Brooks et al. 1996).

At Topaz Lake nitrate export occurred during the latter portion of the growing season during some years (i.e., 1991 and 1993), however, nitrate concentrations were typically low or below detection during late spring or early summer. In addition, peak nitrate concentrations during snowmelt were typically greater than nitrate concentrations

in the spring snowpack (i.e.,  $\sim 2 \mu\text{Eq L}^{-1}$  in snow vs. snowmelt peaks of 6 to  $40 \mu\text{Eq L}^{-1}$ , see Tables III-8 and Figure I-60). Thus, Topaz Lake falls somewhere between Stage 1 of nitrogen saturation (Stoddard 1994; chronic N export during non-growing season and  $[\text{snowpack NO}_3^-] < [\text{peak outflow NO}_3^-]$ ) and Stage 2 (chronic N export during growing season and  $[\text{snowpack NO}_3^-] < [\text{peak outflow NO}_3^-]$ ). However this classification may be inappropriate, since the nitrogen exported during the growing season was likely derived from catchment sources and not atmospheric deposition. At other lakes, during the period of 1990 through 1994, nitrate was exported only during non-growing seasons (primarily snowmelt) and hence would be classified as either Stage 0 (chronic N export during non-growing season and  $[\text{snowpack NO}_3^-] > [\text{peak outflow NO}_3^-]$ ) or Stage 1 of N saturation. Peak nitrate concentrations at Emerald ( $5\text{-}15 \mu\text{Eq L}^{-1}$ ), Marble Fork ( $6\text{-}7 \mu\text{Eq L}^{-1}$ ), Pear ( $7\text{-}10 \mu\text{Eq L}^{-1}$ ), Ruby ( $7\text{-}12 \mu\text{Eq L}^{-1}$ ), and Spuller ( $10\text{-}13 \mu\text{Eq L}^{-1}$ ) would place them at Stage 1 since snowpack concentrations were lower. Lost and Crystal are Stage 0 watersheds since N exports were low and peak nitrate concentrations ( $\sim 2 \mu\text{Eq L}^{-1}$ ) were similar to levels in snow. Given the short growing season and sparse vegetation in the High Sierra and the possibility that much of the nitrate exported during snowmelt derives from catchment sources (Kendall et al. 1995), nitrogen export during non-growing seasons (i.e., Stages 0 and 1) probably represent a natural, undisturbed condition for most of these watersheds and suggests that the N saturation concept should not be strictly applied to all Sierran watersheds.

Prior to 1988, Emerald Lake was close to experiencing Stage 2 symptoms of nitrogen saturation since (1) nitrate export occurred year-round (2) peak outflow concentrations were  $>$  snow concentrations and (3) the catchment was a net sink for nitrogen deposition (Figure I-90 and III-12). After 1988, conditions at Emerald Lake shifted to Stage 1 of nitrogen saturation. As discussed in Chapter One, and in Sickman and Melack (1998) we believe the shift is due to greater retention of N in the terrestrial portions of the catchment. Analytical error and decreased N deposition have been ruled out. Periodic limitation of phytoplankton growth by nitrogen has become more common in Emerald Lake as a consequence of the shift to Stage 1. This conclusion is consistent with recent studies in forested watersheds in the northeastern U.S. (Mitchell et al. 1996) and high elevation catchments of the Alps (Sommaruga-Wögrath et al. 1997) where climate warming stimulated biological activity and demand for N, thereby decreasing nitrate levels in surface waters and lowering N export. A decline in nitrate concentration in Log Creek which was contemporaneous with changes seen in Emerald Lake supports the hypothesis that N dynamics in the Sierra Nevada are susceptible to climate forcings.

### 3.3.6.2. Sources of Nitrate to Surface-waters

One of the most pronounced features of the nitrogen cycle in Sierran watersheds is the release of nitrogen from the snowpack and its transport out of the catchments during snowmelt. Specifically the ionic pulse of nitrogen that occurs on the rising limb of the snowmelt hydrograph is a poorly understood feature of the nitrogen budget. Two possible mechanisms have been invoked to explain the ionic pulse of nitrate. In the first, atmospherically derived nitrate is preferentially eluted from the snowpack and transported to streams during the first fractions of snowmelt. This explanation has been used at Emerald Lake by Williams et al. (1993 and 1995) to explain the ionic pulse of nitrate. As

a further refinement, William et al. (1995) postulated that ammonium in the snowpack is rapidly nitrified in the snowpack and soils and represents a significant percentage of the nitrate pulse in streams during snowmelt. In a second mechanism, microbially produced nitrate in the soil zone is flushed into streams by snowmelt waters. Recently this mechanism was tested at montane watersheds in the eastern U.S. and at Loch Vale watershed in the Rocky Mountain (Kendall et al. 1995). Using the oxygen and nitrogen isotopic compositions of nitrate, these researchers found that the ionic pulse of nitrate was derived primarily from watershed sources. They also found that nitrogen eluted from the snowpack appears to go into storage in catchment soils and/or vegetation.

In our study an ionic pulse of nitrate occurred in all the watersheds. For catchments in the Tokopah Valley, Ruby Lake and Spuller Lake the ionic pulse was found in both lake inflows and outflows. The pulse was muted or absent in outflowing waters from Lost and Crystal lakes, probably owing to uptake of nitrogen by phytoplankton during the snowmelt period. Despite conditions that appear unfavorable for phytoplankton growth, e.g., ice-cover, low-light intensity and cold temperature, phytoplankton blooms have been documented in other ice-covered montane lakes (Spaulding et al. 1992, Sickman 1991). Therefore, it is likely that depressed levels of nitrogen in these lakes during snowmelt are partly the result of biological uptake. Inflowing waters to Lost and Crystal lakes did, however, indicate a nitrate pulse from the watershed; peak concentrations ranged from 5 to 10  $\mu\text{Eq L}^{-1}$ . The concentrations of nitrate in the inflowing waters to the lakes were of similar magnitude to one another and to values measured at Emerald Lake during 1986 and 1987. Concentrations of nitrate in the outflows during the pulse were variable owing to differences in the rates of nitrogen utilization in the lakes (Chapter One). For example, peak nitrate values during the annual pulse at Spuller Lake outflow were 2 to 3 times greater than concentrations measured at the Topaz Lake outflow. Thus, the ionic pulse of nitrate appear to be a universal characteristic of Sierran watersheds, but lake processes appear to alter the timing and magnitude of the pulse.

Solute balances from 1990 through 1994 indicate that the study catchments are net sinks for nitrate most years and for DIN (ammonium + nitrate) in all years (Figure III-12). A relatively small yield of nitrate was found in 4 of the 36 water years in our study. Of these years, two were at Emerald Lake (1986, 1993), one was at Ruby (1993) and one was at Spuller (1993). The finding that on an annual basis nitrate is retained in the catchments supports the atmospheric-source theory since it indicates that most of the nitrate leaving the watersheds can be accounted for snowpack storage. Indeed, if non-winter dry deposition of nitrate (estimated from the Wolverton NOAA station:  $\sim 41$  moles  $\text{ha}^{-1}$ ) is added, net retention of nitrate occurred in all cases. However, when solute balance calculations are done for sequential portions of the snowmelt period, there is insufficient snowpack nitrate to explain the observed export.

We have computed separate solute balances for the rising and falling periods of the snowmelt hydrographs for 1993 and 1986 at Emerald Lake (Tables III-26 and III-27). These years were chosen because (1) they had positive nitrate yield, (2) they had abundant runoff and (3) the chemistry of outflow was measured frequently. The balances show that nitrate transported from the catchment during the rise of the hydrograph exceeded the entire nitrate pool in the snowpack. For example, during the rise of snowmelt in 1986, 6.4

kiloequivalents (kEq) of nitrate were transported from the Emerald Lake catchment. Using published data on SWE and snow chemistry (Williams and Melack 1991) we estimated that the pool of nitrate in the entire snowpack at maximum accumulation was less than 5.2 kEq. Similarly, in 1993 nitrate export from the Emerald Lake watershed was 4.9 kEq while the snowpack reservoir was 4.7 kEq. No major rain-on-snow events occurred during the snowmelt seasons of 1986 and 1993. The data clearly show that even if the entire nitrate content of the snowpack were preferentially eluted it would not be sufficient to explain the output of nitrate from the catchment during the hydrograph rise. If rapid nitrification of snowpack ammonium takes place (within catchment soils or the snowpack), there is sufficient nitrogen to explain the ionic pulse. However, there is no direct evidence that snowpack ammonium is nitrified during snowmelt or that nitrification of ammonium would dominate over sequestration of ammonium by vegetation, microbes and phytoplankton in the catchments. Recent work by Williams et al. (1996) in the Rocky Mountains found no evidence of nitrification in high-elevation snowpacks and ammonium in snowmelt was rapidly immobilized in underlying soils.

In earlier work conducted at Emerald Lake, Williams et al. (1995) stated that DIN released from the snowpack (4.8 kEq; determined from snow lysimeters) was congruent with the amount of DIN transported in inflow streams (4.6 kEq) to the lake during the period of May 5 to June 27, 1986. This finding strongly suggested and was presented as evidence, that the atmospheric-source mechanism, coupled with nitrification of snowmelt-ammonium in soils, explained the nitrate pulse at Emerald Lake. However, these estimates must be carefully examined since they are based on imprecise measurements of inflow discharge and basin-wide melt rates estimated from just 5 small, snow lysimeters. Moreover, solute-balance calculations indicate that 6.2 kEq of DIN was transported out of the catchment (via the lake outflow) during this same period (nitrate concentrations in the lake were equal to or less than levels in inflowing waters). Previous studies of Emerald Lake (Melack et al. 1989) have demonstrated that, during snowmelt, the lake and lake sediments do not contribute to nitrogen exports from the basin. Assuming that the lysimeters provided a reasonable estimate of DIN release from the snowpack, 1.4 kEq or ~25% of N export are unaccounted for, suggesting a watershed source for much of the nitrate in the ionic pulse at the Emerald Lake catchment.

Another problem with the atmospheric-source theory is the lack of large-scale changes in bulk snow chemistry during snowmelt. If preferential elution of ammonium and nitrate were of sufficient magnitude to account for nitrate efflux during snowmelt, then the volume-weighted mean concentration of DIN in the snowpack would decrease markedly. Data from snowpit samples collected as melt progressed (Melack et al. 1997) and similar data from Williams et al. (1995) indicate that the DIN concentration of the snowpack remains relatively constant or decreases only slightly. It is possible that rain-on-snow events may mask the expected decrease; rainfall during snowmelt was found to significantly alter bulk snow chemistry and stream chemistry during 1987 but this phenomenon did not occur in 1986 or 1993. Preferential elution of anions no doubt occurs, but given the spatial and temporal variability of snowmelt in the study catchments it cannot be the only cause of the nitrate ionic-pulse in the Sierra Nevada.

If most of the nitrate exported from Sierran watersheds is catchment derived, where is the nitrate stored and how is it produced? Soil water collected from five sites in

the Emerald basin had low concentrations of nitrate and ammonium prior to and after snowmelt (Williams et al. 1994). Low nitrate concentrations in soil waters prior to melt could be the result of low free-water content in these soils. In contrast, concentrations of nitrate in shallow soil solutions on a ridge in the Emerald basin exceeded  $70 \mu\text{Eq L}^{-1}$  for two consecutive weeks during peak snowmelt runoff in 1987. These nitrate levels are similar to those found in the lake and outflow at Topaz watershed (50 to ca.  $200 \mu\text{Eq L}^{-1}$ ) during baseflow periods in the autumn and winter. The source for this nitrate could not be from preferential elution from the snowpack or precipitation events. At Emerald the highest nitrate and ammonium concentrations measured in snow lysimeters were  $28 \mu\text{Eq L}^{-1}$ . Assuming immobilization of ammonium, nitrate concentrations in snowmelt cannot account for the high soil-water concentrations found in 1987 and one must conclude that the majority of nitrate found in these samples was derived from catchment sources.

Low nitrate concentrations in soil-water following snowmelt is likely the result of biological uptake and storage within the terrestrial portion of the catchment. Large areas of talus have been previously ignored a reservoirs of nitrate in the Emerald Lake basin. In fact, talus fields have recently been identified as potentially large sources of nitrate in alpine catchments of the Rocky Mountains (Campbell et al. 1995). Given the large percentage of talus in the catchments of our study, it is not unreasonable to think that they play a role in the nitrogen cycle in the Sierra Nevada.

Other evidence to support the watershed-derived mechanism comes from a sequence of 1994 storms in the Tokopah Valley. Following a very dry summer, a series of large rain and snow events occurred in during late September and early October. Daily samples of stream chemistry were collected at the Marble Fork gauging station; the first sample was collected about 24 hours after the start of the rain storm. Precipitation chemistry and quantity were measured over the same period at Emerald Lake. Following the storm, pH and ANC in the Marble Fork declined precipitously as did sulfate and the base cations (Figures III-32 through III-34). In contrast, nitrate levels increased markedly. The peak nitrate concentration in the Marble Fork was  $55 \mu\text{Eq L}^{-1}$  (nearly 24 hours after the first rain event) and nitrate in the precipitation was less than  $30 \mu\text{Eq L}^{-1}$ . After this storm, runoff and nitrate levels in the river decreased rapidly. A modest snowfall then occurred in the basin which very quickly began to melt (the nitrate concentration of the snow was less than  $10 \mu\text{Eq L}^{-1}$ ). The time series of nitrate concentration and stream discharge during the next 10 days was an excellent match to the concentration-discharge relationship found during the spring snowmelt season. On the rising limb of the autumn-snowmelt hydrograph, nitrate concentrations increased from 14 to  $25 \mu\text{Eq L}^{-1}$ , peaking just prior to maximum runoff. After the nitrate peak, levels gradually decreased to less than  $10 \mu\text{Eq L}^{-1}$ .

High nitrate levels immediately after the original rain-storm are likely the result of dry deposition being washed off of catchment surfaces and into streams. Elevated nitrate concentrations during the autumn-snowmelt event, however, closely matched nitrate peaks measured in inflowing streams of the study catchments (i.e., peak values of 20 to  $30 \mu\text{Eq L}^{-1}$ ) during spring snowmelt and are caused by a different mechanism. Preferential elution of nitrate from the autumn snowpack may explain the observed nitrate pattern, but there is strong evidence that it does not. Mechanistically, preferential elution is thought to be the result of melt-freeze cycles that cause the outer coating of snow-crystals to become

enriched with solutes (Bales 1992). These coatings are then "washed" from the snowpack during the first release of water from the snowpack. However, this process could not have occurred following the autumn snowstorm because nitrate levels climbed, and snowmelt began, immediately after the storm ended. There was simply no time for melt-freeze cycles to create enriched coatings on ice crystals. More likely, nitrate that was stored in soil solution or other catchment sinks was flushed from the watershed by the melting snow, causing the nitrate pulse. Whether this watershed-derived nitrate was the result of the previous rainstorm or from microbially-produced nitrate is inconsequential to this conclusion. The ionic pulse of nitrate in this autumn-snowmelt phenomenon was derived primarily from nitrate stored in the catchment and not from preferential elution of nitrate in the snowpack.

### 3.4. Conclusions

The volume-weighted mean chemistry of the solute balance components, (winter snowfall, lake outflow and non-winter precipitation) was calculated as the product of chemical concentrations and water fluxes. Dry deposition was not directly quantified, but was measured as part of winter precipitation for the months of December through March. Non-winter dry deposition was ignored for logistical reasons. Snow chemistry was dilute and very similar among the eight study catchments. Samples from the spring snowpack had pH levels typically between 5.3 and 5.6 with an overall mean value of 5.42. After hydrogen-ion, the most abundant ions in solution were compounds of nitrogen, ammonium and nitrate, with mean concentrations of 2.7 and 2.4  $\mu\text{Eq L}^{-1}$ , respectively. Sulfate concentrations in winter snow were slightly lower: 1.0 to 3.0  $\mu\text{Eq L}^{-1}$  (overall mean, 2.0  $\mu\text{Eq L}^{-1}$ ). Of the remaining solutes, only calcium and sodium were found in levels much above the detection limit (mean values: 1.7 and 1.3  $\mu\text{Eq L}^{-1}$ , respectively). Organic anions (acetate and formate) were difficult to measure in snow and were usually found only at low concentrations (mean concentrations ca. 0.5  $\mu\text{Eq L}^{-1}$ ). The solutes that showed the most variability among years and among sites were potassium and the organic anions; acetate and formate. The most consistent solutes in snow during the study were hydrogen-ion and sulfate. Mean annual snowfall during the study was 1027 mm of water equivalence.

Non-winter precipitation (i.e., rain and snow from ca. April through November) varied considerably with respect to chemistry and quantity. Solute concentrations ranged from near detection limits to tens of microequivalents per liter. Most of the variability was due to the timing of the precipitation: spring and autumn storms were the most dilute and summer rains were relatively enriched with solutes. Thus the annual volume-weighted mean concentration of non-winter precipitation depended on the mix of samples obtained. The mean pH of non-winter precipitation in the study was 4.93. Ammonium and nitrate concentrations were 8 to 9 times greater in non-winter precipitation than in winter snowfall (mean values, 23.4 and 20.7  $\mu\text{Eq L}^{-1}$ , respectively). Ammonium levels were usually higher than nitrate, with both nitrogen ions exceeding the mean concentration of sulfate (15.1  $\mu\text{Eq L}^{-1}$ ). The mean chloride level measured in non-winter precipitation was 4.2  $\mu\text{Eq L}^{-1}$  which was only slightly higher than concentrations in winter snowfall. After ammonium and hydrogen-ion the next most abundant cations in non-winter precipitation were calcium (mean, 10.4  $\mu\text{Eq L}^{-1}$ ) and sodium (4.6  $\mu\text{Eq L}^{-1}$ ). In contrast to winter snow,

organic anions were abundant in non-winter precipitation. Mean values for acetate and formate were on the order of 7 to 9  $\mu\text{Eq L}^{-1}$ . The average annual flux of water during non-winter periods of our study was 117 mm.

Precipitation intercepted by Sierran catchments is greatly altered by geochemical processes before exiting the catchments as streamflow. High rates of nitrogen deposition were measured in the study catchments (mean annual nitrogen deposition was 95.6 Eq  $\text{ha}^{-1}$ ). Biological processes and other sinks within the watersheds consumed the large majority of these nutrient inputs. Ammonium was rarely found at detectable levels in outflow streams in our study. Nitrate concentrations were typically higher, but in most cases the input-output budgets showed a net retention of nitrate in the catchments. During most years the majority of nitrogen deposition occurred during non-winter periods.

Hydrogen-ion deposition was also substantial in these catchments and winter snowfall was the main contributor. These inputs were effectively neutralized by the catchments and, on average, the basins consumed 86.7% of the hydrogen-ions deposited in them. Catchments in the eastern Sierra Nevada had significantly ( $p < 0.05$ ) higher outflow ANC and neutralized a higher percentage of acid inputs than did basins in the Tokopah Valley or the Lost Lake watershed. This suggests that watersheds along the eastern slope of the Sierra Nevada may be less susceptible to harm from acid deposition. Since precipitation chemistry varies little from site to site in the Sierra Nevada (Melack et al. 1997), the differences in acid-sensitivity observed among the catchments in our study are due to differences in catchment features such as soils, geology, hydrologic flowpaths (e.g., the predominance of groundwater) and vegetation. Processes, principally mineral weathering and biological uptake of nitrogen, changed the chemical make-up of precipitation so that streamwaters exiting the catchments were a solution composed primarily of ANC (i.e.,  $\text{HCO}_3^-$  or bicarbonate), calcium and dissolved silica.

Research conducted in high elevation watersheds of the Sierra Nevada during the last two decades indicates these ecosystems are potentially sensitive to increased nutrient loading and climatic perturbations (Sickman and Melack 1998). Drought conditions in the Sierra Nevada were probably responsible for increasing the proportion of runoff derived from shallow groundwater in the Ruby Lake basin as evidenced by increased sulfate concentrations (see Chapter One). Climate forcing may also be responsible for increased retention of N in the Emerald Lake catchment. In the Emerald Lake basin, long-term monitoring has revealed a decrease in annual nitrate maxima and minima with a concomitant shift of the lake's phytoplankton community from phosphorus limitation towards nitrogen limitation. These findings supports recent evidence that N uptake in alpine catchments may increase due to climate warming and runs counter to the recent shift of Lake Tahoe to P limitation of phytoplankton. At Emerald Lake, decreases in nitrate represent a shift from Stage 2 to Stage 1 of nitrogen saturation and is a counter example to lakes and streams in the Front Range of the Rocky Mountains. Based on nitrate peaks during snowmelt and nitrate levels in snow, most of the catchments in our study are experiencing Stage 1 symptoms of N-saturation. However, given the severe limitations placed on plant and microbial metabolism (e.g., deep snowpacks, short growing seasons etc..) the traditional concept of N-saturation should not be strictly applied to the High Sierra Nevada, especially since its framework was developed for forested catchments in the eastern U.S..

Further study is needed to accurately describe nitrogen dynamics in high elevation catchments of the Sierra Nevada. A first step would be to partition the nitrate pulse into its source components: snowpack and watershed. To do this, the nitrogen and oxygen isotopic composition of nitrate can be used to apportion nitrate in streams into its source waters, i.e., precipitation or ground/soil water (Kendall et al. 1995). Transformations of nitrogen that occur in the watersheds and particularly during snowmelt are poorly understood. To investigate these processes, a catchment-scale or plot-scale isotopic enrichment experiment should be done. The catchment or plot would need to be small, with a well defined drainage area and have accurately gauged outflow. In this type of experiment, the drainage or plot is spiked with a sufficient quantity of  $^{15}\text{N}$  labeled nitrogen to substantially alter the isotopic composition of nitrogen in the catchment. Surface and soil waters and vegetation would be sampled intensively during the experiment to measure the progression of the  $^{15}\text{N}$  labeled nitrogen through the biotic and abiotic systems of the catchment. Gauging catchment outflow allows a quantitative assessment of the transformations and retention of ammonium and nitrate. A combination of enrichment experiments, analysis of the nitrogen and oxygen isotopes of nitrate and the detailed mass balance studies of the seasonal snowpack and catchment would provide a more complete picture of nitrogen dynamics in seasonally snow-covered regions in the Sierra Nevada.

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Table III-1. Sources of non-winter precipitation data used in solute and water balances for water years 1990 through 1994. Precipitation gauge location identifies the primary site where non-winter precipitation was measured for each watershed. Precipitation collector location identifies the site where precipitation chemistry for each watershed was determined. Alternate station is a backup gauge used to fill in gaps in the primary rain gauge record caused by instrument malfunction. Source for April, May and November precipitation list the station locations used to estimate precipitation at each watershed during spring and late autumn when the tipping bucket gauges were not operated. The following abbreviations are used:

- MLRS - U.S. Forest Service Ranger Station, Mammoth Lakes, California
- LMS - Lake Mary store, Mammoth Lakes California
- LPRS - U.S. National Park Service Ranger Station, Lodgepole, Sequoia N.P.
- SB - Snowboard within watershed
- SP - Snowpit within watershed
- EML - Emerald Lake

At the two ranger stations and the Lake Mary store, precipitation was measured in a U.S. Forest Service approve rain/snow gauge (Belfort). Eastern Brook Lake and the Carnegie Station are part of the Alpine Deposition Monitoring network operated by UCSB. Eastern Brook Lake is located in the Rock Creek Canyon, approximately 4 km and 220 meters lower than the outlet to Ruby Lake. The Carnegie Station is located about 3 km north of and 140 meters lower than Spuller Lake.

Watershed	Precip. Gauge Location	Precip. Collector Location	Alternate Station for Gauge	Source for April, May, November Precip.
Crystal	Lake outlet	Mammoth Mt.	Mammoth Mt.	MLRS, LMS
Emerald	Lake inlet	Lake inlet	Topaz Lake	SB, SP, LPRS
Lost	Angora Lake	Angora Lake	None	None
Marble Fork	Emerald Lake	Emerald Lake	Topaz Lake	EML, LPRS
Pear	Emerald Lake	Emerald Lake	Topaz Lake	EML, LPRS
Ruby	Lake outlet	Eastern Brook LK.	Mammoth Mt.	MLRS, LMS
Spuller	Lake outlet	Carnegie Station	Mammoth Mt.	MLRS, LMS
Topaz	Lake outlet	Emerald Lake	Emerald Lake	EML, LPRS



Table III-2. Summary of unsampled rain and snow included in the solute balances for the study catchments. The amounts are expressed as a percentage of total non-winter precipitation (rain) and total winter precipitation (snow). For any watershed, chemistry for unsampled snow that fell after the spring snow-survey was estimated to equal the volume-weighted mean chemistry from the spring snowpack at that catchment. Similarly, for any watershed, chemistry of unsampled rain that fell during the period of ~May through October was estimated to equal the volume-weighted mean chemistry for non-winter precipitation at that catchment. The relatively high percentages of unsampled rain in water year 1990 are due to the fact that rain chemistry from the autumn of 1989 was unavailable. Note: no unsampled rain or snow was estimated from alternate sites for Lost Lake. All precipitation that fell during 1985 through 1987 at Emerald Lake was sampled (Williams and Melack 1991)

<b>Unsampled Rain:</b>					
	1990	1991	1992	1993	1994
Crystal	71%	5.7%	0.0%	0.0%	-
Emerald	51%	0.0%	2.9%	0.0%	0.0%
Marble Fork	51%	0.0%	0.0%	0.0%	0.0%
Pear	51%	0.0%	0.0%	0.0%	-
Ruby	53%	32%	18%	0.0%	31%
Spuller	30%	19%	0.0%	0.0%	32%
Topaz	51%	0.0%	0.0%	0.0%	-

<b>Unsampled Snow:</b>					
	1990	1991	1992	1993	1994
Crystal	6.7%	4.7%	2.0%	4.9%	-
Emerald	2.6%	5.5%	4.2%	0.0%	20%
Marble Fork	2.6%	5.5%	4.2%	0.0%	20%
Pear	2.2%	5.9%	5.0%	0.0%	-
Ruby	2.7%	5.4%	1.0%	1.0%	9.0%
Spuller	6.8%	3.9%	0.0%	0.8%	6.3%
Topaz	2.8%	6.6%	5.0%	0.0%	-

Table III-3. Number of outflow samples collected during snowmelt in the eight study catchments. Snowmelt was defined as the period from March 1 through August 31. Data followed by an asterisk were derived from samples collected by an ISCO automated stream sampler.

Catchment	1985	1986	1987	1990	1991	1992	1993	1994
Crystal	-	-	1	15	11	7	18	-
Emerald	15	21	27	9	11	13	95*	85*
Lost	-	-	-	9	9	12	70*	-
Pear	-	-	3	7	7	10	17	2
Ruby	-	-	5	12	13	10	14	5
Spuller	-	-	-	11	11	9	14	5
Topaz	-	-	3	7	8	8	24*	2
Marble Fork	-	-	-	-	-	-	16	52*

Table III-4. Summary of statistical analyses of VWM outflow chemistry from 1990 through 1993. For each catchment, data from all years were combined for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate differences ( $p < 0.05$ ) among catchments. Catchments not sharing letter designations are statistically different and the differences are ranked by their letter designations, i.e.,  $a < b < c$  etc.. Data from 1994 were not available for all study sites and therefore this year was not included in the analyses. Marble Fork data were only available for 1993 and 1994 and are also not included in the analyses.

Solute	Crystal	Emerald	Lost	Pear	Ruby	Spuller	Topaz
H <sup>+</sup>	a	ab	b	ab	a	ab	a
ANC	e	a	a	a	d	c	b
NH <sub>4</sub> <sup>+</sup>	a	ab	a	b	a	a	ab
Cl <sup>-</sup>	a	a	a	a	a	a	a
NO <sub>3</sub> <sup>-</sup>	a	b	a	b	b	b	a
SO <sub>4</sub> <sup>2-</sup>	a	a	a	a	b	b	a
Ca <sup>2+</sup>	c	a	a	a	d	c	b
Mg <sup>2+</sup>	c	a	a	a	ab	b	b
Na <sup>+</sup>	c	b	a	a	b	ab	ab
K <sup>+</sup>	d	a	a	a	c	a	bc
Silicate	c	b	ab	a	b	b	b

Table III-5. Summary of statistical analyses of VWM snow chemistry from 1990 through 1993. For each catchment, data from all years were combined for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among catchments. Catchments not sharing letter designations are statistically different and the differences are ranked by their letter designations, i.e.,  $a < b < c$  etc.. Letters in parenthesis indicate significant differences at  $p < 0.1$  level. Data from 1994 were not available for all study sites and therefore this year was not included in the analyses. Marble Fork data were only available for 1993 and 1994 and are also not included in the analyses.

Solute	Crystal	Emerald	Lost	Pear	Ruby	Spuller	Topaz
H <sup>+</sup>	a	a	a	a	a	a	a
NH <sub>4</sub> <sup>+</sup>	a	a	a	a	a	a	a
Cl <sup>-</sup>	a	a	a	a	a	a	a
NO <sub>3</sub> <sup>-</sup>	a	a	a	a	a	a	a
SO <sub>4</sub> <sup>2-</sup>	(b)	(a)	(a)	(a)	(a)	(a)	(a)
Ca <sup>2+</sup>	a	a	a	a	a	a	a
Mg <sup>2+</sup>	b	a	a	a	a	a	a
Na <sup>+</sup>	a	a	a	a	a	a	a
K <sup>+</sup>	a	a	a	a	a	a	a
Acetate	a	a	a	a	a	a	a
Formate	a	a	a	a	a	a	a

Table III-6. Volume-weighted mean (VWM) concentration of solute balance components for Emerald Lake, water years 1985 through 1994. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Data from 1985, 1986 and 1987 are from Williams and Melack (1991). The approximate standard error of the means is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
85 RAIN	8.6 (0.3)	0.0 (NA)	24.4 (1.2)	5.9 (0.1)	17.9 (0.3)	12.6 (0.7)	10.4 (0.1)	1.6 (0.1)	4.9 (0.5)	1.9 (0.1)	0.0 (NA)	NA (NA)	NA (NA)
85 SNOW	5.3 (0.2)	0.0 (NA)	0.9 (0.0)	4.0 (0.2)	2.3 (0.1)	3.0 (0.2)	2.2 (0.2)	0.7 (0.0)	1.9 (0.1)	0.9 (0.0)	0.0 (NA)	NA (NA)	NA (NA)
85 OUTFLOW	0.6 (0.1)	25.7 (2.5)	0.2 (0.1)	2.3 (0.4)	6.8 (1.5)	5.7 (0.4)	20.4 (2.1)	4.0 (0.4)	10.5 (0.9)	3.0 (0.3)	32.0 (2.9)	0.0 (NA)	0.0 (NA)
85 LOADING	5.6 (0.2)	0.0 (NA)	3.0 (0.2)	4.2 (0.2)	3.7 (0.1)	3.9 (0.3)	2.9 (0.2)	0.8 (0.1)	2.2 (0.2)	1.0 (0.1)	0.0 (NA)	NA (NA)	NA (NA)
86 RAIN	7.8 (0.2)	0.0 (NA)	22.0 (1.1)	4.4 (0.1)	15.5 (0.3)	10.9 (0.6)	8.2 (0.1)	1.3 (0.1)	3.2 (0.3)	1.5 (0.1)	0.0 (NA)	NA (NA)	NA (NA)
86 SNOW	4.6 (0.1)	0.0 (NA)	1.4 (0.1)	3.1 (0.2)	1.8 (0.0)	1.6 (0.1)	0.6 (0.0)	0.3 (0.0)	1.4 (0.1)	0.8 (0.0)	0.0 (NA)	NA (NA)	NA (NA)
86 OUTFLOW	1.3 (0.2)	20.6 (2.7)	0.1 (0.0)	3.1 (0.4)	4.9 (0.6)	5.3 (0.3)	20.6 (2.0)	3.7 (0.3)	9.5 (1.0)	2.1 (0.2)	29.1 (3.0)	0.0 (NA)	0.0 (NA)
86 LOADING	4.9 (0.2)	0.0 (NA)	3.3 (0.2)	3.2 (0.2)	3.0 (0.1)	2.4 (0.2)	1.3 (0.1)	0.4 (0.0)	1.6 (0.2)	0.9 (0.1)	0.0 (NA)	NA (NA)	NA (NA)
87 RAIN	12.4 (0.4)	0.0 (NA)	61.1 (3.1)	8.4 (0.1)	45.8 (0.9)	39.8 (2.3)	22.0 (0.2)	4.8 (0.2)	15.5 (1.6)	3.4 (0.2)	0.0 (NA)	13.1 (0.9)	13.1 (0.9)
87 SNOW	4.6 (0.1)	0.0 (NA)	3.8 (0.2)	1.5 (0.1)	4.2 (0.1)	2.9 (0.2)	1.8 (0.1)	1.1 (0.1)	0.7 (0.0)	0.4 (0.0)	0.0 (NA)	0.5 (0.1)	0.3 (0.0)
87 OUTFLOW	0.9 (0.1)	28.8 (2.4)	0.1 (0.0)	4.0 (0.3)	7.8 (0.6)	7.0 (0.3)	24.9 (1.5)	4.7 (0.2)	11.7 (0.9)	4.6 (0.3)	26.3 (1.1)	0.0 (NA)	0.0 (NA)
87 LOADING	6.1 (0.3)	0.0 (NA)	14.7 (1.0)	2.8 (0.2)	12.1 (0.4)	9.9 (0.8)	5.6 (0.4)	1.8 (0.1)	3.5 (0.4)	1.0 (0.1)	0.0 (NA)	2.9 (0.4)	2.7 (0.3)
90 RAIN	5.1 (1.3)	0.0 (NA)	11.8 (3.1)	3.7 (0.9)	16.5 (4.2)	13.5 (3.5)	9.6 (2.4)	2.5 (0.6)	3.9 (1.1)	4.5 (1.2)	0.0 (NA)	NA (NA)	NA (NA)
90 SNOW	4.7 (0.1)	0.0 (NA)	4.6 (0.2)	2.1 (0.1)	2.6 (0.1)	2.6 (0.1)	1.3 (0.1)	0.6 (0.0)	1.8 (0.1)	0.5 (0.0)	0.0 (NA)	1.0 (0.1)	0.4 (0.0)
90 OUTFLOW	0.8 (0.1)	24.8 (2.4)	0.3 (0.1)	4.1 (0.4)	4.5 (0.5)	6.9 (0.3)	19.5 (1.5)	3.4 (0.2)	12.7 (0.9)	2.8 (0.2)	36.2 (1.7)	0.0 (NA)	0.0 (NA)
90 LOADING	4.8 (1.2)	0.0 (NA)	6.2 (1.6)	2.4 (0.6)	5.6 (1.4)	5.0 (1.3)	3.1 (0.8)	1.0 (0.3)	2.3 (0.6)	1.4 (0.4)	0.0 (NA)	NA (NA)	NA (NA)
91 RAIN	8.8 (0.3)	0.0 (NA)	67.4 (3.4)	5.3 (0.1)	36.1 (0.7)	23.8 (1.4)	14.6 (0.1)	5.6 (0.2)	4.5 (0.5)	6.1 (0.3)	0.0 (NA)	11.0 (0.8)	19.6 (1.4)
91 SNOW	3.3 (0.1)	0.0 (NA)	2.9 (0.1)	1.2 (0.1)	1.7 (0.0)	1.2 (0.1)	1.1 (0.1)	0.4 (0.0)	1.0 (0.1)	0.3 (0.0)	0.0 (NA)	0.2 (0.0)	0.3 (0.0)
91 OUTFLOW	1.7 (0.3)	22.7 (1.9)	0.1 (0.1)	3.0 (0.6)	5.6 (0.8)	6.8 (0.4)	17.5 (1.7)	3.5 (0.2)	12.6 (1.1)	3.0 (0.2)	34.8 (2.1)	0.0 (NA)	0.0 (NA)
91 LOADING	3.8 (0.2)	0.0 (NA)	8.3 (0.6)	1.5 (0.1)	4.6 (0.2)	3.1 (0.2)	2.2 (0.2)	0.8 (0.1)	1.3 (0.1)	0.8 (0.1)	0.0 (NA)	1.1 (0.1)	1.9 (0.2)
92 RAIN	3.5 (0.1)	0.0 (NA)	11.6 (0.6)	3.6 (0.1)	14.1 (0.3)	12.6 (0.7)	5.2 (0.1)	1.3 (0.1)	4.9 (0.5)	2.5 (0.1)	0.0 (NA)	5.7 (0.4)	4.0 (0.3)
92 SNOW	2.8 (0.1)	0.0 (NA)	3.4 (0.2)	1.7 (0.1)	3.0 (0.1)	1.9 (0.1)	2.5 (0.2)	0.5 (0.0)	0.9 (0.0)	0.1 (0.0)	0.0 (NA)	0.6 (0.1)	0.6 (0.1)
92 OUTFLOW	0.6 (0.1)	26.0 (1.8)	0.2 (0.1)	2.6 (0.2)	3.6 (0.4)	5.8 (0.2)	21.3 (1.2)	3.8 (0.2)	12.0 (0.8)	2.6 (0.2)	31.6 (4.2)	0.0 (NA)	0.0 (NA)
92 LOADING	2.9 (0.1)	0.0 (NA)	5.2 (0.4)	2.1 (0.1)	5.4 (0.2)	4.2 (0.3)	3.1 (0.2)	0.7 (0.0)	1.8 (0.2)	0.6 (0.0)	0.0 (NA)	1.7 (0.2)	1.3 (0.2)
93 RAIN	4.8 (0.1)	0.0 (NA)	5.8 (0.3)	0.9 (0.0)	5.4 (0.1)	4.1 (0.2)	1.0 (0.0)	0.2 (0.0)	0.8 (0.1)	0.5 (0.0)	0.0 (NA)	2.1 (0.1)	4.7 (0.3)
93 SNOW	5.2 (0.2)	0.0 (NA)	2.2 (0.1)	1.9 (0.1)	1.8 (0.0)	2.4 (0.1)	0.9 (0.1)	0.5 (0.0)	0.9 (0.0)	0.3 (0.0)	0.0 (NA)	0.6 (0.1)	0.2 (0.0)
93 OUTFLOW	0.7 (0.0)	21.0 (1.8)	0.5 (0.1)	2.2 (0.2)	4.6 (0.3)	6.0 (0.2)	17.2 (1.2)	3.5 (0.2)	10.0 (0.7)	3.0 (0.4)	30.4 (1.2)	0.0 (NA)	0.0 (NA)
93 LOADING	5.2 (0.2)	0.0 (NA)	2.5 (0.2)	1.8 (0.1)	2.1 (0.1)	2.5 (0.2)	0.9 (0.1)	0.5 (0.0)	0.9 (0.1)	0.3 (0.0)	0.0 (NA)	0.7 (0.1)	0.6 (0.1)
94 RAIN	5.5 (0.2)	0.0 (NA)	17.9 (0.9)	9.0 (0.1)	18.3 (0.3)	10.7 (0.6)	8.0 (0.1)	2.1 (0.1)	7.5 (0.8)	3.6 (0.2)	0.0 (NA)	2.5 (0.2)	3.8 (0.3)
94 SNOW	2.9 (0.1)	0.0 (NA)	3.5 (0.2)	2.1 (0.1)	2.7 (0.1)	1.5 (0.1)	2.6 (0.2)	0.5 (0.0)	1.4 (0.1)	0.6 (0.0)	0.0 (NA)	0.0 (0.0)	0.6 (0.1)
94 OUTFLOW	0.6 (0.0)	21.2 (1.1)	0.2 (0.0)	3.1 (0.2)	4.8 (0.3)	6.1 (0.2)	17.8 (0.8)	3.1 (0.2)	11.4 (0.7)	2.6 (0.1)	29.7 (0.8)	0.0 (NA)	0.0 (NA)
94 LOADING	3.2 (0.2)	0.0 (NA)	5.0 (0.4)	2.8 (0.2)	4.4 (0.2)	2.5 (0.2)	3.2 (0.3)	0.7 (0.1)	2.0 (0.2)	0.9 (0.1)	0.0 (NA)	0.3 (0.0)	0.9 (0.1)

Table III-7. Volume-weighted mean (VWM) concentration of solute balance components for Pear Lake, water years 1990 through 1993. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain chemistry is from Emerald Watershed. The approximate standard error of the means is given in parentheses.

YR/COMPONENT	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	5.1 (1.3)	0.0 (NA)	11.8 (3.1)	3.7 (0.9)	16.5 (4.2)	13.5 (3.5)	9.6 (2.4)	2.5 (0.6)	3.9 (1.1)	4.5 (1.2)	0.0 (NA)	NA (NA)	NA (NA)
90 SNOW	4.3 (0.1)	0.0 (NA)	4.1 (0.2)	2.2 (0.1)	2.2 (0.1)	2.7 (0.1)	1.0 (0.1)	0.5 (0.0)	1.7 (0.1)	0.3 (0.0)	0.0 (NA)	0.5 (0.1)	0.6 (0.1)
90 OUTFLOW	0.9 (0.1)	22.5 (1.6)	0.4 (0.3)	4.2 (0.3)	4.1 (1.5)	6.6 (0.3)	17.6 (1.0)	3.0 (0.2)	9.3 (0.7)	3.1 (0.2)	22.8 (1.6)	0.0 (NA)	0.0 (NA)
90 LOADING	4.5 (1.1)	0.0 (NA)	5.6 (1.5)	2.5 (0.6)	4.9 (1.3)	4.7 (1.3)	2.6 (0.7)	0.9 (0.2)	2.1 (0.6)	1.1 (0.3)	0.0 (NA)	NA (NA)	NA (NA)
91 RAIN	8.8 (0.3)	0.0 (NA)	67.4 (3.4)	5.3 (0.1)	36.1 (0.7)	23.8 (1.4)	14.6 (0.1)	5.6 (0.2)	4.5 (0.5)	6.1 (0.3)	0.0 (NA)	11.0 (0.8)	19.6 (1.4)
91 SNOW	3.6 (0.1)	0.0 (NA)	4.0 (0.2)	1.1 (0.1)	2.6 (0.1)	1.7 (0.1)	1.4 (0.1)	0.5 (0.0)	1.0 (0.1)	0.3 (0.0)	0.0 (NA)	0.5 (0.1)	1.1 (0.1)
91 OUTFLOW	1.7 (0.2)	20.0 (2.7)	0.4 (0.3)	3.4 (0.6)	6.1 (1.6)	6.6 (0.4)	17.6 (1.7)	3.4 (0.3)	9.5 (1.1)	3.5 (0.3)	23.0 (2.4)	0.0 (NA)	0.0 (NA)
91 LOADING	4.1 (0.2)	0.0 (NA)	9.6 (0.7)	1.5 (0.1)	5.6 (0.2)	3.7 (0.3)	2.6 (0.2)	1.0 (0.1)	1.3 (0.2)	0.8 (0.1)	0.0 (NA)	1.4 (0.2)	2.7 (0.3)
92 RAIN	3.5 (0.1)	0.0 (NA)	11.6 (0.6)	3.6 (0.1)	14.1 (0.3)	12.6 (0.7)	5.2 (0.1)	1.3 (0.1)	4.9 (0.5)	2.5 (0.1)	0.0 (NA)	5.7 (0.4)	4.0 (0.3)
92 SNOW	3.4 (0.1)	0.0 (NA)	3.8 (0.2)	1.2 (0.1)	2.9 (0.1)	1.9 (0.1)	1.4 (0.1)	0.4 (0.0)	1.1 (0.1)	0.2 (0.0)	0.0 (NA)	0.3 (0.0)	0.7 (0.1)
92 OUTFLOW	0.9 (0.2)	24.3 (1.8)	0.5 (0.3)	2.7 (0.3)	3.0 (0.8)	5.6 (0.2)	18.7 (1.2)	3.4 (0.2)	9.0 (0.7)	3.0 (0.2)	15.4 (4.3)	0.0 (NA)	0.0 (NA)
92 LOADING	3.4 (0.1)	0.0 (NA)	5.6 (0.4)	1.7 (0.1)	5.4 (0.2)	4.3 (0.3)	2.3 (0.2)	0.6 (0.0)	2.0 (0.2)	0.7 (0.0)	0.0 (NA)	1.5 (0.2)	1.4 (0.2)
93 RAIN	4.8 (0.1)	0.0 (NA)	5.8 (0.3)	0.9 (0.0)	5.4 (0.1)	4.1 (0.2)	1.0 (0.0)	0.2 (0.0)	0.8 (0.1)	0.5 (0.0)	0.0 (NA)	2.1 (0.1)	4.7 (0.3)
93 SNOW	3.3 (0.1)	0.0 (NA)	1.9 (0.1)	1.9 (0.1)	1.6 (0.0)	2.0 (0.1)	1.0 (0.1)	0.4 (0.0)	1.4 (0.1)	0.3 (0.0)	0.0 (NA)	0.6 (0.1)	0.2 (0.0)
93 OUTFLOW	1.5 (0.1)	17.4 (1.5)	0.6 (0.2)	1.9 (0.3)	2.7 (0.5)	5.5 (0.2)	14.5 (1.1)	2.8 (0.2)	6.2 (0.5)	2.3 (0.3)	20.5 (1.3)	0.0 (NA)	0.0 (NA)
93 LOADING	3.4 (0.1)	0.0 (NA)	2.2 (0.2)	1.8 (0.1)	1.9 (0.1)	2.2 (0.2)	1.0 (0.1)	0.4 (0.0)	1.3 (0.2)	0.3 (0.0)	0.0 (NA)	0.7 (0.1)	0.6 (0.1)

Table III-8. Volume-weighted mean (VWM) concentration of solute balance components for Topaz Lake, water years 1990 through 1993. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain chemistry is from Emerald Watershed. The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	5.1 (1.3)	0.0 (NA)	11.8 (3.1)	3.7 (0.9)	16.5 (4.2)	13.5 (3.5)	9.6 (2.4)	2.5 (0.6)	3.9 (1.1)	4.5 (1.2)	0.0 (NA)	NA (NA)	NA (NA)
90 SNOW	4.0 (0.1)	0.0 (NA)	3.2 (0.2)	2.0 (0.1)	2.4 (0.1)	2.3 (0.1)	0.7 (0.0)	0.4 (0.0)	1.5 (0.1)	0.5 (0.0)	0.0 (NA)	1.3 (0.1)	0.6 (0.1)
90 OUTFLOW	0.6 (0.1)	41.3 (3.8)	0.1 (0.0)	4.2 (0.5)	1.6 (0.5)	5.7 (0.7)	28.7 (2.7)	4.1 (0.4)	10.8 (1.4)	4.6 (0.5)	42.1 (3.8)	0.0 (NA)	0.0 (NA)
90 LOADING	4.3 (1.1)	0.0 (NA)	5.2 (1.4)	2.4 (0.6)	5.6 (1.4)	4.9 (1.3)	2.7 (0.7)	0.9 (0.2)	2.1 (0.6)	1.4 (0.4)	0.0 (NA)	NA (NA)	NA (NA)
91 RAIN	8.8 (0.3)	0.0 (NA)	67.4 (3.4)	5.3 (0.1)	36.1 (0.7)	23.8 (1.4)	14.6 (0.1)	5.6 (0.2)	4.5 (0.5)	6.1 (0.3)	0.0 (NA)	11.0 (0.8)	19.6 (1.4)
91 SNOW	3.9 (0.1)	0.0 (NA)	2.0 (0.1)	0.6 (0.0)	1.7 (0.0)	1.2 (0.1)	3.0 (0.2)	0.3 (0.0)	0.9 (0.0)	0.2 (0.0)	0.0 (NA)	0.6 (0.1)	0.8 (0.1)
91 OUTFLOW	1.2 (0.1)	34.9 (5.4)	0.2 (0.2)	3.1 (0.8)	2.8 (1.3)	6.0 (0.9)	26.5 (4.6)	4.8 (0.8)	10.6 (1.9)	4.7 (0.9)	29.1 (5.0)	0.0 (NA)	0.0 (NA)
91 LOADING	4.4 (0.2)	0.0 (NA)	8.4 (0.6)	1.1 (0.1)	5.1 (0.2)	3.4 (0.3)	4.1 (0.3)	0.8 (0.1)	1.3 (0.1)	0.8 (0.1)	0.0 (NA)	1.6 (0.2)	2.7 (0.3)
92 RAIN	3.5 (0.1)	0.0 (NA)	11.6 (0.6)	3.6 (0.1)	14.1 (0.3)	12.6 (0.7)	5.2 (0.1)	1.3 (0.1)	4.9 (0.5)	2.5 (0.1)	0.0 (NA)	5.7 (0.4)	4.0 (0.3)
92 SNOW	3.4 (0.1)	0.0 (NA)	2.6 (0.1)	1.4 (0.1)	2.5 (0.1)	1.7 (0.1)	1.4 (0.1)	0.4 (0.0)	0.6 (0.0)	1.2 (0.1)	0.0 (NA)	0.2 (0.0)	0.3 (0.0)
92 OUTFLOW	0.8 (0.1)	41.8 (3.1)	0.8 (0.5)	3.5 (0.6)	2.6 (1.0)	4.8 (0.4)	30.0 (3.7)	4.7 (0.5)	12.9 (1.1)	4.3 (0.3)	25.9 (10.1)	0.0 (NA)	0.0 (NA)
92 LOADING	3.4 (0.1)	0.0 (NA)	4.8 (0.3)	1.9 (0.1)	5.3 (0.2)	4.4 (0.3)	2.3 (0.2)	0.6 (0.0)	1.6 (0.2)	1.5 (0.1)	0.0 (NA)	1.5 (0.2)	1.2 (0.1)
93 RAIN	4.8 (0.1)	0.0 (NA)	5.8 (0.3)	0.9 (0.0)	5.4 (0.1)	4.1 (0.2)	1.0 (0.0)	0.2 (0.0)	0.8 (0.1)	0.5 (0.0)	0.0 (NA)	2.1 (0.1)	4.7 (0.3)
93 SNOW	3.3 (0.1)	0.0 (NA)	2.1 (0.1)	1.9 (0.1)	1.6 (0.0)	2.2 (0.1)	1.7 (0.1)	0.4 (0.0)	1.8 (0.1)	0.3 (0.0)	0.0 (NA)	0.5 (0.0)	0.3 (0.0)
93 OUTFLOW	0.6 (0.1)	33.5 (2.8)	0.3 (0.2)	2.3 (0.4)	0.8 (0.7)	4.6 (0.5)	23.7 (3.2)	3.8 (0.4)	9.2 (1.0)	3.0 (0.4)	29.7 (2.5)	0.0 (NA)	0.0 (NA)
93 LOADING	3.5 (0.1)	0.0 (NA)	2.6 (0.2)	1.8 (0.1)	2.1 (0.1)	2.4 (0.2)	1.6 (0.1)	0.4 (0.0)	1.7 (0.2)	0.3 (0.0)	0.0 (NA)	0.7 (0.1)	0.9 (0.1)

Table III-9. Volume-weighted mean (VWM) concentration of solute balance components for upper Marble Fork of the Kaweah River drainage, water years 1993 and 1994. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain and snow chemistry are from Emerald Watershed. The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
93 RAIN	4.8 (0.1)	0.0 (NA)	5.8 (0.3)	0.9 (0.0)	5.4 (0.1)	4.1 (0.2)	1.0 (0.0)	0.2 (0.0)	0.8 (0.1)	0.5 (0.0)	0.0 (NA)	2.1 (0.1)	4.7 (0.3)
93 SNOW	5.2 (0.2)	0.0 (NA)	2.2 (0.1)	2.8 (0.2)	1.8 (0.0)	2.4 (0.1)	0.9 (0.1)	0.5 (0.0)	1.5 (0.1)	0.3 (0.0)	0.0 (NA)	0.6 (0.1)	0.2 (0.0)
93 OUTFLOW	0.9 (0.2)	34.5 (3.9)	0.2 (0.1)	4.4 (1.0)	2.1 (0.4)	7.2 (1.6)	22.6 (2.6)	3.3 (0.3)	10.4 (1.7)	3.1 (0.3)	37.1 (2.8)	0.0 (NA)	0.0 (NA)
93 LOADING	5.2 (0.2)	0.0 (NA)	2.6 (0.2)	2.6 (0.1)	2.2 (0.1)	2.6 (0.2)	0.9 (0.1)	0.5 (0.0)	1.4 (0.2)	0.3 (0.0)	0.0 (NA)	0.7 (0.1)	0.6 (0.1)
94 RAIN	5.5 (0.2)	0.0 (NA)	17.9 (0.9)	9.0 (0.1)	18.3 (0.3)	10.7 (0.6)	8.0 (0.1)	2.1 (0.1)	7.5 (0.8)	3.6 (0.2)	0.0 (NA)	2.5 (0.2)	3.8 (0.3)
94 SNOW	2.9 (0.1)	0.0 (NA)	3.5 (0.2)	1.6 (0.1)	2.7 (0.1)	1.5 (0.1)	2.6 (0.2)	0.5 (0.0)	1.4 (0.1)	0.6 (0.0)	0.0 (NA)	0.0 (0.0)	0.6 (0.1)
94 OUTFLOW	0.4 (0.0)	30.6 (3.7)	0.2 (0.1)	2.9 (0.5)	2.7 (0.5)	8.8 (2.2)	25.3 (2.5)	3.6 (0.2)	12.3 (1.3)	3.4 (0.2)	30.8 (2.2)	0.0 (NA)	0.0 (NA)
94 LOADING	3.2 (0.2)	0.0 (NA)	5.2 (0.4)	2.5 (0.2)	4.6 (0.2)	2.6 (0.2)	3.3 (0.3)	0.7 (0.1)	2.1 (0.3)	1.0 (0.1)	0.0 (NA)	0.3 (0.0)	1.0 (0.1)

Table III-10. Volume-weighted mean (VWM) concentration of solute balance components for Crystal Lake, water years 1990 through 1993. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain chemistry is from Mammoth Mountain. The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	22.3 (8.0)	0.0 (NA)	27.3 (9.8)	5.1 (1.8)	27.9 (9.9)	15.7 (5.7)	11.6 (4.1)	2.2 (0.8)	5.2 (1.9)	2.0 (0.7)	0.0 (NA)	7.8 (2.8)	15.4 (5.6)
90 SNOW	4.8 (0.2)	0.0 (NA)	3.1 (0.2)	2.0 (0.1)	3.3 (0.1)	2.5 (0.1)	2.2 (0.2)	0.6 (0.0)	2.4 (0.1)	1.0 (0.1)	0.0 (NA)	1.4 (0.1)	1.0 (0.1)
90 OUTFLOW	0.6 (0.1)	73.1 (4.4)	0.1 (0.0)	3.5 (0.2)	0.2 (0.0)	6.1 (0.2)	35.4 (1.6)	12.4 (0.5)	21.5 (1.3)	6.2 (0.2)	63.2 (6.7)	0.0 (NA)	0.0 (NA)
90 LOADING	7.9 (2.8)	0.0 (NA)	7.4 (2.7)	2.5 (0.9)	7.7 (2.7)	4.8 (1.8)	3.8 (1.4)	0.9 (0.3)	2.9 (1.1)	1.2 (0.4)	0.0 (NA)	2.5 (0.9)	3.6 (1.3)
91 RAIN	18.3 (0.8)	0.0 (NA)	29.0 (1.7)	5.0 (0.2)	28.0 (1.0)	21.2 (1.4)	16.6 (0.5)	2.1 (0.1)	9.1 (1.0)	1.8 (0.1)	0.0 (NA)	10.6 (0.8)	14.0 (1.1)
91 SNOW	3.3 (0.1)	0.0 (NA)	5.5 (0.3)	2.0 (0.1)	4.5 (0.1)	2.3 (0.1)	4.2 (0.3)	0.9 (0.0)	2.0 (0.1)	1.0 (0.0)	0.0 (NA)	0.8 (0.1)	0.9 (0.1)
91 OUTFLOW	1.1 (0.2)	63.1 (3.5)	0.0 (0.0)	3.0 (0.3)	0.8 (0.2)	6.4 (0.3)	35.4 (1.8)	12.5 (0.6)	22.3 (1.5)	7.6 (0.3)	71.9 (1.9)	0.0 (NA)	0.0 (NA)
91 LOADING	4.5 (0.2)	0.0 (NA)	7.3 (0.6)	2.2 (0.1)	6.3 (0.3)	3.8 (0.3)	5.2 (0.4)	1.0 (0.1)	2.6 (0.3)	1.1 (0.1)	0.0 (NA)	1.6 (0.2)	1.9 (0.2)
92 RAIN	15.3 (0.5)	0.0 (NA)	23.5 (1.2)	1.5 (0.0)	19.4 (0.4)	14.9 (0.9)	6.5 (0.1)	1.5 (0.1)	2.2 (0.2)	0.9 (0.0)	0.0 (NA)	7.6 (0.5)	7.5 (0.5)
92 SNOW	3.7 (0.1)	0.0 (NA)	4.0 (0.2)	1.1 (0.1)	3.2 (0.1)	3.0 (0.2)	4.0 (0.3)	1.4 (0.1)	1.1 (0.1)	2.2 (0.1)	0.0 (NA)	0.5 (0.1)	0.8 (0.1)
92 OUTFLOW	0.5 (0.1)	61.4 (3.9)	0.0 (0.0)	4.0 (0.2)	0.5 (0.2)	6.1 (0.2)	34.4 (1.5)	12.1 (0.4)	21.3 (1.4)	6.6 (0.2)	57.3 (10.1)	0.0 (NA)	0.0 (NA)
92 LOADING	5.2 (0.2)	0.0 (NA)	6.6 (0.5)	1.2 (0.1)	5.4 (0.2)	4.6 (0.4)	4.3 (0.3)	1.4 (0.1)	1.2 (0.1)	2.0 (0.1)	0.0 (NA)	1.4 (0.2)	1.7 (0.2)
93 RAIN	5.9 (0.2)	0.0 (NA)	18.4 (0.9)	1.3 (0.0)	11.0 (0.2)	10.4 (0.6)	3.1 (0.0)	0.8 (0.0)	1.3 (0.1)	0.6 (0.0)	0.0 (NA)	2.0 (0.1)	3.8 (0.3)
93 SNOW	3.4 (0.1)	0.0 (NA)	1.7 (0.1)	0.7 (0.0)	1.4 (0.0)	1.7 (0.1)	1.4 (0.1)	0.5 (0.0)	0.9 (0.0)	0.2 (0.0)	0.0 (NA)	0.4 (0.0)	0.2 (0.0)
93 OUTFLOW	0.7 (0.1)	62.4 (3.5)	0.1 (0.0)	2.7 (0.3)	0.5 (0.1)	6.0 (0.2)	35.9 (1.5)	12.3 (0.5)	19.4 (1.2)	6.5 (0.3)	72.9 (1.9)	0.0 (NA)	0.0 (NA)
93 LOADING	3.5 (0.2)	0.0 (NA)	2.6 (0.2)	0.7 (0.0)	1.9 (0.1)	2.2 (0.2)	1.5 (0.1)	0.5 (0.0)	0.9 (0.1)	0.2 (0.0)	0.0 (NA)	0.5 (0.1)	0.4 (0.0)

Table III-11. Volume-weighted mean (VWM) concentration of solute balance components for Ruby Lake, water years 1990 through 1994. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain chemistry is from Eastern Brook Lake. The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	18.7 (4.9)	0.0 (NA)	22.8 (6.1)	5.3 (1.4)	23.9 (6.3)	15.5 (4.2)	22.9 (6.0)	3.3 (0.9)	4.6 (1.3)	1.2 (0.3)	0.0 (NA)	4.4 (1.2)	9.7 (2.6)
90 SNOW	5.2 (0.2)	0.0 (NA)	1.9 (0.1)	1.0 (0.1)	2.8 (0.1)	2.3 (0.1)	2.0 (0.1)	0.5 (0.0)	1.1 (0.1)	0.3 (0.0)	0.0 (NA)	1.0 (0.1)	0.7 (0.1)
90 OUTFLOW	0.5 (0.0)	56.9 (3.6)	0.1 (0.0)	2.9 (0.4)	3.2 (0.4)	9.3 (0.4)	45.8 (2.3)	3.1 (0.2)	11.2 (1.1)	4.1 (0.3)	34.9 (2.0)	0.0 (NA)	0.0 (NA)
90 LOADING	7.6 (2.0)	0.0 (NA)	5.7 (1.5)	1.8 (0.5)	6.6 (1.8)	4.7 (1.3)	5.8 (1.6)	1.0 (0.3)	1.7 (0.5)	0.5 (0.1)	0.0 (NA)	1.6 (0.5)	2.3 (0.7)
91 RAIN	21.8 (3.6)	0.0 (NA)	34.0 (5.7)	4.3 (0.7)	27.9 (4.5)	19.5 (3.3)	11.3 (1.8)	2.0 (0.3)	3.1 (0.6)	1.5 (0.2)	0.0 (NA)	9.8 (1.7)	13.4 (2.3)
91 SNOW	2.7 (0.1)	0.0 (NA)	2.7 (0.1)	0.6 (0.0)	1.7 (0.0)	1.4 (0.1)	2.4 (0.2)	0.3 (0.0)	0.5 (0.0)	0.2 (0.0)	0.0 (NA)	0.4 (0.0)	1.4 (0.1)
91 OUTFLOW	1.1 (0.2)	51.4 (4.0)	0.1 (0.1)	2.5 (0.2)	5.3 (1.0)	9.5 (0.4)	44.4 (2.2)	4.2 (0.3)	12.3 (0.9)	5.1 (0.4)	36.6 (1.3)	0.0 (NA)	0.0 (NA)
91 LOADING	5.6 (0.9)	0.0 (NA)	7.4 (1.3)	1.2 (0.2)	5.7 (0.9)	4.1 (0.7)	3.7 (0.7)	0.6 (0.1)	0.9 (0.2)	0.4 (0.1)	0.0 (NA)	1.8 (0.4)	3.2 (0.6)
92 RAIN	21.8 (2.1)	0.0 (NA)	26.2 (2.7)	3.4 (0.3)	27.2 (2.5)	23.0 (2.5)	12.2 (1.1)	2.7 (0.3)	4.5 (0.6)	1.9 (0.2)	0.0 (NA)	8.6 (1.0)	9.3 (1.1)
92 SNOW	3.6 (0.1)	0.0 (NA)	2.1 (0.1)	0.7 (0.0)	2.3 (0.1)	1.9 (0.1)	2.0 (0.1)	0.4 (0.0)	1.1 (0.1)	0.2 (0.0)	0.0 (NA)	0.4 (0.0)	0.4 (0.0)
92 OUTFLOW	0.4 (0.1)	54.0 (3.5)	0.0 (0.0)	3.0 (0.4)	5.1 (1.2)	12.1 (0.9)	50.5 (2.1)	4.2 (0.1)	12.9 (0.8)	4.6 (0.2)	36.2 (1.1)	0.0 (NA)	0.0 (NA)
92 LOADING	6.2 (0.6)	0.0 (NA)	5.6 (0.6)	1.1 (0.1)	5.9 (0.6)	5.0 (0.6)	3.5 (0.4)	0.7 (0.1)	1.6 (0.2)	0.4 (0.0)	0.0 (NA)	1.6 (0.2)	1.7 (0.3)
93 RAIN	6.1 (0.2)	0.0 (NA)	8.0 (0.4)	1.8 (0.0)	8.8 (0.2)	8.3 (0.5)	8.6 (0.1)	1.4 (0.1)	1.7 (0.2)	1.2 (0.1)	0.0 (NA)	2.7 (0.2)	4.8 (0.3)
93 SNOW	3.8 (0.1)	0.0 (NA)	1.2 (0.1)	0.9 (0.0)	1.6 (0.0)	1.9 (0.1)	1.5 (0.1)	0.3 (0.0)	0.7 (0.0)	0.2 (0.0)	0.0 (NA)	0.5 (0.1)	0.2 (0.0)
93 OUTFLOW	0.4 (0.1)	49.4 (3.4)	0.4 (0.3)	1.9 (0.3)	5.3 (1.3)	11.8 (0.4)	48.7 (2.4)	4.1 (0.2)	12.1 (0.8)	4.6 (0.3)	41.6 (1.2)	0.0 (NA)	0.0 (NA)
93 LOADING	3.9 (0.2)	0.0 (NA)	1.4 (0.1)	0.9 (0.1)	1.8 (0.1)	2.1 (0.2)	1.7 (0.1)	0.3 (0.0)	0.7 (0.1)	0.2 (0.0)	0.0 (NA)	0.6 (0.1)	0.3 (0.0)
94 RAIN	11.4 (1.8)	0.0 (NA)	10.5 (1.7)	2.6 (0.4)	9.8 (1.5)	8.9 (1.5)	4.0 (0.6)	0.8 (0.1)	1.5 (0.3)	0.6 (0.1)	0.0 (NA)	2.1 (0.4)	1.8 (0.3)
94 SNOW	3.3 (0.1)	0.0 (NA)	4.0 (0.2)	1.1 (0.1)	3.3 (0.1)	2.1 (0.1)	2.1 (0.2)	0.4 (0.0)	1.0 (0.1)	0.4 (0.0)	0.0 (NA)	1.1 (0.1)	0.0 (0.0)
94 OUTFLOW	0.2 (0.1)	54.1 (3.0)	0.4 (0.1)	2.4 (0.2)	1.5 (0.4)	11.4 (0.4)	48.6 (2.2)	3.4 (0.6)	13.5 (0.9)	5.0 (0.5)	42.1 (3.4)	0.0 (NA)	0.0 (NA)
94 LOADING	4.6 (0.7)	0.0 (NA)	5.0 (0.9)	1.3 (0.2)	4.3 (0.7)	3.2 (0.6)	2.4 (0.4)	0.5 (0.1)	1.1 (0.2)	0.4 (0.1)	0.0 (NA)	1.3 (0.3)	0.3 (0.1)

Table III-12. Volume-weighted mean (VWM) concentration of solute balance components for Spuller Lake, water years 1990 through 1994. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	18.7 (2.8)	0.0 (NA)	27.3 (4.3)	7.9 (1.2)	30.0 (4.5)	18.2 (2.9)	13.9 (2.1)	3.2 (0.5)	13.3 (2.4)	4.4 (0.7)	0.0 (NA)	20.6 (3.4)	13.2 (2.2)
90 SNOW	5.6 (0.2)	0.0 (NA)	1.6 (0.1)	1.3 (0.1)	1.5 (0.0)	1.3 (0.1)	0.9 (0.1)	0.3 (0.0)	0.7 (0.0)	0.4 (0.0)	0.0 (NA)	0.3 (0.0)	0.2 (0.0)
90 OUTFLOW	0.6 (0.1)	43.0 (3.4)	0.1 (0.0)	2.8 (0.2)	4.5 (1.2)	9.7 (1.3)	39.2 (3.5)	3.9 (0.3)	10.9 (0.7)	3.0 (0.1)	32.6 (6.0)	0.0 (NA)	0.0 (NA)
90 LOADING	7.6 (1.2)	0.0 (NA)	5.4 (0.9)	2.3 (0.4)	5.7 (0.9)	3.8 (0.6)	2.8 (0.5)	0.7 (0.1)	2.6 (0.5)	1.0 (0.2)	0.0 (NA)	3.3 (0.6)	2.1 (0.4)
91 RAIN	25.8 (2.5)	0.0 (NA)	34.8 (3.7)	5.5 (0.5)	31.8 (3.0)	23.0 (2.5)	15.6 (1.5)	2.8 (0.3)	5.3 (0.7)	2.2 (0.2)	0.0 (NA)	10.4 (1.2)	12.8 (1.5)
91 SNOW	3.9 (0.1)	0.0 (NA)	2.2 (0.1)	1.1 (0.1)	2.1 (0.1)	1.7 (0.1)	2.0 (0.1)	0.4 (0.0)	1.0 (0.0)	0.7 (0.0)	0.0 (NA)	0.5 (0.1)	0.7 (0.1)
91 OUTFLOW	1.5 (0.2)	36.1 (4.2)	0.1 (0.0)	2.6 (0.3)	5.3 (0.8)	9.5 (1.1)	34.3 (3.5)	4.2 (0.5)	10.0 (1.1)	3.7 (0.3)	27.7 (2.8)	0.0 (NA)	0.0 (NA)
91 LOADING	5.5 (0.6)	0.0 (NA)	4.6 (0.5)	1.4 (0.2)	4.3 (0.4)	3.3 (0.4)	3.0 (0.4)	0.6 (0.1)	1.3 (0.2)	0.8 (0.1)	0.0 (NA)	1.2 (0.2)	1.6 (0.2)
92 RAIN	22.7 (0.7)	0.0 (NA)	20.0 (1.0)	3.1 (0.0)	19.5 (0.4)	16.6 (1.0)	7.2 (0.1)	1.9 (0.1)	3.3 (0.3)	1.3 (0.1)	0.0 (NA)	9.0 (0.6)	9.9 (0.7)
92 SNOW	3.5 (0.1)	0.0 (NA)	2.7 (0.1)	1.0 (0.1)	3.0 (0.1)	2.2 (0.1)	1.8 (0.1)	0.6 (0.0)	0.9 (0.0)	1.0 (0.0)	0.0 (NA)	0.5 (0.1)	0.5 (0.1)
92 OUTFLOW	0.5 (0.1)	44.5 (4.1)	0.0 (0.0)	1.9 (0.3)	5.5 (1.9)	12.0 (1.2)	43.7 (3.5)	5.1 (0.4)	13.3 (1.2)	2.8 (0.2)	32.7 (4.1)	0.0 (NA)	0.0 (NA)
92 LOADING	7.6 (0.3)	0.0 (NA)	6.4 (0.5)	1.4 (0.1)	6.5 (0.2)	5.3 (0.4)	3.0 (0.2)	0.9 (0.1)	1.4 (0.2)	1.1 (0.1)	0.0 (NA)	2.3 (0.3)	2.5 (0.3)
93 RAIN	25.3 (0.8)	0.0 (NA)	26.5 (1.3)	3.8 (0.1)	30.0 (0.6)	21.1 (1.2)	7.4 (0.1)	2.7 (0.1)	5.3 (0.6)	2.9 (0.1)	0.0 (NA)	8.3 (0.6)	7.1 (0.5)
93 SNOW	3.1 (0.1)	0.0 (NA)	1.7 (0.1)	1.1 (0.1)	1.4 (0.0)	1.7 (0.1)	1.9 (0.1)	0.5 (0.0)	0.9 (0.0)	0.3 (0.0)	0.0 (NA)	0.8 (0.1)	0.1 (0.0)
93 OUTFLOW	1.1 (0.3)	37.1 (3.4)	0.0 (0.0)	1.1 (0.2)	3.2 (0.9)	8.3 (0.9)	33.0 (3.4)	4.2 (0.3)	9.7 (0.7)	2.7 (0.1)	36.0 (1.6)	0.0 (NA)	0.0 (NA)
93 LOADING	3.6 (0.2)	0.0 (NA)	2.2 (0.2)	1.2 (0.1)	2.0 (0.1)	2.1 (0.2)	2.0 (0.1)	0.5 (0.0)	1.0 (0.1)	0.4 (0.0)	0.0 (NA)	1.0 (0.1)	0.3 (0.0)
94 RAIN	10.8 (1.8)	0.0 (NA)	20.9 (3.5)	2.5 (0.4)	18.4 (3.0)	12.6 (2.2)	18.4 (3.0)	1.5 (0.2)	2.5 (0.5)	1.3 (0.2)	0.0 (NA)	4.0 (0.7)	8.0 (1.4)
94 SNOW	3.5 (0.1)	0.0 (NA)	2.4 (0.1)	1.0 (0.1)	2.9 (0.1)	1.8 (0.1)	1.3 (0.1)	0.3 (0.0)	0.8 (0.0)	0.2 (0.0)	0.0 (NA)	0.2 (0.0)	0.1 (0.0)
94 OUTFLOW	0.2 (0.1)	35.9 (31.4)	0.2 (0.6)	2.6 (0.2)	2.6 (1.7)	11.5 (1.3)	32.2 (23.0)	3.8 (2.5)	12.3 (6.2)	3.2 (1.4)	42.0 (9.1)	0.0 (NA)	0.0 (NA)
94 LOADING	4.4 (0.7)	0.0 (NA)	4.6 (0.8)	1.2 (0.2)	4.7 (0.8)	3.1 (0.6)	3.3 (0.6)	0.4 (0.1)	1.0 (0.2)	0.3 (0.1)	0.0 (NA)	0.7 (0.1)	1.0 (0.2)

Table III-13. Volume-weighted mean (VWM) concentration of solute balance components for Lost Lake, water years 1990 through 1993. Units are microequivalents per liter for all solutes except for silicate with units of micromoles per liter. Rain is the concentration of solutes from non-winter precipitation (i.e. ~April through November). Snow is the concentration of solutes from winter precipitation (i.e. ~December through March). Outflow is the concentrations of solutes from the outflow of the catchment. Loading is the VWM concentration of the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Rain chemistry and quantity are from Angora Lake. The approximate standard error for the means is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	14.3 (0.4)	0.0 (NA)	21.5 (1.1)	5.9 (0.3)	26.5 (0.7)	18.2 (1.0)	13.2 (0.9)	4.1 (0.2)	6.2 (0.3)	3.2 (0.2)	0.0 (NA)	17.6 (1.8)	4.0 (0.4)
90 SNOW	4.3 (0.1)	0.0 (NA)	2.4 (0.1)	2.1 (0.1)	2.9 (0.1)	2.1 (0.1)	1.1 (0.1)	0.5 (0.0)	1.7 (0.1)	0.4 (0.0)	0.0 (NA)	0.8 (0.1)	0.1 (0.0)
90 OUTFLOW	1.2 (0.1)	26.0 (2.6)	0.2 (0.0)	3.4 (0.3)	0.7 (0.2)	6.7 (0.4)	18.1 (1.5)	3.3 (0.2)	8.7 (0.8)	2.8 (0.2)	31.7 (1.8)	0.0 (NA)	0.0 (NA)
90 LOADING	5.2 (0.2)	0.0 (NA)	4.1 (0.3)	2.4 (0.2)	5.0 (0.2)	3.5 (0.3)	2.2 (0.2)	0.8 (0.1)	2.1 (0.1)	0.6 (0.0)	0.0 (NA)	2.3 (0.3)	0.4 (0.1)
91 RAIN	13.5 (0.4)	0.0 (NA)	20.2 (1.0)	4.7 (0.3)	19.2 (0.5)	13.2 (0.7)	7.1 (0.5)	2.5 (0.1)	7.0 (0.3)	1.9 (0.1)	0.0 (NA)	12.0 (1.2)	9.4 (0.9)
91 SNOW	3.3 (0.1)	0.0 (NA)	3.3 (0.2)	2.1 (0.1)	2.5 (0.1)	1.9 (0.1)	1.4 (0.1)	0.7 (0.0)	1.4 (0.1)	0.3 (0.0)	0.0 (NA)	0.6 (0.1)	1.0 (0.1)
91 OUTFLOW	2.5 (0.4)	21.6 (2.9)	0.0 (0.0)	2.8 (0.2)	0.6 (0.2)	5.6 (0.5)	16.5 (1.9)	3.6 (0.3)	8.9 (1.0)	2.5 (0.2)	23.7 (3.0)	0.0 (NA)	0.0 (NA)
91 LOADING	4.3 (0.2)	0.0 (NA)	5.0 (0.4)	2.4 (0.2)	4.2 (0.1)	3.0 (0.2)	2.0 (0.2)	0.9 (0.1)	2.0 (0.1)	0.5 (0.0)	0.0 (NA)	1.8 (0.2)	1.9 (0.3)
92 RAIN	16.0 (0.5)	0.0 (NA)	10.1 (0.5)	1.4 (0.1)	18.6 (0.5)	15.6 (0.8)	7.9 (0.6)	1.7 (0.1)	3.3 (0.2)	1.7 (0.1)	0.0 (NA)	4.1 (0.4)	4.2 (0.4)
92 SNOW	3.7 (0.1)	0.0 (NA)	1.7 (0.1)	1.2 (0.1)	1.6 (0.0)	1.3 (0.1)	1.3 (0.1)	0.6 (0.0)	1.3 (0.1)	0.5 (0.0)	0.0 (NA)	0.5 (0.1)	0.6 (0.1)
92 OUTFLOW	1.8 (0.4)	23.9 (3.7)	0.0 (0.0)	3.3 (0.8)	0.5 (0.1)	6.9 (1.1)	18.6 (2.7)	3.9 (0.5)	10.7 (2.2)	2.8 (0.4)	19.6 (10.1)	0.0 (NA)	0.0 (NA)
92 LOADING	5.3 (0.2)	0.0 (NA)	2.8 (0.2)	1.2 (0.1)	3.8 (0.1)	3.1 (0.2)	2.1 (0.2)	0.7 (0.1)	1.6 (0.1)	0.7 (0.0)	0.0 (NA)	1.0 (0.1)	1.1 (0.1)
93 RAIN	2.2 (0.1)	0.0 (NA)	23.0 (1.2)	10.0 (0.5)	24.7 (0.6)	15.6 (0.8)	7.4 (0.5)	2.4 (0.1)	6.7 (0.3)	2.5 (0.1)	0.0 (NA)	11.9 (1.2)	18.9 (1.9)
93 SNOW	2.9 (0.1)	0.0 (NA)	3.3 (0.2)	2.1 (0.1)	2.3 (0.1)	2.3 (0.1)	2.2 (0.2)	0.3 (0.0)	1.6 (0.1)	0.3 (0.0)	0.0 (NA)	0.7 (0.1)	0.5 (0.1)
93 OUTFLOW	1.4 (0.3)	19.6 (1.9)	0.2 (0.1)	2.3 (0.4)	0.7 (0.2)	5.3 (0.7)	16.0 (2.0)	3.3 (0.3)	6.5 (0.7)	2.0 (0.2)	18.9 (2.4)	0.0 (NA)	0.0 (NA)
93 LOADING	2.9 (0.1)	0.0 (NA)	3.5 (0.2)	2.2 (0.2)	2.5 (0.1)	2.4 (0.2)	2.3 (0.2)	0.3 (0.0)	1.6 (0.1)	0.3 (0.0)	0.0 (NA)	0.8 (0.1)	0.7 (0.1)

Table III-14. Average of volume-weighted mean snow chemistry from 1985 through 1994 for the eight study sites in this report. Chemistry shown is for winter precipitation (i.e., December through March) only. Shown are the arithmetic means for each constituent ( $\mu\text{Eq L}^{-1}$ ) along with the coefficient of variation (C.V.) and the range of values measured for the 36 catchment-years of record. Deposition is precipitation quantity in millimeters.

Solute	Mean	C.V.	Range
Hydrogen	3.8	0.21	2.7 - 5.6
Ammonium	2.7	0.38	0.9 - 5.5
Chloride	1.7	0.51	0.6 - 4.4
Nitrate	2.4	0.33	1.2 - 4.5
Sulfate	2.0	0.26	1.2 - 3.0
Calcium	1.7	0.46	0.6 - 4.2
Magnesium	0.5	0.43	0.3 - 1.4
Sodium	1.3	0.48	0.5 - 4.0
Potassium	0.5	0.90	0.1 - 2.3
Acetate	0.6	0.68	0.0 - 2.2
Formate	0.5	0.66	0.0 - 1.4
Deposition	1027	0.60	501 - 3017

Table III-15. Average of volume-weighted mean chemistry of non-winter precipitation from 1985 through 1994 for the eight study sites in this report. Chemistry shown is for non-winter precipitation (i.e. April through November) only. Shown are the arithmetic means for each major constituent ( $\mu\text{Eq L}^{-1}$ ) along with the coefficient of variation (C.V.) and the range of values measured for the 36 catchment-years of record. Deposition is precipitation quantity in millimeters.

Solute	Mean	C.V.	Range
Hydrogen	11.7	0.61	2.2 - 25.8
Ammonium	23.4	0.70	5.8 - 67.4
Chloride	4.2	0.53	0.9 - 10.0
Nitrate	20.7	0.46	5.4 - 45.8
Sulfate	15.1	0.45	4.1 - 39.8
Calcium	10.4	0.59	1.0 - 22.9
Magnesium	2.3	0.62	0.2 - 5.6
Sodium	4.6	0.66	0.8 - 15.5
Potassium	2.4	0.68	0.5 - 6.1
Acetate	7.3	0.63	2.0 - 20.6
Formate	9.1	0.58	2.6 - 19.6
Deposition	117	0.51	8 - 236

Table III-16. Average of volume-weighted mean precipitation chemistry from 1985 through 1994 for the eight study sites in this report. Precipitation is the sum of winter and non-winter deposition. Shown are the arithmetic means for each major constituent ( $\mu\text{Eq L}^{-1}$ ) along with the coefficient of variation (C.V.) and the range of values measured for the 36 catchment-years of record. Deposition is precipitation quantity in millimeters.

Solute	Mean	C.V.	Range
Hydrogen	4.7	0.28	2.9 - 8.0
Ammonium	5.1	0.50	1.3 - 14.7
Chloride	2.0	0.41	0.7 - 4.2
Nitrate	4.6	0.45	1.5 - 12.1
Sulfate	3.6	0.40	1.8 - 9.9
Calcium	2.8	0.44	0.9 - 6.4
Magnesium	0.7	0.41	0.3 - 1.8
Sodium	1.7	0.41	0.7 - 3.5
Potassium	0.8	0.60	0.2 - 2.0
Acetate	1.4	0.51	0.3 - 2.9
Formate	1.5	0.64	0.1 - 3.5
Deposition	1144	0.52	664 - 3031

Table III-17. Average of volume-weighted mean outflow chemistry from 1985 through 1994 (excluding 1988 and 1989) for the eight study sites in this report. Shown are the arithmetic means for each major constituent ( $\mu\text{Eq L}^{-1}$ ) along with the coefficient of variation (C.V.) and the range of values measured for the 36 catchment-years of record. Runoff is the equivalent water depth of outflow discharge in millimeters. Data from Crystal Lake were not included in the runoff statistic because of large sub-surface water loss. Acetate and formate are undetectable in surface waters of the Sierra Nevada.

Solute	Mean	C.V.	Range
Hydrogen	0.9	0.56	0.2 - 2.5
ANC	36.2	0.42	17.4 - 73.1
Ammonium	0.2	0.91	0.0 - 0.8
Chloride	2.9	0.26	1.1 - 4.4
Nitrate	3.2	0.64	0.2 - 7.8
Sulfate	7.4	0.30	4.6 - 12.1
Calcium	28.2	0.39	14.5 - 50.5
Magnesium	4.7	0.59	2.8 - 12.5
Sodium	11.9	0.31	6.2 - 22.3
Potassium	3.7	0.37	2.0 - 7.6
Silicate	34.7	0.58	15.4 - 72.9
Outflow	787	0.62	389 - 2,359

Table III-18. Summary of statistical analyses of year-to-year differences in VWM snow chemistry from all seven lake-basins from 1990 through 1993. For each year, data from all catchments were averaged for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among years. Years not sharing letter designations are statistically different and the differences are ranked by their letter designations i.e.  $a < b < c$  etc.. Data from 1994 were not available for all study sites and therefore this year was not included in the analyses. Marble Fork data were only available for 1993 and 1994 and are also not included in the analyses.

Solute	1990	1991	1992	1993
H <sup>+</sup>	b	a	a	a
NH <sub>4</sub> <sup>+</sup>	a	a	a	a
Cl <sup>-</sup>	a	a	a	a
NO <sub>3</sub> <sup>-</sup>	a	a	a	a
SO <sub>4</sub> <sup>2-</sup>	a	a	a	a
Ca <sup>2+</sup>	a	a	a	a
Mg <sup>2+</sup>	a	a	a	a
Na <sup>+</sup>	a	a	a	a
K <sup>+</sup>	a	a	a	a
Acetate	a	b	a	a
Formate	b	a	a	a

Table III-19. Summary of statistical analyses of year-to-year differences in VWM outflow chemistry from all seven lake-basins from 1990 through 1993. For each year, data from all catchments were averaged for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among years. Years not sharing letter designations are statistically different and the differences are ranked by their letter designations i.e.  $a < b < c$  etc.. Data from 1994 were not available for all study sites and therefore this year was not included in the analyses. Marble Fork data were only available for 1993 and 1994 and are also not included in the analyses.

Solute	1990	1991	1992	1993
H <sup>+</sup>	a	b	a	a
ANC	a	a	a	a
NH <sub>4</sub> <sup>+</sup>	a	a	a	a
Cl <sup>-</sup>	b	b	b	a
NO <sub>3</sub> <sup>-</sup>	a	a	a	a
SO <sub>4</sub> <sup>2-</sup>	a	a	a	a
Ca <sup>2+</sup>	a	a	a	a
Mg <sup>2+</sup>	a	a	a	a
Na <sup>+</sup>	a	a	a	a
K <sup>+</sup>	a	a	a	a
Silicate	a	a	a	a

Table III-20. Solute balance summary for Emerald Lake watershed. Data are from all water years with complete records during the period of 1985 through 1994. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. ~April through November). Snow is the input of solutes from winter precipitation (i.e. ~December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare

O = outflow flux of solute (same units)

R = input of solute from non-winter precipitation (same units)

S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
85 RAIN	9 (1)	0 (NA)	25 (3)	6 (1)	19 (2)	13 (1)	11 (1)	2 (0)	5 (1)	2 (0)	0 (NA)	NA (NA)	NA (NA)
85 SNOW	56 (3)	0 (NA)	9 (1)	42 (3)	24 (1)	32 (2)	23 (2)	7 (1)	20 (1)	9 (1)	0 (NA)	NA (NA)	NA (NA)
85 OUTFLOW	3 (1)	143 (26)	1 (1)	15 (3)	38 (10)	32 (5)	114 (21)	22 (4)	59 (10)	17 (3)	179 (31)	0 (NA)	0 (NA)
85 LOADING	65 (3)	0 (NA)	35 (3)	48 (3)	43 (2)	45 (3)	34 (2)	9 (1)	25 (2)	11 (1)	0 (NA)	NA (NA)	NA (NA)
85 YIELD	-61 (3)	143 (26)	-34 (3)	-35 (4)	-5 (10)	-13 (6)	80 (21)	13 (4)	34 (10)	5 (3)	179 (31)	NA (NA)	NA (NA)
86 RAIN	18 (2)	0 (NA)	52 (5)	10 (1)	37 (3)	26 (3)	19 (2)	3 (0)	8 (1)	3 (0)	0 (NA)	NA (NA)	NA (NA)
86 SNOW	110 (6)	0 (NA)	33 (2)	74 (5)	43 (2)	38 (3)	14 (1)	7 (1)	33 (2)	19 (1)	0 (NA)	NA (NA)	NA (NA)
86 OUTFLOW	23 (4)	379 (63)	2 (1)	57 (9)	89 (14)	96 (11)	377 (53)	68 (9)	175 (25)	38 (5)	534 (76)	0 (NA)	0 (NA)
86 LOADING	128 (7)	0 (NA)	85 (6)	85 (6)	80 (4)	64 (4)	34 (2)	10 (1)	41 (3)	23 (1)	0 (NA)	NA (NA)	NA (NA)
86 YIELD	-105 (8)	379 (63)	-83 (6)	-27 (10)	10 (15)	32 (12)	344 (53)	58 (9)	134 (25)	15 (6)	534 (76)	NA (NA)	NA (NA)
87 RAIN	23 (2)	0 (NA)	111 (11)	15 (1)	83 (7)	72 (8)	40 (3)	9 (1)	28 (4)	6 (1)	0 (NA)	24 (3)	24 (3)
87 SNOW	36 (2)	0 (NA)	30 (2)	12 (1)	33 (2)	23 (2)	14 (1)	9 (1)	5 (0)	3 (0)	0 (NA)	4 (0)	2 (0)
87 OUTFLOW	6 (1)	197 (25)	1 (0)	28 (3)	54 (7)	48 (5)	170 (20)	32 (4)	80 (10)	32 (4)	180 (19)	0 (NA)	0 (NA)
87 LOADING	58 (3)	0 (NA)	141 (11)	27 (2)	116 (8)	95 (8)	54 (4)	17 (1)	34 (4)	9 (1)	0 (NA)	28 (3)	26 (3)
87 YIELD	-52 (3)	197 (25)	-141 (11)	1 (4)	-62 (10)	-47 (9)	116 (20)	15 (4)	46 (11)	22 (4)	180 (19)	-28 (3)	-26 (3)
90 RAIN	8 (2)	0 (NA)	19 (5)	6 (2)	26 (7)	21 (6)	15 (4)	4 (1)	6 (2)	7 (2)	0 (NA)	NA (NA)	NA (NA)
90 SNOW	27 (2)	0 (NA)	26 (2)	12 (1)	15 (1)	15 (1)	7 (1)	3 (0)	10 (1)	3 (0)	0 (NA)	6 (1)	2 (0)
90 OUTFLOW	4 (1)	137 (19)	2 (1)	23 (3)	25 (4)	38 (4)	107 (13)	19 (2)	70 (9)	15 (2)	199 (22)	0 (NA)	0 (NA)
90 LOADING	35 (3)	0 (NA)	45 (5)	18 (2)	41 (7)	36 (6)	23 (4)	7 (1)	16 (2)	10 (2)	0 (NA)	NA (NA)	NA (NA)
90 YIELD	-30 (3)	137 (19)	-43 (5)	5 (4)	-16 (8)	2 (7)	85 (14)	11 (2)	54 (9)	5 (3)	199 (22)	NA (NA)	NA (NA)
91 RAIN	8 (1)	0 (NA)	59 (6)	5 (0)	32 (3)	21 (2)	13 (1)	5 (0)	4 (1)	5 (1)	0 (NA)	10 (1)	17 (2)
91 SNOW	32 (2)	0 (NA)	28 (2)	12 (1)	16 (1)	12 (1)	11 (1)	4 (0)	10 (1)	3 (0)	0 (NA)	2 (0)	3 (0)
91 OUTFLOW	14 (2)	189 (18)	1 (1)	25 (5)	46 (7)	56 (4)	146 (16)	29 (2)	104 (10)	25 (2)	290 (23)	0 (NA)	0 (NA)
91 LOADING	40 (2)	0 (NA)	88 (6)	16 (1)	48 (3)	33 (2)	24 (1)	9 (1)	14 (1)	8 (1)	0 (NA)	12 (1)	20 (2)
91 YIELD	-26 (3)	189 (18)	-86 (6)	9 (5)	-2 (7)	24 (5)	122 (16)	21 (2)	91 (10)	17 (2)	290 (23)	-12 (1)	-20 (2)
92 RAIN	6 (1)	0 (NA)	20 (2)	6 (1)	24 (2)	21 (2)	9 (1)	2 (0)	8 (1)	4 (0)	0 (NA)	10 (1)	7 (1)
92 SNOW	17 (1)	0 (NA)	21 (1)	10 (1)	19 (1)	12 (1)	15 (1)	3 (0)	6 (0)	1 (0)	0 (NA)	4 (0)	4 (0)
92 OUTFLOW	4 (0)	148 (13)	1 (0)	15 (2)	21 (3)	33 (2)	121 (9)	21 (1)	68 (6)	15 (1)	180 (26)	0 (NA)	0 (NA)
92 LOADING	23 (1)	0 (NA)	41 (2)	17 (1)	43 (2)	33 (2)	24 (2)	5 (0)	14 (1)	5 (0)	0 (NA)	13 (1)	10 (1)
92 YIELD	-20 (1)	148 (13)	-40 (3)	-2 (2)	-22 (3)	-0 (3)	97 (9)	16 (1)	54 (6)	10 (1)	180 (26)	-13 (1)	-10 (1)
93 RAIN	10 (1)	0 (NA)	11 (1)	2 (0)	11 (1)	8 (1)	2 (0)	0 (0)	2 (0)	1 (0)	0 (NA)	4 (0)	9 (1)
93 SNOW	114 (7)	0 (NA)	48 (3)	42 (3)	39 (2)	52 (4)	20 (2)	11 (1)	20 (1)	7 (0)	0 (NA)	13 (1)	4 (0)
93 OUTFLOW	12 (1)	338 (34)	8 (2)	36 (4)	75 (6)	97 (6)	277 (23)	56 (4)	161 (14)	48 (7)	489 (31)	0 (NA)	0 (NA)
93 LOADING	123 (7)	0 (NA)	60 (4)	43 (3)	50 (2)	61 (4)	22 (2)	11 (1)	21 (1)	7 (0)	0 (NA)	17 (2)	14 (1)
93 YIELD	-112 (7)	338 (34)	-52 (4)	-7 (5)	25 (6)	37 (7)	255 (23)	45 (4)	140 (15)	40 (7)	489 (31)	-17 (2)	-14 (1)
94 RAIN	5 (1)	0 (NA)	18 (2)	9 (1)	18 (2)	11 (1)	8 (1)	2 (0)	7 (1)	4 (0)	0 (NA)	2 (0)	4 (0)
94 SNOW	24 (2)	0 (NA)	29 (2)	17 (1)	23 (2)	13 (1)	22 (2)	4 (0)	12 (1)	5 (0)	0 (NA)	0 (0)	5 (1)
94 OUTFLOW	4 (0)	152 (11)	1 (0)	22 (2)	34 (3)	44 (3)	128 (9)	23 (2)	82 (7)	19 (1)	214 (12)	0 (NA)	0 (NA)
94 LOADING	30 (2)	0 (NA)	47 (3)	26 (2)	41 (2)	23 (2)	30 (2)	6 (0)	19 (1)	9 (1)	0 (NA)	2 (0)	9 (1)
94 YIELD	-26 (2)	152 (11)	-46 (3)	-4 (2)	-6 (4)	21 (3)	98 (9)	16 (2)	63 (7)	10 (1)	214 (12)	-2 (0)	-9 (1)

Table III-21. Solute balance summary for Pear Lake watershed, water years 1990 through 1993. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. ~April through November). Snow is the input of solutes from winter precipitation (i.e. ~December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

- Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	8 (2)	0 (NA)	19 (5)	6 (2)	26 (7)	21 (6)	15 (4)	4 (1)	6 (2)	7 (2)	0 (NA)	NA (NA)	NA (NA)
90 SNOW	29 (2)	0 (NA)	28 (2)	15 (1)	15 (1)	18 (1)	7 (1)	3 (0)	12 (1)	2 (0)	0 (NA)	3 (0)	4 (0)
90 OUTFLOW	4 (1)	104 (27)	2 (2)	19 (5)	19 (8)	31 (8)	82 (21)	14 (4)	43 (11)	14 (4)	106 (27)	0 (NA)	0 (NA)
90 LOADING	37 (3)	0 (NA)	47 (5)	21 (2)	41 (7)	40 (6)	22 (4)	7 (1)	18 (2)	9 (2)	0 (NA)	NA (NA)	NA (NA)
90 YIELD	-33 (3)	104 (27)	-45 (6)	-2 (5)	-22 (11)	-9 (10)	60 (21)	6 (4)	26 (12)	5 (4)	106 (27)	NA (NA)	NA (NA)
91 RAIN	8 (1)	0 (NA)	59 (6)	5 (0)	32 (3)	21 (2)	13 (1)	5 (0)	4 (1)	5 (1)	0 (NA)	10 (1)	17 (2)
91 SNOW	32 (2)	0 (NA)	36 (3)	10 (1)	23 (1)	15 (1)	13 (1)	5 (0)	9 (1)	3 (0)	0 (NA)	5 (1)	10 (1)
91 OUTFLOW	8 (2)	91 (26)	2 (1)	15 (5)	28 (10)	30 (8)	81 (22)	15 (4)	44 (12)	16 (4)	105 (29)	0 (NA)	0 (NA)
91 LOADING	40 (2)	0 (NA)	96 (6)	15 (1)	55 (3)	36 (2)	25 (2)	9 (1)	13 (1)	8 (1)	0 (NA)	14 (1)	27 (2)
91 YIELD	-33 (3)	91 (26)	-94 (7)	1 (5)	-28 (11)	-6 (8)	55 (22)	6 (4)	31 (12)	8 (4)	105 (29)	-14 (1)	-27 (2)
92 RAIN	6 (1)	0 (NA)	20 (2)	6 (1)	24 (2)	21 (2)	9 (1)	2 (0)	8 (1)	4 (0)	0 (NA)	10 (1)	7 (1)
92 SNOW	20 (1)	0 (NA)	22 (2)	7 (1)	17 (1)	11 (1)	8 (1)	2 (0)	6 (0)	1 (0)	0 (NA)	2 (0)	4 (0)
92 OUTFLOW	4 (1)	104 (17)	2 (1)	12 (2)	13 (4)	24 (4)	80 (13)	15 (2)	39 (7)	13 (2)	66 (21)	0 (NA)	0 (NA)
92 LOADING	26 (1)	0 (NA)	42 (3)	13 (1)	41 (2)	32 (2)	17 (1)	4 (0)	15 (1)	5 (0)	0 (NA)	11 (1)	11 (1)
92 YIELD	-22 (2)	104 (17)	-40 (3)	-1 (2)	-28 (5)	-8 (4)	63 (13)	10 (2)	24 (7)	7 (2)	66 (21)	-11 (1)	-11 (1)
93 RAIN	10 (1)	0 (NA)	11 (1)	2 (0)	11 (1)	8 (1)	2 (0)	0 (0)	2 (0)	1 (0)	0 (NA)	4 (0)	9 (1)
93 SNOW	66 (4)	0 (NA)	38 (3)	38 (3)	32 (2)	40 (3)	20 (2)	8 (1)	28 (2)	6 (0)	0 (NA)	12 (1)	4 (0)
93 OUTFLOW	22 (4)	254 (44)	9 (3)	27 (6)	39 (9)	80 (12)	212 (35)	40 (7)	91 (16)	33 (7)	300 (49)	0 (NA)	0 (NA)
93 LOADING	76 (4)	0 (NA)	50 (3)	40 (3)	43 (2)	48 (3)	22 (2)	8 (1)	30 (2)	7 (0)	0 (NA)	16 (1)	13 (1)
93 YIELD	-54 (6)	254 (44)	-41 (4)	-13 (7)	-4 (9)	32 (13)	189 (35)	32 (7)	61 (16)	26 (7)	300 (49)	-16 (1)	-13 (1)

Table III-22. Solute balance summary for Topaz Lake watershed, water years 1990 through 1993. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	8 (2)	0 (NA)	19 (5)	6 (2)	26 (7)	21 (6)	15 (4)	4 (1)	6 (2)	7 (2)	0 (NA)	NA (NA)	NA (NA)
90 SNOW	21 (1)	0 (NA)	17 (1)	11 (1)	13 (1)	12 (1)	4 (0)	2 (0)	8 (1)	3 (0)	0 (NA)	7 (1)	3 (0)
90 OUTFLOW	2 (1)	161 (35)	0 (0)	16 (4)	6 (2)	22 (5)	111 (25)	16 (3)	42 (10)	18 (4)	163 (36)	0 (NA)	0 (NA)
90 LOADING	29 (3)	0 (NA)	36 (5)	17 (2)	39 (7)	34 (6)	19 (4)	6 (1)	14 (2)	10 (2)	0 (NA)	NA (NA)	NA (NA)
90 YIELD	-27 (3)	161 (35)	-35 (5)	-0 (4)	-33 (7)	-12 (8)	92 (25)	10 (4)	28 (10)	8 (4)	163 (36)	NA (NA)	NA (NA)
91 RAIN	8 (1)	0 (NA)	59 (6)	5 (0)	32 (3)	21 (2)	13 (1)	5 (0)	4 (1)	5 (1)	0 (NA)	10 (1)	17 (2)
91 SNOW	31 (2)	0 (NA)	16 (1)	5 (0)	14 (1)	10 (1)	24 (2)	2 (0)	7 (1)	2 (0)	0 (NA)	5 (1)	6 (1)
91 OUTFLOW	5 (1)	156 (39)	1 (1)	14 (5)	12 (6)	27 (7)	118 (31)	21 (6)	47 (13)	21 (6)	130 (34)	0 (NA)	0 (NA)
91 LOADING	39 (2)	0 (NA)	76 (6)	10 (1)	46 (3)	31 (2)	37 (2)	7 (1)	11 (1)	7 (1)	0 (NA)	15 (1)	24 (2)
91 YIELD	-34 (2)	156 (39)	-75 (6)	4 (5)	-33 (7)	-4 (7)	81 (31)	14 (6)	36 (13)	14 (6)	130 (34)	-15 (1)	-24 (2)
92 RAIN	6 (1)	0 (NA)	20 (2)	6 (1)	24 (2)	21 (2)	9 (1)	2 (0)	8 (1)	4 (0)	0 (NA)	10 (1)	7 (1)
92 SNOW	18 (1)	0 (NA)	14 (1)	7 (1)	13 (1)	9 (1)	7 (1)	2 (0)	3 (0)	6 (0)	0 (NA)	1 (0)	2 (0)
92 OUTFLOW	3 (1)	176 (29)	3 (2)	15 (3)	11 (5)	20 (4)	126 (24)	20 (4)	54 (9)	18 (3)	109 (47)	0 (NA)	0 (NA)
92 LOADING	24 (1)	0 (NA)	33 (2)	14 (1)	37 (2)	30 (2)	16 (1)	4 (0)	12 (1)	11 (1)	0 (NA)	11 (1)	8 (1)
92 YIELD	-20 (1)	176 (29)	-30 (3)	1 (4)	-26 (5)	-10 (4)	110 (25)	15 (4)	43 (9)	8 (3)	109 (47)	-11 (1)	-8 (1)
93 RAIN	10 (1)	0 (NA)	12 (1)	2 (0)	11 (1)	8 (1)	2 (0)	0 (0)	2 (0)	1 (0)	0 (NA)	4 (0)	9 (1)
93 SNOW	40 (2)	0 (NA)	26 (2)	23 (2)	19 (1)	27 (2)	21 (2)	5 (0)	22 (2)	4 (0)	0 (NA)	6 (1)	4 (0)
93 OUTFLOW	7 (1)	392 (67)	3 (2)	27 (7)	10 (8)	53 (10)	278 (56)	45 (8)	107 (20)	35 (7)	348 (60)	0 (NA)	0 (NA)
93 LOADING	50 (2)	0 (NA)	38 (2)	25 (2)	30 (1)	35 (2)	23 (2)	5 (0)	24 (2)	5 (0)	0 (NA)	10 (1)	14 (1)
93 YIELD	-43 (3)	392 (67)	-34 (3)	2 (7)	-21 (9)	18 (10)	254 (56)	39 (8)	83 (20)	30 (7)	348 (60)	-10 (1)	-14 (1)

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Table III-23. Solute balance summary for the upper Marble Fork drainage of the Kaweah River, water years 1993 and 1994. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
93 RAIN	10 (1)	0 (NA)	11 (1)	2 (0)	11 (1)	8 (1)	2 (0)	0 (0)	2 (0)	1 (0)	0 (NA)	4 (0)	9 (1)
93 SNOW	94 (5)	0 (NA)	40 (3)	51 (4)	32 (2)	43 (3)	16 (1)	9 (1)	27 (2)	5 (0)	0 (NA)	11 (1)	4 (0)
93 OUTFLOW	15 (5)	591 (136)	4 (2)	75 (23)	35 (9)	124 (37)	387 (89)	57 (12)	178 (46)	54 (12)	636 (136)	0 (NA)	0 (NA)
93 LOADING	103 (6)	0 (NA)	51 (3)	52 (4)	43 (2)	51 (3)	18 (1)	9 (1)	29 (2)	6 (0)	0 (NA)	15 (1)	13 (1)
93 YIELD	-88 (7)	591 (136)	-47 (4)	23 (23)	-8 (10)	73 (37)	368 (89)	48 (12)	149 (46)	48 (12)	636 (136)	-15 (1)	-13 (1)
94 RAIN	5 (1)	0 (NA)	18 (2)	9 (1)	18 (2)	11 (1)	8 (1)	2 (0)	7 (1)	4 (0)	0 (NA)	2 (0)	4 (0)
94 SNOW	21 (1)	0 (NA)	25 (2)	12 (1)	20 (1)	11 (1)	19 (2)	4 (0)	10 (1)	4 (0)	0 (NA)	0 (0)	4 (1)
94 OUTFLOW	3 (0)	238 (46)	2 (1)	23 (5)	21 (5)	68 (20)	197 (35)	28 (4)	96 (18)	26 (4)	239 (40)	0 (NA)	0 (NA)
94 LOADING	27 (2)	0 (NA)	43 (3)	21 (1)	38 (2)	22 (1)	27 (2)	6 (0)	18 (1)	8 (0)	0 (NA)	2 (0)	8 (1)
94 YIELD	-24 (2)	238 (46)	-42 (3)	2 (5)	-17 (5)	47 (20)	170 (35)	22 (4)	78 (18)	18 (4)	239 (40)	-2 (0)	-8 (1)

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Table III-24. Solute balance summary for Crystal Lake, water years 1990 through 1993. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	27 (10)	0 (NA)	33 (12)	6 (2)	34 (12)	19 (7)	14 (5)	3 (1)	6 (2)	2 (1)	0 (NA)	10 (4)	19 (7)
90 SNOW	27 (3)	0 (NA)	18 (1)	11 (1)	19 (1)	14 (1)	12 (1)	4 (0)	14 (1)	6 (0)	0 (NA)	8 (1)	6 (1)
90 OUTFLOW	1 (0)	187 (30)	0 (0)	9 (1)	1 (0)	16 (2)	90 (14)	32 (5)	55 (9)	16 (2)	161 (30)	0 (NA)	0 (NA)
90 LOADING	54 (11)	0 (NA)	51 (12)	17 (2)	53 (13)	33 (7)	27 (5)	6 (1)	20 (3)	8 (1)	0 (NA)	17 (4)	25 (7)
90 YIELD	-53 (11)	187 (30)	-51 (12)	-9 (3)	-52 (13)	-18 (8)	64 (15)	25 (5)	35 (9)	8 (3)	161 (30)	-17 (4)	-25 (7)
91 RAIN	12 (1)	0 (NA)	18 (2)	3 (0)	18 (2)	13 (1)	10 (1)	1 (0)	6 (1)	1 (0)	0 (NA)	7 (1)	9 (1)
91 SNOW	25 (1)	0 (NA)	42 (3)	15 (1)	34 (2)	18 (1)	32 (3)	7 (1)	15 (1)	8 (1)	0 (NA)	6 (1)	7 (1)
91 OUTFLOW	3 (1)	202 (32)	0 (0)	10 (2)	3 (1)	21 (3)	113 (18)	40 (6)	71 (12)	24 (4)	230 (35)	0 (NA)	0 (NA)
91 LOADING	37 (2)	0 (NA)	60 (4)	18 (1)	52 (3)	31 (2)	43 (3)	8 (1)	21 (1)	9 (1)	0 (NA)	13 (1)	16 (1)
91 YIELD	-33 (2)	202 (32)	-60 (4)	-9 (2)	-49 (3)	-10 (4)	71 (18)	32 (6)	50 (12)	16 (4)	230 (35)	-13 (1)	-16 (1)
92 RAIN	19 (2)	0 (NA)	29 (3)	2 (0)	24 (2)	18 (2)	8 (1)	2 (0)	3 (0)	1 (0)	0 (NA)	9 (1)	9 (1)
92 SNOW	30 (2)	0 (NA)	32 (2)	9 (1)	26 (1)	24 (2)	32 (3)	11 (1)	9 (1)	18 (1)	0 (NA)	4 (0)	6 (1)
92 OUTFLOW	1 (0)	148 (18)	0 (0)	10 (1)	1 (1)	15 (2)	83 (9)	29 (3)	51 (6)	16 (2)	138 (28)	0 (NA)	0 (NA)
92 LOADING	49 (2)	0 (NA)	61 (4)	11 (1)	50 (3)	43 (3)	40 (3)	13 (1)	12 (1)	19 (1)	0 (NA)	13 (1)	16 (1)
92 YIELD	-48 (2)	148 (18)	-61 (4)	-1 (1)	-49 (3)	-28 (3)	43 (10)	16 (3)	40 (6)	-3 (2)	138 (28)	-13 (1)	-16 (1)
93 RAIN	6 (1)	0 (NA)	19 (2)	1 (0)	11 (1)	11 (1)	3 (0)	1 (0)	1 (0)	1 (0)	0 (NA)	2 (0)	4 (0)
93 SNOW	59 (3)	0 (NA)	29 (2)	12 (1)	24 (1)	29 (2)	24 (2)	9 (1)	16 (1)	3 (0)	0 (NA)	7 (1)	3 (0)
93 OUTFLOW	6 (1)	549 (63)	1 (0)	24 (3)	4 (1)	53 (6)	316 (34)	109 (12)	171 (20)	57 (6)	642 (66)	0 (NA)	0 (NA)
93 LOADING	65 (4)	0 (NA)	49 (3)	13 (1)	36 (2)	40 (2)	27 (2)	9 (1)	17 (1)	4 (0)	0 (NA)	9 (1)	7 (1)
93 YIELD	-59 (4)	549 (63)	-48 (3)	10 (3)	-31 (2)	13 (6)	289 (34)	99 (12)	154 (20)	53 (6)	642 (66)	-9 (1)	-7 (1)

Table III-25. Solute balance summary for Ruby Lake watershed, water years 1990 through 1994. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	25 (8)	0 (NA)	31 (9)	7 (2)	32 (10)	21 (6)	31 (9)	4 (1)	6 (2)	2 (0)	0 (NA)	6 (2)	13 (4)
90 SNOW	32 (2)	0 (NA)	12 (1)	6 (0)	17 (1)	14 (1)	12 (1)	3 (0)	7 (0)	2 (0)	0 (NA)	6 (1)	4 (0)
90 OUTFLOW	2 (0)	266 (43)	1 (0)	14 (3)	15 (3)	43 (7)	214 (34)	14 (2)	52 (9)	19 (3)	163 (26)	0 (NA)	0 (NA)
90 LOADING	57 (8)	0 (NA)	43 (9)	13 (2)	50 (10)	35 (6)	43 (9)	8 (1)	13 (2)	3 (1)	0 (NA)	12 (2)	17 (4)
90 YIELD	-55 (8)	266 (43)	-42 (9)	0 (4)	-35 (10)	8 (9)	171 (35)	7 (3)	39 (9)	16 (3)	163 (26)	-12 (2)	-17 (4)
91 RAIN	22 (5)	0 (NA)	34 (7)	4 (1)	28 (6)	20 (4)	11 (2)	2 (0)	3 (1)	2 (0)	0 (NA)	10 (2)	14 (3)
91 SNOW	15 (1)	0 (NA)	15 (1)	3 (0)	10 (1)	8 (1)	14 (1)	2 (0)	3 (0)	1 (0)	0 (NA)	2 (0)	8 (1)
91 OUTFLOW	5 (1)	228 (38)	1 (0)	11 (2)	24 (6)	42 (7)	197 (31)	19 (3)	54 (9)	23 (4)	162 (25)	0 (NA)	0 (NA)
91 LOADING	37 (5)	0 (NA)	50 (7)	8 (1)	38 (6)	28 (4)	25 (3)	4 (0)	6 (1)	3 (0)	0 (NA)	12 (2)	22 (3)
91 YIELD	-32 (5)	228 (38)	-49 (7)	3 (2)	-14 (8)	15 (8)	172 (31)	15 (3)	48 (9)	20 (4)	162 (25)	-12 (2)	-22 (3)
92 RAIN	22 (4)	0 (NA)	27 (5)	3 (1)	28 (4)	23 (4)	12 (2)	3 (0)	5 (1)	2 (0)	0 (NA)	9 (2)	9 (2)
92 SNOW	22 (1)	0 (NA)	13 (1)	4 (0)	14 (1)	11 (1)	12 (1)	2 (0)	7 (0)	1 (0)	0 (NA)	2 (0)	2 (0)
92 OUTFLOW	2 (0)	239 (28)	0 (0)	13 (2)	23 (6)	54 (7)	224 (24)	19 (2)	57 (7)	20 (2)	161 (17)	0 (NA)	0 (NA)
92 LOADING	44 (4)	0 (NA)	39 (5)	8 (1)	42 (5)	35 (4)	24 (2)	5 (0)	11 (1)	3 (0)	0 (NA)	11 (2)	12 (2)
92 YIELD	-42 (4)	239 (28)	-39 (5)	6 (2)	-19 (7)	19 (8)	200 (24)	14 (2)	46 (7)	17 (2)	161 (17)	-11 (2)	-12 (2)
93 RAIN	3 (0)	0 (NA)	4 (1)	1 (0)	4 (1)	4 (1)	4 (1)	1 (0)	1 (0)	1 (0)	0 (NA)	1 (0)	2 (0)
93 SNOW	57 (3)	0 (NA)	18 (1)	14 (1)	24 (1)	29 (2)	23 (2)	5 (0)	11 (1)	3 (0)	0 (NA)	8 (1)	3 (0)
93 OUTFLOW	3 (1)	366 (44)	3 (2)	14 (2)	39 (10)	88 (9)	361 (40)	30 (3)	89 (11)	34 (4)	309 (32)	0 (NA)	0 (NA)
93 LOADING	60 (3)	0 (NA)	22 (1)	14 (1)	28 (1)	32 (2)	26 (2)	5 (0)	11 (1)	4 (0)	0 (NA)	9 (1)	5 (0)
93 YIELD	-57 (3)	366 (44)	-18 (2)	-0 (3)	11 (10)	56 (10)	335 (40)	25 (3)	78 (11)	30 (4)	309 (32)	-9 (1)	-5 (0)
94 RAIN	13 (3)	0 (NA)	12 (3)	3 (1)	11 (2)	10 (2)	5 (1)	1 (0)	2 (0)	1 (0)	0 (NA)	2 (1)	2 (0)
94 SNOW	20 (1)	0 (NA)	25 (2)	7 (1)	20 (1)	13 (1)	13 (1)	2 (0)	6 (0)	2 (0)	0 (NA)	7 (1)	0 (0)
94 OUTFLOW	1 (0)	237 (27)	2 (1)	11 (1)	7 (2)	50 (5)	212 (23)	15 (3)	59 (7)	22 (3)	184 (24)	0 (NA)	0 (NA)
94 LOADING	33 (3)	0 (NA)	36 (3)	10 (1)	31 (3)	23 (2)	17 (1)	3 (0)	8 (1)	3 (0)	0 (NA)	9 (1)	2 (0)
94 YIELD	-32 (3)	237 (27)	-35 (3)	1 (2)	-25 (3)	27 (6)	195 (23)	12 (3)	51 (7)	19 (3)	184 (24)	-9 (1)	-2 (0)

Table III-26. Solute balance summary for Spuller Lake watershed, water years 1990 through 1994. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	24 (5)	0 (NA)	35 (7)	10 (2)	39 (8)	23 (5)	18 (4)	4 (1)	17 (4)	6 (1)	0 (NA)	27 (6)	17 (4)
90 SNOW	41 (2)	0 (NA)	12 (1)	10 (1)	11 (1)	10 (1)	7 (1)	2 (0)	5 (0)	3 (0)	0 (NA)	2 (0)	1 (0)
90 OUTFLOW	3 (1)	236 (51)	0 (0)	15 (3)	25 (8)	53 (13)	215 (47)	21 (5)	60 (13)	16 (3)	179 (49)	0 (NA)	0 (NA)
90 LOADING	65 (5)	0 (NA)	47 (7)	20 (2)	50 (8)	33 (5)	25 (4)	6 (1)	22 (4)	9 (1)	0 (NA)	29 (6)	18 (4)
90 YIELD	-62 (6)	236 (51)	-47 (7)	-4 (4)	-25 (11)	20 (14)	190 (47)	15 (5)	38 (13)	8 (4)	179 (49)	-29 (6)	-18 (4)
91 RAIN	19 (3)	0 (NA)	26 (4)	4 (1)	24 (4)	17 (3)	12 (2)	2 (0)	4 (1)	2 (0)	0 (NA)	8 (1)	10 (2)
91 SNOW	37 (2)	0 (NA)	21 (1)	10 (1)	20 (1)	16 (1)	19 (2)	4 (0)	9 (1)	7 (0)	0 (NA)	5 (1)	7 (1)
91 OUTFLOW	12 (2)	291 (38)	1 (0)	21 (3)	43 (7)	76 (10)	277 (33)	34 (4)	81 (10)	30 (3)	223 (26)	0 (NA)	0 (NA)
91 LOADING	56 (4)	0 (NA)	47 (5)	15 (1)	44 (4)	33 (3)	31 (3)	6 (0)	13 (1)	8 (1)	0 (NA)	13 (1)	16 (2)
91 YIELD	-44 (4)	291 (38)	-46 (5)	7 (3)	-1 (8)	43 (10)	246 (33)	28 (4)	67 (10)	21 (3)	223 (26)	-13 (1)	-16 (2)
92 RAIN	43 (6)	0 (NA)	38 (5)	6 (1)	37 (5)	32 (5)	14 (2)	4 (1)	6 (1)	2 (0)	0 (NA)	17 (3)	19 (3)
92 SNOW	24 (1)	0 (NA)	19 (1)	7 (1)	21 (1)	15 (1)	13 (1)	4 (0)	6 (0)	7 (0)	0 (NA)	3 (0)	3 (0)
92 OUTFLOW	3 (0)	255 (28)	0 (0)	11 (2)	31 (11)	69 (8)	250 (25)	29 (3)	76 (8)	16 (1)	187 (26)	0 (NA)	0 (NA)
92 LOADING	68 (6)	0 (NA)	57 (6)	13 (1)	58 (5)	47 (5)	26 (2)	8 (1)	13 (1)	9 (1)	0 (NA)	21 (3)	22 (3)
92 YIELD	-65 (6)	255 (28)	-57 (6)	-2 (2)	-27 (12)	22 (9)	224 (25)	21 (3)	63 (8)	7 (2)	187 (26)	-21 (3)	-22 (3)
93 RAIN	11 (2)	0 (NA)	12 (2)	2 (0)	13 (2)	9 (1)	3 (0)	1 (0)	2 (0)	1 (0)	0 (NA)	4 (1)	3 (0)
93 SNOW	61 (4)	0 (NA)	33 (2)	22 (2)	27 (2)	33 (3)	37 (3)	10 (1)	18 (1)	6 (0)	0 (NA)	16 (2)	2 (0)
93 OUTFLOW	15 (4)	501 (55)	0 (0)	14 (2)	43 (12)	111 (13)	445 (53)	57 (6)	130 (13)	37 (3)	486 (36)	0 (NA)	0 (NA)
93 LOADING	72 (4)	0 (NA)	45 (3)	23 (2)	41 (2)	43 (3)	41 (3)	11 (1)	20 (1)	7 (0)	0 (NA)	19 (2)	5 (1)
93 YIELD	-57 (5)	501 (55)	-45 (3)	-9 (3)	3 (13)	69 (14)	404 (53)	46 (6)	110 (13)	30 (3)	486 (36)	-19 (2)	-5 (1)
94 RAIN	13 (3)	0 (NA)	25 (5)	3 (1)	22 (5)	15 (3)	22 (5)	2 (0)	3 (1)	2 (0)	0 (NA)	5 (1)	9 (2)
94 SNOW	31 (2)	0 (NA)	21 (2)	9 (1)	25 (1)	16 (1)	11 (1)	3 (0)	7 (0)	2 (0)	0 (NA)	2 (0)	1 (0)
94 OUTFLOW	1 (1)	240 (210)	1 (4)	18 (2)	18 (11)	76 (10)	215 (154)	25 (17)	82 (42)	21 (10)	281 (63)	0 (NA)	0 (NA)
94 LOADING	43 (3)	0 (NA)	46 (6)	12 (1)	47 (5)	31 (3)	33 (5)	4 (0)	10 (1)	3 (0)	0 (NA)	6 (1)	10 (2)
94 YIELD	-42 (3)	240 (210)	-44 (7)	6 (2)	-29 (12)	46 (10)	182 (154)	21 (17)	72 (42)	18 (10)	281 (63)	-6 (1)	-10 (2)

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Table III-27. Solute balance summary for Lost Lake watershed, water years 1990 through 1993. Units are equivalents per hectare per year for all solutes except for silicate with units of moles per hectare per year. Rain is the input of solutes from non-winter precipitation (i.e. April through November). Snow is the input of solutes from winter precipitation (i.e. December through March). Outflow is the loss of solutes from the watershed via the outflow of the catchment. Loading is the sum of inputs from non-winter precipitation (Rain) and winter precipitation (Snow). Yield is defined as:

$$Y = O - (R+S)$$

Where: Y = yield of solute in equivalent or moles per hectare  
 O = outflow flux of solute (same units)  
 R = input of solute from non-winter precipitation (same units)  
 S = input of solute from winter precipitation (same units)

A negative yield indicates the solute showed a net retention (sink) within the watershed. A positive yield indicates that there was a net output of solute (source) from the watershed. The approximate standard error of the flux estimates is given in parentheses.

YR/COMPONENT	H+	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE	ACETATE	FORMATE
90 RAIN	13 (2)	0 (NA)	19 (3)	5 (1)	24 (3)	16 (2)	12 (2)	4 (1)	6 (1)	3 (0)	0 (NA)	16 (3)	4 (1)
90 SNOW	40 (2)	0 (NA)	22 (2)	20 (1)	27 (2)	20 (1)	10 (1)	5 (0)	16 (1)	4 (0)	0 (NA)	7 (1)	1 (0)
90 OUTFLOW	9 (2)	203 (45)	1 (0)	26 (6)	5 (2)	52 (11)	141 (30)	25 (5)	68 (15)	22 (4)	247 (52)	0 (NA)	0 (NA)
90 LOADING	53 (3)	0 (NA)	42 (3)	25 (2)	51 (4)	36 (3)	22 (2)	8 (1)	21 (1)	7 (0)	0 (NA)	23 (3)	5 (1)
90 YIELD	-44 (4)	203 (45)	-40 (3)	1 (6)	-45 (4)	16 (11)	119 (31)	17 (5)	47 (15)	15 (5)	247 (52)	-23 (3)	-5 (1)
91 RAIN	15 (2)	0 (NA)	22 (3)	5 (1)	21 (3)	14 (2)	8 (1)	3 (0)	8 (1)	2 (0)	0 (NA)	13 (2)	10 (2)
91 SNOW	31 (2)	0 (NA)	31 (2)	20 (1)	24 (1)	18 (1)	13 (1)	7 (0)	13 (1)	3 (0)	0 (NA)	6 (1)	10 (1)
91 OUTFLOW	20 (5)	177 (43)	0 (0)	23 (5)	5 (2)	46 (10)	135 (31)	29 (6)	73 (17)	21 (5)	194 (46)	0 (NA)	0 (NA)
91 LOADING	46 (3)	0 (NA)	53 (4)	25 (2)	45 (3)	32 (2)	21 (2)	9 (1)	21 (1)	5 (0)	0 (NA)	19 (2)	20 (2)
91 YIELD	-26 (6)	177 (43)	-53 (4)	-2 (5)	-40 (4)	14 (10)	114 (31)	20 (6)	52 (17)	16 (5)	194 (46)	-19 (2)	-20 (2)
92 RAIN	20 (3)	0 (NA)	13 (2)	2 (0)	24 (3)	20 (3)	10 (2)	2 (0)	4 (1)	2 (0)	0 (NA)	5 (1)	5 (1)
92 SNOW	32 (2)	0 (NA)	15 (1)	10 (1)	14 (1)	11 (1)	11 (1)	5 (0)	11 (1)	4 (0)	0 (NA)	4 (0)	5 (1)
92 OUTFLOW	15 (4)	211 (45)	0 (0)	30 (9)	4 (1)	60 (13)	163 (34)	35 (7)	95 (24)	25 (5)	173 (93)	0 (NA)	0 (NA)
92 LOADING	53 (3)	0 (NA)	28 (2)	12 (1)	38 (3)	31 (3)	21 (2)	7 (0)	16 (1)	7 (0)	0 (NA)	10 (1)	11 (1)
92 YIELD	-37 (5)	211 (45)	-28 (2)	18 (9)	-33 (3)	29 (13)	141 (34)	27 (7)	79 (24)	19 (5)	173 (93)	-10 (1)	-11 (1)
93 RAIN	1 (0)	0 (NA)	7 (1)	3 (0)	7 (1)	5 (1)	2 (0)	1 (0)	2 (0)	1 (0)	0 (NA)	3 (1)	6 (1)
93 SNOW	87 (5)	0 (NA)	100 (7)	63 (5)	69 (4)	69 (5)	66 (6)	9 (1)	48 (3)	9 (1)	0 (NA)	21 (2)	15 (2)
93 OUTFLOW	33 (9)	462 (83)	5 (2)	55 (12)	16 (6)	126 (24)	378 (73)	78 (14)	152 (29)	47 (8)	446 (88)	0 (NA)	0 (NA)
93 LOADING	88 (5)	0 (NA)	106 (7)	66 (5)	77 (4)	74 (5)	69 (6)	10 (1)	50 (3)	10 (1)	0 (NA)	25 (2)	21 (2)
93 YIELD	-55 (11)	462 (83)	-101 (7)	-11 (13)	-61 (7)	52 (25)	309 (73)	68 (14)	102 (29)	37 (8)	446 (88)	-25 (2)	-21 (2)

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Table III-28. Summary of statistical analyses of solute yields from 1990 through 1992. For each catchment, data from all years were combined for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among catchments. Catchments not sharing letter designations are statistically different and the differences are ranked by their letter designations, i.e.,  $a < b < c$  etc.. Water year 1993 was not included in the analysis because high runoff caused yields for most solutes to be 2-4 times greater than during the period of 1990-1992. This large difference in turn raised the standard error for the mean yields at each station thereby greatly reducing the power of the ANOVA to detect significant differences.

Solute	Crystal	Emerald	Lost	Pear	Ruby	Spuller	Topaz
H <sup>+</sup>	a	b	b	b	a	a	b
ANC	b	b	b	a	c	c	b
NH <sub>4</sub> <sup>+</sup>	a	a	a	a	a	a	a
Cl <sup>-</sup>	a	a	a	a	a	a	a
NO <sub>3</sub> <sup>-</sup>	a	c	ab	bc	bc	c	bc
SO <sub>4</sub> <sup>2-</sup>	a	ab	b	a	b	b	a
Ca <sup>2+</sup>	a	b	b	a	c	d	ab
Mg <sup>2+</sup>	b	b	b	a	ab	b	ab
Na <sup>+</sup>	ab	b	ab	a	ab	ab	ab
K <sup>+</sup>	a	a	a	a	a	a	a
Silicate	ab	b	b	a	ab	b	ab

Table III-29. Summary of statistical analyses of solute exports from 1990 through 1992. For each catchment, data from all years were combined for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among catchments. Catchments not sharing letter designations are statistically different and the differences are ranked by their letter designations i.e.  $a < b < c$  etc.. Water year 1993 was not included in the analysis because high runoff caused yields for most solutes to be 2-4 times greater than during the period of 1990-1992. This large difference in turn raised the standard error for the mean yields at each station thereby greatly reducing the power of the ANOVA to detect significant differences.

Solute	Crystal	Emerald	Lost	Pear	Ruby	Spuller	Topaz
H <sup>+</sup>	a	a	b	a	a	a	a
ANC	b	b	b	a	cd	d	b
NH <sub>4</sub> <sup>+</sup>	a	a	a	a	a	a	a
Cl <sup>-</sup>	a	bc	c	ab	ab	ab	ab
NO <sub>3</sub> <sup>-</sup>	a	c	ab	bc	bc	c	ab
SO <sub>4</sub> <sup>2-</sup>	a	b	bc	a	b	c	a
Ca <sup>2+</sup>	ab	bc	c	a	d	e	bc
Mg <sup>2+</sup>	c	abc	c	a	a	bc	ab
Na <sup>+</sup>	ab	b	b	a	ab	b	a
K <sup>+</sup>	a	a	a	a	a	a	a
Silicate	ab	b	b	a	ab	b	ab

Table III-30. Summary of statistical analyses of year-to-year differences in solute yields from 1990 through 1993. For each year, data from all catchments were combined for the analyses. An one-way ANOVA and multiple-comparison test (Student-Newman-Keuls) were used to detect and isolate significant differences ( $p < 0.05$ ) among years. Years not sharing letter designations are statistically different and the differences are ranked by their letter designations i.e.  $a < b < c$  etc.. Data from 1994 were not available for all study sites and therefore were not included in the analyses. Marble Fork data were only available for 1993 and 1994 and are also not included in the analyses.

Solute	1990	1991	1992	1993
H <sup>+</sup>	b	b	b	a
ANC	a	a	a	b
NH <sub>4</sub> <sup>+</sup>	a	a	a	a
Cl <sup>-</sup>	a	a	a	a
NO <sub>3</sub> <sup>-</sup>	a	a	a	b
SO <sub>4</sub> <sup>2-</sup>	a	a	a	b
Ca <sup>2+</sup>	a	a	a	b
Mg <sup>2+</sup>	a	a	a	b
Na <sup>+</sup>	a	a	a	b
K <sup>+</sup>	a	a	a	b
Silicate	a	a	a	b

Table III-31. Average of annual solute yield from 1985 through 1994 (excluding 1988 and 1989) for the eight study sites in this report. Yield is the difference between solute export and inputs and is expressed on an areal basis. Shown are the mean values for each major constituent ( $\text{Eq ha}^{-1} \text{yr}^{-1}$ ) along with the coefficient of variation (C.V.) and the range of values measured.

Solute	Mean	C.V.	Range
Hydrogen	-45.0	0.48	-111 - 18.9
ANC	250	0.49	91.4 - 591
Ammonium	-50.5	0.46	-140 - -17.6
Chloride	-0.6	18.5	-35.2 - 25.3
Nitrate	-21.5	0.94	-62.5 - 24.8
Sulfate	17.0	1.62	-47.3 - 76.4
Calcium	171	0.57	42.7 - 407
Magnesium	25.6	0.75	6.2 - 99.5
Sodium	66.4	0.53	24.5 - 154
Potassium	18.1	0.68	-2.9 - 53.5
Silicate	252	0.57	66.1 - 642
Acetate	0.0	-	-
Formate	0.0	-	-

Table III-32. Average of annual solute loading from 1985 through 1994 for the eight study sites in this report. Loading is the sum of solute deposition from winter and non-winter precipitation. Shown are the mean values for each major constituent ( $\text{Eq ha}^{-1}\text{yr}^{-1}$ ) along with the coefficient of variation and the range of values measured.

Solute	Mean	C.V.	Range
Hydrogen	51.9	0.48	22.5 - 128
Ammonium	50.8	0.47	20.8 - 141
Chloride	22.5	0.73	7.7 - 84.5
Nitrate	44.8	0.37	26.8 - 116
Sulfate	37.4	0.39	16.4 - 94.9
Calcium	28.0	0.39	15.9 - 67.4
Magnesium	7.4	0.38	3.7 - 17.3
Sodium	18.1	0.50	6.0 - 49.2
Potassium	7.7	0.54	2.6 - 22.6
Acetate	13.7	0.41	2.6 - 27.7
Formate	13.7	0.52	2.5 - 26.6

Table III-33. Percent of annual solute loading contributed by non-winter precipitation by site for the period of 1990 through 1993. Also shown is the average loading fraction for all sites by year. Precip is the ratio of non-winter precipitation to annual precipitation. Some data are from Melack et al. (1997). The following abbreviations were used: AM-Alpine Meadows, AN-Angora Lake, CR-Crystal Lake, EB-Eastern Brook Lake, EM-Emerald Lake, MK-Mineral King, MM-Mammoth Mountain, OV-Onion Valley, PR-Pear Lake, RB-Ruby Lake, SL-South Lake, SN-Sonora Pass, TG-Tioga Pass (Spuller Lake), TZ-Topaz Lake.

Site/Year	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	Precip
AM-90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
AN-90	24%	46%	21%	47%	45%	52%	46%	26%	43%	68%	75%	9%
CR-90	35%	53%	24%	52%	44%	40%	30%	21%	19%	40%	63%	10%
EB-90	53%	73%	50%	72%	79%	87%	80%	74%	53%	95%	100%	22%
EM-90	19%	35%	29%	59%	51%	63%	49%	44%	73%	NA	NA	17%
MK-90	23%	66%	33%	66%	66%	47%	34%	43%	17%	12%	40%	13%
MM-90	21%	35%	22%	42%	35%	40%	60%	27%	32%	34%	76%	7%
OV-90	50%	82%	56%	78%	78%	43%	44%	55%	20%	87%	94%	27%
PR-90	17%	34%	25%	59%	46%	64%	47%	41%	78%	NA	NA	15%
RB-90	36%	65%	45%	57%	51%	63%	51%	40%	36%	41%	67%	13%
SL-90	63%	73%	46%	67%	73%	68%	68%	64%	49%	75%	84%	25%
SN-90	37%	83%	53%	77%	78%	70%	56%	61%	41%	76%	98%	18%
TG-90	33%	72%	46%	74%	68%	68%	59%	74%	60%	90%	88%	12%
TZ-90	16%	36%	24%	53%	46%	68%	51%	40%	66%	NA	NA	13%
1990 AVG	32.8%	58.0%	36.4%	61.6%	58.6%	59.4%	52.0%	46.9%	45.1%	61.9%	78.5%	15.5%
AM-91	45%	51%	28%	59%	55%	66%	17%	48%	53%	80%	79%	18%
AN-91	31%	40%	20%	46%	43%	36%	27%	36%	45%	67%	51%	10%
CR-91	35%	35%	19%	38%	47%	27%	19%	30%	15%	56%	59%	9%
EB-91	47%	80%	45%	79%	75%	62%	42%	50%	44%	88%	81%	17%
EM-91	24%	67%	29%	65%	65%	57%	58%	29%	66%	81%	85%	12%
KP-91	28%	40%	21%	31%	47%	27%	40%	20%	53%	57%	34%	9%
MK-91	28%	34%	33%	46%	65%	62%	38%	33%	34%	20%	12%	16%
MM-91	25%	39%	18%	41%	43%	44%	28%	35%	28%	61%	51%	7%
OV-91	21%	42%	23%	33%	43%	36%	39%	30%	22%	44%	41%	6%
PR-91	25%	62%	32%	58%	58%	53%	55%	31%	70%	69%	62%	14%
RB-91	51%	62%	47%	67%	64%	38%	44%	42%	53%	75%	55%	11%
SL-91	37%	70%	39%	67%	56%	45%	48%	39%	33%	51%	77%	11%
SN-91	63%	73%	37%	77%	55%	48%	36%	21%	43%	93%	83%	14%
TG-91	34%	54%	29%	53%	50%	38%	30%	25%	14%	63%	59%	7%
TZ-91	25%	78%	50%	70%	68%	36%	64%	36%	79%	66%	71%	15%
1991 AVG	34.6%	55.2%	31.3%	55.3%	55.7%	44.9%	39.1%	33.7%	43.4%	64.6%	60.0%	11.7%
AM-92	31%	63%	32%	65%	64%	61%	47%	44%	52%	75%	81%	11%
AN-92	39%	51%	35%	66%	67%	52%	37%	39%	39%	64%	65%	15%
CR-92	36%	48%	15%	48%	42%	19%	13%	22%	5%	70%	59%	14%
EB-92	64%	74%	44%	67%	73%	58%	24%	50%	35%	89%	79%	22%
EM-92	32%	53%	36%	61%	65%	33%	37%	58%	84%	87%	83%	27%
KP-92	29%	58%	30%	71%	77%	65%	52%	39%	50%	52%	93%	20%
MK-92	53%	51%	34%	58%	67%	45%	34%	47%	51%	88%	91%	31%
MM-92	33%	51%	15%	42%	40%	30%	25%	19%	15%	80%	53%	12%
OV-92	20%	55%	38%	37%	38%	38%	37%	26%	22%	75%	55%	8%
PR-92	30%	52%	47%	64%	68%	48%	44%	57%	82%	94%	80%	29%
RB-92	49%	66%	44%	65%	66%	49%	52%	39%	58%	78%	77%	14%
SL-92	62%	77%	39%	67%	79%	60%	59%	56%	57%	86%	76%	21%
SN-92	61%	70%	35%	67%	71%	46%	32%	51%	14%	85%	73%	18%
TG-92	63%	66%	44%	63%	67%	51%	48%	50%	25%	83%	84%	21%
TZ-92	31%	62%	43%	68%	71%	49%	42%	73%	39%	96%	91%	29%
1992 AVG	42.3%	59.8%	35.3%	60.6%	63.6%	47.0%	38.9%	44.6%	42.0%	80.0%	76.1%	19.5%
AM-93	5%	25%	7%	38%	24%	14%	6%	6%	8%	9%	20%	5%
AN-93	2%	7%	1%	12%	9%	3%	10%	2%	19%	0%	0%	1%
CR-93	11%	30%	10%	27%	24%	9%	6%	7%	11%	15%	49%	6%
EB-93	13%	35%	9%	28%	22%	19%	10%	17%	6%	42%	54%	6%
EM-93	5%	18%	3%	16%	12%	10%	4%	5%	15%	12%	48%	4%
KP-93	4%	16%	7%	29%	13%	16%	14%	8%	16%	45%	75%	2%
MK-93	8%	27%	5%	33%	16%	5%	5%	6%	28%	26%	48%	2%
MM-93	9%	23%	5%	19%	16%	8%	7%	5%	6%	12%	37%	5%
OV-93	12%	24%	13%	28%	31%	16%	8%	14%	8%	14%	60%	4%
PR-93	8%	22%	5%	19%	14%	9%	5%	6%	14%	13%	54%	4%
RB-93	4%	13%	4%	12%	9%	10%	8%	5%	11%	11%	33%	2%
SL-93	8%	16%	6%	13%	8%	7%	6%	8%	13%	9%	5%	1%
SN-93	9%	25%	6%	24%	16%	7%	5%	11%	9%	25%	20%	2%
TG-93	5%	17%	3%	16%	10%	3%	3%	3%	6%	5%	41%	2%
TZ-93	17%	30%	9%	29%	21%	3%	9%	7%	22%	26%	54%	7%
1993 AVG	8.0%	21.9%	6.2%	22.9%	16.3%	9.3%	7.1%	7.3%	12.6%	17.6%	39.8%	3.6%

Table III-34. Summary of analytical errors for rain, snow and outflow samples. Errors were estimated from analytical accuracies determined by spike recoveries and analyses of standard reference materials. Acetate and formate were below the detection limit in outflow samples. Silicate and ANC were undetectable in precipitation samples. Errors for rain and snow are from Melack et al. (1997).

Solute	Rain	Snow	Outflow
H+	3.0%	3.0%	3.0%
Ammonium	5.0%	5.0%	10.0%
Chloride	1.5%	5.4%	5.0%
Nitrate	1.9%	2.5%	2.0%
Sulfate	5.8%	5.4%	3.0%
Calcium	1.0%	7.0%	4.0%
Magnesium	4.1%	5.3%	3.0%
Sodium	10.4%	4.9%	6.0%
Potassium	4.5%	4.8%	3.0%
Acetate	7.0%	10.0%	NA
Formate	7.0%	10.0%	NA
ANC	NA	NA	5.0%
Silicate	NA	NA	2.0%

Table III-35. Sampling errors for rain and snow during water years 1990 through 1994. Sampling errors were calculated on the basis of the amount of unsampled rain or snow (i.e., no chemistry) that fell at a catchment. The unsampled-precipitation volume was estimated from gauges or snowboards in the catchment or from an alternative station (see Table III-1). In the case of rain, unsampled precipitation was assigned the volume-weighted mean chemistry for the catchment during the water year in which it fell. In the case of snow that fell after the spring surveys, the VWM chemistry from that catchment's previous snow survey (snowpits) was used. In the analyses we assumed that extrapolation of VWM rain chemistry caused a 50% error in the chemistry for unsampled rain. For snow, we assumed that extrapolation of VWM snow chemistry caused a 20% error in the chemistry for unsampled snow. To estimate the sampling-error contribution to uncertainty in VWM chemistry the uncertainty in unsampled rain (or snow) chemistry was multiplied by the ratio of unsampled rain (or snow) volume to total rain (or snow) volume. If all rain or snow was sampled, the sampling error was zero. In the case of Lost Lake, we were unable to estimate the quantity of unsampled rain or snow owing to a lack of reliable alternate station. Relatively large sampling errors for rain during 1990 are due to unsampled rainfall from the autumn of 1989. Routine rain collection did not begin until the summer of 1990. Sampling errors for 1985 through 1987 were assumed to be zero since all precipitation was sampled (Williams and Melack 1991).

Rain							
Year	Crystal	Emerald	Marble Fork	Pear	Ruby	Spuller	Topaz
1990	35.6%	25.5%	25.5%	25.5%	26.3%	14.9%	25.5%
1991	2.9%	0.0%	0.0%	0.0%	16.0%	9.2%	0.0%
1992	0.0%	0.0%	0.0%	0.0%	9.0%	0.0%	0.0%
1993	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1994	-	0.0%	0.0%	-	15.7%	16.2%	-

Snow							
Year	Crystal	Emerald	Marble Fork	Pear	Ruby	Spuller	Topaz
1990	1.3%	0.5%	0.5%	0.4%	0.5%	1.4%	0.6%
1991	0.9%	1.1%	1.1%	1.2%	1.1%	0.8%	1.3%
1992	0.4%	0.8%	0.8%	1.0%	0.2%	0.0%	1.0%
1993	1.0%	0.0%	0.0%	0.0%	0.2%	1.6%	0.0%
1994	-	4.0%	4.0%	-	1.8%	1.3%	-

Table III-36. Sampling error for volume-weighted mean outflow concentrations derived from Tukey's jackknife procedure. The jackknife method provides a measure of the variability of a given statistic (in this case VWM chemistry) as the statistic is iteratively computed with a different one of the observations (i.e. outflow chemistry samples) ignored each time. The variability of these values is subsequently used to compute an approximate sampling error for the statistic (VWM chemistry). The magnitude of the sampling error was dependent on sampling intensity (more samples yields less error) and the annual variability of solute concentrations (greater variability results in larger error). In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE
CR-1990	10.4%	3.2%	11.9%	2.2%	12.8%	1.1%	2.3%	2.1%	0.9%	1.5%	10.3%
CR-1991	15.7%	2.5%	106.6%	9.4%	23.2%	4.0%	3.1%	3.8%	2.7%	2.6%	1.7%
CR-1992	24.8%	4.0%	118.4%	1.8%	45.7%	2.4%	2.1%	1.7%	2.5%	2.1%	17.6%
CR-1993	18.0%	2.5%	53.2%	7.9%	18.0%	2.1%	1.4%	2.9%	1.7%	2.7%	1.6%
EM-1985	17.9%	8.5%	46.0%	16.6%	22.5%	6.7%	9.6%	10.4%	5.5%	7.9%	8.9%
EM-1986	13.2%	12.2%	38.1%	10.2%	11.9%	4.6%	8.8%	7.7%	8.4%	9.7%	9.9%
EM-1987	10.7%	6.5%	14.4%	5.5%	7.7%	2.5%	4.3%	3.2%	4.6%	6.0%	3.5%
EM-1990	7.1%	8.4%	24.3%	8.0%	10.6%	2.4%	6.3%	4.4%	4.3%	5.5%	4.2%
EM-1991	15.9%	6.7%	80.9%	17.8%	13.8%	5.3%	9.0%	5.6%	6.1%	6.1%	5.6%
EM-1992	10.6%	4.8%	44.4%	7.6%	11.0%	1.7%	4.1%	3.6%	2.5%	5.3%	13.1%
EM-1993	4.3%	7.2%	20.2%	7.8%	5.9%	1.4%	5.4%	3.9%	4.5%	13.5%	3.3%
EM-1994	4.1%	2.1%	27.9%	3.5%	5.9%	1.3%	2.2%	4.7%	1.6%	2.2%	1.7%
LO-1990	9.1%	8.5%	22.7%	5.6%	26.1%	5.6%	7.1%	7.0%	7.2%	4.6%	5.4%
LO-1991	15.7%	12.7%	66.1%	6.6%	31.5%	8.2%	10.6%	7.5%	9.0%	8.6%	12.5%
LO-1992	22.1%	14.6%	104.9%	23.6%	17.2%	15.6%	14.1%	11.2%	19.3%	13.0%	51.6%
LO-1993	23.3%	8.4%	38.9%	15.7%	36.5%	11.9%	11.6%	9.7%	9.9%	8.4%	12.7%
MF-1993	22.7%	10.2%	43.4%	22.3%	17.5%	21.7%	10.6%	7.9%	14.8%	9.3%	7.2%
MF-1994	5.3%	11.0%	48.3%	15.8%	17.2%	24.3%	9.0%	4.0%	8.6%	6.5%	6.7%
PE-1990	10.5%	5.3%	74.4%	4.5%	35.5%	3.0%	4.0%	4.5%	5.0%	6.0%	6.5%
PE-1991	9.0%	12.7%	77.6%	15.8%	26.9%	5.9%	8.6%	7.6%	9.8%	7.1%	10.4%
PE-1992	16.6%	5.5%	52.0%	9.5%	25.5%	2.9%	5.2%	4.8%	4.5%	6.4%	27.9%
PE-1993	9.5%	7.0%	27.2%	15.5%	17.8%	2.4%	6.1%	5.8%	6.4%	12.7%	5.8%
RU-1990	5.6%	3.8%	14.1%	13.2%	13.9%	3.6%	3.1%	5.2%	7.4%	5.9%	5.4%
RU-1991	13.2%	5.9%	46.7%	5.8%	18.6%	2.9%	3.0%	6.8%	3.6%	6.7%	2.9%
RU-1992	22.7%	4.1%	101.3%	11.0%	24.0%	6.7%	1.3%	1.6%	2.3%	3.8%	2.3%
RU-1993	17.5%	4.7%	61.0%	12.8%	23.6%	1.7%	2.8%	3.0%	2.7%	5.4%	1.9%
RU-1994	41.9%	2.5%	31.4%	8.0%	29.5%	1.1%	2.0%	16.4%	2.1%	10.1%	7.9%
SP-1990	19.3%	6.2%	37.4%	7.3%	26.1%	13.5%	7.9%	7.6%	3.2%	2.9%	18.4%
SP-1991	12.2%	10.6%	62.8%	11.3%	15.0%	10.9%	9.4%	10.7%	9.3%	8.7%	9.8%
SP-1992	12.9%	7.8%	104.6%	14.7%	34.9%	9.9%	6.9%	7.3%	6.7%	5.5%	12.4%
SP-1993	22.9%	7.6%	63.1%	14.4%	27.8%	10.0%	9.6%	7.2%	4.7%	3.6%	3.9%
SP-1994	64.4%	87.4%	293.9%	3.8%	62.6%	10.8%	71.3%	66.1%	50.2%	44.4%	21.5%
TO-1990	13.2%	7.6%	44.4%	10.8%	32.9%	11.2%	8.4%	8.0%	11.7%	10.0%	8.8%
TO-1991	7.4%	14.7%	108.5%	25.4%	46.6%	15.3%	17.0%	16.7%	16.9%	19.9%	17.2%
TO-1992	12.4%	5.6%	60.4%	17.4%	39.0%	8.8%	11.7%	10.3%	6.0%	5.3%	40.3%
TO-1993	11.3%	6.7%	53.5%	18.4%	87.4%	9.9%	13.1%	11.2%	9.7%	14.1%	8.2%

Table III-37. Estimated error in rain VWM solute concentrations for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the sampling error with the analytical error for each solute. In the table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>3</sub> <sup>-</sup>
CR-1990	35.7%	35.9%	35.6%	35.6%	36.0%	35.6%	35.8%	37.0%	35.8%	36.2%	36.2%
CR-1991	4.1%	5.8%	3.2%	3.4%	6.5%	3.0%	5.0%	10.8%	5.3%	7.6%	7.6%
CR-1992	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
CR-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1985	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1986	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1987	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1988	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1989	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1990	25.6%	26.0%	25.5%	25.5%	26.1%	25.5%	25.8%	27.5%	25.9%	26.4%	26.4%
EM-1991	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1992	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
EM-1994	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
LO-1990	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1991	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1992	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
MF-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
MF-1994	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
PE-1990	25.6%	26.0%	25.5%	25.5%	26.1%	25.5%	25.8%	27.5%	25.9%	26.4%	26.4%
PE-1991	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
PE-1992	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
PE-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
RU-1990	26.4%	26.7%	26.3%	26.3%	26.9%	26.3%	26.6%	28.2%	26.6%	27.2%	27.2%
RU-1991	16.3%	16.8%	16.1%	16.2%	17.1%	16.1%	16.6%	19.1%	16.7%	17.5%	17.5%
RU-1992	9.4%	10.3%	9.1%	9.2%	10.7%	9.0%	9.9%	13.7%	10.0%	11.4%	11.4%
RU-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
RU-1994	16.0%	16.5%	15.8%	15.8%	16.7%	15.7%	16.2%	18.8%	16.3%	17.2%	17.2%
SP-1990	15.2%	15.7%	15.0%	15.0%	16.0%	14.9%	15.4%	18.2%	15.5%	16.4%	16.4%
SP-1991	9.7%	10.5%	9.4%	9.4%	10.9%	9.3%	10.1%	13.9%	10.3%	11.6%	11.6%
SP-1992	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
SP-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
SP-1994	16.4%	16.9%	16.2%	16.3%	17.2%	16.2%	16.7%	19.2%	16.8%	17.6%	17.6%
TO-1990	25.6%	26.0%	25.5%	25.5%	26.1%	25.5%	25.8%	27.5%	25.9%	26.4%	26.4%
TO-1991	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
TO-1992	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%
TO-1993	3.0%	5.0%	1.5%	1.9%	5.8%	1.0%	4.1%	10.4%	4.5%	7.0%	7.0%

Table III-38. Estimated error in snow VWM solute concentrations for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the sampling error with the analytical error for each solute. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>2</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
CR-1990	3.3%	5.2%	5.6%	2.8%	5.6%	7.1%	5.5%	5.1%	5.0%	10.1%	10.1%
CR-1991	3.1%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.0%	10.0%
CR-1992	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
CR-1993	3.2%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.0%	10.0%
EM-1985	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1986	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1987	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1988	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1989	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1990	3.0%	5.0%	5.4%	2.6%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1991	3.2%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.1%	10.1%
EM-1992	3.1%	5.1%	5.5%	2.6%	5.5%	7.1%	5.4%	5.0%	4.9%	10.0%	10.0%
EM-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
EM-1994	5.0%	6.4%	6.7%	4.7%	6.7%	8.1%	6.6%	6.3%	6.2%	10.8%	10.8%
LO-1990	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1991	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1992	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
LO-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
MF-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
MF-1994	5.0%	6.4%	6.7%	4.7%	6.7%	8.1%	6.6%	6.3%	6.2%	10.8%	10.8%
PE-1990	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
PE-1991	3.2%	5.1%	5.5%	2.8%	5.5%	7.1%	5.4%	5.0%	4.9%	10.1%	10.1%
PE-1992	3.2%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.0%	10.0%
PE-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
RU-1990	3.0%	5.0%	5.4%	2.6%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
RU-1991	3.2%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.1%	10.1%
RU-1992	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
RU-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
RU-1994	3.5%	5.3%	5.7%	3.1%	5.7%	7.2%	5.6%	5.2%	5.1%	10.2%	10.2%
SP-1990	3.3%	5.2%	5.6%	2.8%	5.6%	7.1%	5.5%	5.1%	5.0%	10.1%	10.1%
SP-1991	3.1%	5.1%	5.5%	2.6%	5.5%	7.0%	5.4%	5.0%	4.9%	10.0%	10.0%
SP-1992	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
SP-1993	3.4%	5.2%	5.6%	3.0%	5.6%	7.2%	5.5%	5.2%	5.1%	10.1%	10.1%
SP-1994	3.3%	5.2%	5.5%	2.8%	5.5%	7.1%	5.4%	5.1%	5.0%	10.1%	10.1%
TO-1990	3.1%	5.0%	5.4%	2.6%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%
TO-1991	3.3%	5.2%	5.6%	2.8%	5.6%	7.1%	5.5%	5.1%	5.0%	10.1%	10.1%
TO-1992	3.2%	5.1%	5.5%	2.7%	5.5%	7.1%	5.4%	5.0%	4.9%	10.0%	10.0%
TO-1993	3.0%	5.0%	5.4%	2.5%	5.4%	7.0%	5.3%	4.9%	4.8%	10.0%	10.0%

Table III-39. Estimated error in outflow VWM solute concentrations for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the sampling error derived from Tukey's jackknife procedure with the analytical error for each solute. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE
CR-1990	10.4%	3.2%	11.9%	2.2%	12.8%	1.1%	2.3%	2.1%	0.9%	1.5%	10.3%
CR-1991	15.7%	2.5%	106.6%	9.4%	23.2%	4.0%	3.1%	3.8%	2.7%	2.6%	1.7%
CR-1992	24.8%	4.0%	118.4%	1.8%	45.7%	2.4%	2.1%	1.7%	2.5%	2.1%	17.6%
CR-1993	18.0%	2.5%	53.2%	7.9%	18.0%	2.1%	1.4%	2.9%	1.7%	2.7%	1.6%
EM-1985	17.9%	8.5%	46.0%	16.6%	22.5%	6.7%	9.6%	10.4%	5.5%	7.9%	8.9%
EM-1986	13.2%	12.2%	38.1%	10.2%	11.9%	4.6%	8.8%	7.7%	8.4%	9.7%	9.9%
EM-1987	10.7%	6.5%	14.4%	5.5%	7.7%	2.5%	4.3%	3.2%	4.6%	6.0%	3.5%
EM-1990	7.1%	8.4%	24.3%	8.0%	10.6%	2.4%	6.3%	4.4%	4.3%	5.5%	4.2%
EM-1991	15.9%	6.7%	80.9%	17.8%	13.8%	5.3%	9.0%	5.6%	6.1%	6.1%	5.6%
EM-1992	10.6%	4.8%	44.4%	7.6%	11.0%	1.7%	4.1%	3.6%	2.5%	5.3%	13.1%
EM-1993	4.3%	7.2%	20.2%	7.8%	5.9%	1.4%	5.4%	3.9%	4.5%	13.5%	3.3%
EM-1994	4.1%	2.1%	27.9%	3.5%	5.9%	1.3%	2.2%	4.7%	1.6%	2.2%	1.7%
LO-1990	9.1%	8.5%	22.7%	5.6%	26.1%	5.6%	7.1%	7.0%	7.2%	4.6%	5.4%
LO-1991	15.7%	12.7%	66.1%	6.6%	31.5%	8.2%	10.6%	7.5%	9.0%	8.6%	12.5%
LO-1992	22.1%	14.6%	104.9%	23.6%	17.2%	15.6%	14.1%	11.2%	19.3%	13.0%	51.6%
LO-1993	23.3%	8.4%	38.9%	15.7%	36.5%	11.9%	11.6%	9.7%	9.9%	8.4%	12.7%
MF-1993	22.7%	10.2%	43.4%	22.3%	17.5%	21.7%	10.6%	7.9%	14.8%	9.3%	7.2%
MF-1994	5.3%	11.0%	48.3%	15.8%	17.2%	24.3%	9.0%	4.0%	8.6%	6.5%	6.7%
PE-1990	10.5%	5.3%	74.4%	4.5%	35.5%	3.0%	4.0%	4.5%	5.0%	6.0%	6.5%
PE-1991	9.0%	12.7%	77.6%	15.8%	26.9%	5.9%	8.6%	7.6%	9.8%	7.1%	10.4%
PE-1992	16.6%	5.5%	52.0%	9.5%	25.5%	2.9%	5.2%	4.8%	4.5%	6.4%	27.9%
PE-1993	9.5%	7.0%	27.2%	15.5%	17.8%	2.4%	6.1%	5.8%	6.4%	12.7%	5.8%
RU-1990	5.6%	3.8%	14.1%	13.2%	13.9%	3.6%	3.1%	5.2%	7.4%	5.9%	5.4%
RU-1991	13.2%	5.9%	46.7%	5.8%	18.6%	2.9%	3.0%	6.8%	3.6%	6.7%	2.9%
RU-1992	22.7%	4.1%	101.3%	11.0%	24.0%	6.7%	1.3%	1.6%	2.3%	3.8%	2.3%
RU-1993	17.5%	4.7%	61.0%	12.8%	23.6%	1.7%	2.8%	3.0%	2.7%	5.4%	1.9%
RU-1994	41.9%	2.5%	31.4%	8.0%	29.5%	1.1%	2.0%	16.4%	2.1%	10.1%	7.9%
SP-1990	19.3%	6.2%	37.4%	7.3%	26.1%	13.5%	7.9%	7.6%	3.2%	2.9%	18.4%
SP-1991	12.2%	10.6%	62.8%	11.3%	15.0%	10.9%	9.4%	10.7%	9.3%	8.7%	9.8%
SP-1992	12.9%	7.8%	104.6%	14.7%	34.9%	9.9%	6.9%	7.3%	6.7%	5.5%	12.4%
SP-1993	22.9%	7.6%	63.1%	14.4%	27.8%	10.0%	9.6%	7.2%	4.7%	3.6%	3.9%
SP-1994	64.4%	87.4%	293.9%	3.8%	62.6%	10.8%	71.3%	66.1%	50.2%	44.4%	21.5%
TO-1990	13.2%	7.6%	44.4%	10.8%	32.9%	11.2%	8.4%	8.0%	11.7%	10.0%	8.8%
TO-1991	7.4%	14.7%	108.5%	25.4%	46.6%	15.3%	17.0%	16.7%	16.9%	19.9%	17.2%
TO-1992	12.4%	5.6%	60.4%	17.4%	39.0%	8.8%	11.7%	10.3%	6.0%	5.3%	40.3%
TO-1993	11.3%	6.7%	53.5%	18.4%	87.4%	9.9%	13.1%	11.2%	9.7%	14.1%	8.2%

Table III-40. Estimated error in rain solute flux for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the error in VWM rain chemistry with the error for rain volume. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
CR-1990	36.7%	36.9%	36.6%	36.6%	37.0%	36.6%	36.8%	38.0%	36.9%	37.3%	37.3%
CR-1991	9.6%	10.4%	9.2%	9.3%	10.8%	9.2%	10.0%	13.8%	10.2%	11.5%	11.5%
CR-1992	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
CR-1993	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1985	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1986	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1987	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1988	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1989	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1990	27.1%	27.4%	26.9%	27.0%	27.5%	26.9%	27.2%	28.8%	27.3%	27.8%	27.8%
EM-1991	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1992	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1993	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
EM-1994	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
LO-1990	13.7%	14.3%	14.4%	13.6%	14.4%	15.1%	14.4%	14.3%	14.2%	16.7%	16.7%
LO-1991	13.7%	14.3%	14.4%	13.6%	14.4%	15.1%	14.4%	14.3%	14.2%	16.7%	16.7%
LO-1992	13.7%	14.3%	14.4%	13.6%	14.4%	15.1%	14.4%	14.3%	14.2%	16.7%	16.7%
LO-1993	13.7%	14.3%	14.4%	13.6%	14.4%	15.1%	14.4%	14.3%	14.2%	16.7%	16.7%
MF-1993	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
MF-1994	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
PE-1990	27.1%	27.4%	26.9%	27.0%	27.5%	26.9%	27.2%	28.8%	27.3%	27.8%	27.8%
PE-1991	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
PE-1992	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
PE-1993	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
RU-1990	29.6%	29.9%	29.5%	29.5%	30.0%	29.5%	29.8%	31.3%	29.8%	30.3%	30.3%
RU-1991	21.1%	21.5%	21.0%	21.0%	21.7%	20.9%	21.3%	23.3%	21.4%	22.0%	22.0%
RU-1992	16.4%	16.9%	16.2%	16.2%	17.1%	16.1%	16.6%	19.2%	16.7%	17.6%	17.6%
RU-1993	13.7%	14.3%	13.5%	13.5%	14.6%	13.4%	14.0%	17.0%	14.1%	15.1%	15.1%
RU-1994	20.8%	21.2%	20.7%	20.7%	21.4%	20.7%	21.0%	23.1%	21.1%	21.8%	21.8%
SP-1990	20.3%	20.6%	20.1%	20.1%	20.9%	20.1%	20.4%	22.6%	20.5%	21.2%	21.2%
SP-1991	16.6%	17.0%	16.3%	16.4%	17.3%	16.3%	16.8%	19.3%	16.9%	17.7%	17.7%
SP-1992	13.7%	14.3%	13.5%	13.5%	14.6%	13.4%	14.0%	17.0%	14.1%	15.1%	15.1%
SP-1993	13.7%	14.3%	13.5%	13.5%	14.6%	13.4%	14.0%	17.0%	14.1%	15.1%	15.1%
SP-1994	21.2%	21.6%	21.0%	21.1%	21.8%	21.0%	21.4%	23.4%	21.5%	22.1%	22.1%
TO-1990	27.1%	27.4%	26.9%	27.0%	27.5%	26.9%	27.2%	28.8%	27.3%	27.8%	27.8%
TO-1991	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
TO-1992	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%
TO-1993	9.2%	10.0%	8.8%	8.9%	10.4%	8.7%	9.6%	13.5%	9.8%	11.1%	11.1%

Table III-41. Estimated error in snow solute flux for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the error in VWM snow chemistry with the error for snow volume. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>2</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
CR-1990	12.8%	7.2%	7.5%	5.7%	7.5%	8.7%	7.4%	7.1%	7.1%	11.3%	11.3%
CR-1991	5.9%	7.1%	7.4%	5.7%	7.4%	8.7%	7.3%	7.1%	7.0%	11.2%	11.2%
CR-1992	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
CR-1993	5.9%	7.1%	7.4%	5.7%	7.4%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
EM-1985	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1986	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1987	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1988	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1989	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1990	5.9%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	7.0%	11.2%	11.2%
EM-1991	5.9%	7.2%	7.4%	5.7%	7.4%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
EM-1992	5.9%	7.1%	7.4%	5.7%	7.4%	8.6%	7.3%	7.1%	7.0%	11.2%	11.2%
EM-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
EM-1994	7.1%	8.1%	8.4%	6.9%	8.4%	9.5%	8.3%	8.1%	8.0%	11.9%	11.9%
LO-1990	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
LO-1991	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
LO-1992	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
LO-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
MF-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
MF-1994	7.1%	8.1%	8.4%	6.9%	8.4%	9.5%	8.3%	8.1%	8.0%	11.9%	11.9%
PE-1990	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
PE-1991	5.9%	7.2%	7.5%	5.7%	7.5%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
PE-1992	5.9%	7.1%	7.4%	5.7%	7.4%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
PE-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
RU-1990	5.9%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	7.0%	11.2%	11.2%
RU-1991	5.9%	7.2%	7.4%	5.7%	7.4%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
RU-1992	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
RU-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
RU-1994	6.1%	7.3%	7.6%	5.9%	7.6%	8.8%	7.5%	7.2%	7.2%	11.3%	11.3%
SP-1990	6.0%	7.2%	7.5%	5.8%	7.5%	8.7%	7.4%	7.1%	7.1%	11.3%	11.3%
SP-1991	5.9%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	7.0%	11.2%	11.2%
SP-1992	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%
SP-1993	6.0%	7.2%	7.5%	5.8%	7.5%	8.7%	7.5%	7.2%	7.1%	11.3%	11.3%
SP-1994	6.0%	7.2%	7.5%	5.7%	7.5%	8.7%	7.4%	7.1%	7.0%	11.3%	11.3%
TO-1990	5.9%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	7.0%	11.2%	11.2%
TO-1991	6.0%	7.2%	7.5%	5.7%	7.5%	8.7%	7.4%	7.1%	7.1%	11.3%	11.3%
TO-1992	5.9%	7.1%	7.4%	5.7%	7.4%	8.7%	7.4%	7.1%	7.0%	11.2%	11.2%
TO-1993	5.8%	7.1%	7.4%	5.6%	7.4%	8.6%	7.3%	7.0%	6.9%	11.2%	11.2%

Table III-42. Estimated error in outflow solute export for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the VWM chemistry errors with the errors for outflow discharge. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SILICATE
CR-1990	18.5%	16.1%	21.6%	16.0%	19.8%	15.3%	15.7%	15.4%	16.2%	15.4%	18.3%
CR-1991	21.9%	16.0%	108.1%	18.4%	27.7%	15.8%	15.8%	15.8%	16.4%	15.5%	15.2%
CR-1992	26.9%	11.9%	119.3%	11.3%	46.8%	10.7%	11.0%	10.6%	11.9%	10.6%	20.3%
CR-1993	20.8%	11.5%	55.0%	13.7%	20.7%	10.6%	10.9%	10.8%	11.8%	10.8%	10.3%
EM-1985	23.6%	17.9%	49.4%	22.9%	27.1%	16.7%	18.3%	18.5%	17.1%	17.2%	17.6%
EM-1986	16.8%	16.6%	40.7%	15.1%	15.7%	11.4%	13.9%	13.0%	14.4%	14.3%	14.2%
EM-1987	15.0%	12.9%	20.2%	12.5%	12.8%	10.7%	11.6%	10.9%	12.5%	12.0%	10.8%
EM-1990	12.6%	14.0%	28.1%	13.7%	14.7%	10.7%	12.5%	11.3%	12.4%	11.8%	11.0%
EM-1991	17.0%	9.7%	81.7%	19.1%	14.8%	7.9%	11.1%	8.1%	9.9%	8.5%	7.8%
EM-1992	12.1%	8.6%	45.8%	10.4%	12.2%	6.1%	7.6%	6.9%	8.2%	7.9%	14.2%
EM-1993	7.3%	10.1%	23.1%	10.5%	8.0%	6.0%	8.4%	7.0%	9.0%	14.7%	6.3%
EM-1994	7.1%	7.4%	30.1%	7.9%	8.0%	6.0%	6.8%	7.5%	8.0%	6.2%	5.6%
LO-1990	22.2%	22.3%	31.8%	21.4%	32.9%	21.0%	21.6%	21.4%	22.1%	20.7%	20.8%
LO-1991	25.6%	24.2%	69.8%	21.6%	37.3%	21.8%	23.0%	21.6%	22.7%	22.0%	23.6%
LO-1992	26.9%	21.5%	106.4%	28.4%	22.9%	21.9%	21.0%	18.9%	25.2%	20.1%	53.7%
LO-1993	27.9%	17.9%	42.9%	22.3%	39.5%	19.4%	19.4%	18.1%	19.0%	17.4%	19.8%
MF-1993	30.4%	23.0%	48.8%	30.4%	26.6%	29.6%	23.0%	21.7%	25.6%	22.3%	21.4%
MF-1994	16.2%	19.3%	51.6%	22.4%	22.9%	28.7%	17.9%	15.8%	18.3%	16.6%	16.6%
PE-1990	27.3%	26.0%	79.1%	25.9%	43.5%	25.4%	25.6%	25.6%	26.2%	25.9%	25.9%
PE-1991	26.7%	28.5%	82.1%	30.0%	36.8%	25.9%	26.7%	26.3%	27.5%	26.2%	27.2%
PE-1992	22.6%	16.7%	55.0%	18.5%	29.6%	15.6%	16.4%	16.0%	16.8%	16.6%	31.8%
PE-1993	18.0%	17.3%	32.6%	22.1%	23.3%	15.5%	16.7%	16.4%	17.4%	19.9%	16.2%
RU-1990	16.3%	16.3%	22.9%	20.6%	20.5%	15.7%	15.8%	16.2%	17.8%	16.4%	16.1%
RU-1991	20.2%	16.9%	50.0%	16.9%	24.0%	15.6%	15.8%	16.8%	16.6%	16.7%	15.4%
RU-1992	25.0%	11.9%	102.2%	15.7%	26.0%	12.4%	10.9%	10.6%	11.9%	11.1%	10.5%
RU-1993	20.4%	12.1%	62.6%	17.0%	25.7%	10.6%	11.1%	10.9%	12.0%	11.8%	10.4%
RU-1994	43.1%	11.4%	34.5%	13.7%	31.2%	10.5%	11.0%	19.5%	11.8%	14.5%	12.9%
SP-1990	28.0%	21.5%	43.6%	21.9%	32.9%	24.3%	21.9%	21.6%	21.1%	20.4%	27.3%
SP-1991	13.9%	13.2%	63.9%	13.8%	16.3%	12.8%	11.8%	12.6%	12.6%	11.0%	11.7%
SP-1992	14.6%	11.0%	105.2%	16.7%	35.5%	11.9%	10.0%	9.9%	10.8%	8.7%	13.9%
SP-1993	23.8%	10.9%	64.1%	16.4%	28.5%	12.1%	12.0%	9.8%	9.7%	7.6%	7.5%
SP-1994	64.7%	87.8%	294.1%	8.7%	62.9%	12.7%	71.7%	66.4%	51.0%	44.9%	22.4%
TO-1990	24.2%	22.0%	49.7%	23.3%	38.5%	23.1%	22.1%	21.7%	23.9%	22.6%	21.9%
TO-1991	21.5%	25.3%	110.8%	32.7%	50.7%	25.3%	26.6%	26.2%	26.9%	28.4%	26.5%
TO-1992	19.7%	16.8%	63.0%	23.5%	41.9%	17.7%	19.4%	18.5%	17.2%	16.2%	43.1%
TO-1993	19.0%	17.2%	56.4%	24.3%	88.7%	18.2%	20.3%	19.0%	18.8%	20.8%	17.2%

Table III-43. Estimated error in annual solute loading (rain + snow flux) for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the flux errors for rain and snow. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP.

SITE/YEAR	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>2</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
CR-1990	19.5%	24.2%	13.9%	23.6%	21.5%	19.9%	16.4%	13.0%	11.9%	21.2%	28.5%
CR-1991	5.1%	5.9%	6.3%	4.9%	6.3%	6.9%	6.4%	6.4%	6.2%	8.0%	8.1%
CR-1992	5.0%	6.0%	6.3%	5.2%	6.1%	7.1%	6.4%	6.2%	6.6%	8.5%	8.0%
CR-1993	5.4%	5.9%	6.8%	4.8%	6.1%	7.7%	6.8%	6.6%	6.2%	9.0%	7.9%
EM-1985	5.2%	7.5%	6.5%	5.0%	6.0%	6.5%	6.2%	6.2%	6.0%	NA	NA
EM-1986	5.2%	6.7%	6.5%	5.1%	6.1%	6.2%	5.8%	6.2%	6.1%	NA	NA
EM-1987	5.0%	8.0%	5.9%	6.6%	8.1%	6.8%	6.0%	11.4%	6.9%	9.7%	10.2%
EM-1990	7.8%	12.1%	10.2%	17.4%	16.6%	18.3%	15.0%	11.7%	19.7%	NA	NA
EM-1991	5.1%	7.2%	5.9%	6.2%	7.2%	6.2%	6.3%	6.4%	6.8%	9.5%	9.7%
EM-1992	5.0%	6.1%	5.7%	5.6%	7.2%	6.3%	5.8%	8.6%	8.6%	8.6%	8.2%
EM-1993	5.4%	6.0%	7.1%	4.8%	6.5%	7.8%	7.1%	6.6%	6.2%	8.9%	8.4%
EM-1994	6.0%	6.3%	6.3%	5.5%	6.6%	7.3%	6.4%	7.2%	6.2%	11.1%	8.3%
LO-1990	5.5%	7.6%	6.6%	7.0%	7.7%	9.0%	7.5%	6.4%	7.3%	11.9%	13.5%
LO-1991	5.9%	7.2%	6.6%	7.0%	7.6%	7.8%	6.6%	6.8%	7.2%	12.1%	10.2%
LO-1992	6.4%	7.6%	6.6%	8.8%	9.6%	8.4%	6.7%	6.4%	6.6%	10.4%	10.1%
LO-1993	5.8%	6.7%	7.1%	5.2%	7.0%	8.3%	6.8%	6.7%	6.5%	9.9%	9.3%
MF-1993	5.4%	5.9%	7.1%	4.7%	6.4%	7.7%	7.0%	6.7%	6.1%	8.7%	8.6%
MF-1994	5.9%	6.3%	6.1%	5.6%	6.7%	7.2%	6.3%	7.4%	6.2%	11.1%	8.2%
PE-1990	7.4%	11.8%	9.3%	17.3%	15.2%	18.8%	15.0%	11.0%	21.3%	NA	NA
PE-1991	5.1%	6.8%	5.8%	5.7%	6.8%	6.2%	6.1%	6.4%	6.9%	8.4%	8.2%
PE-1992	5.0%	6.0%	5.7%	5.7%	7.3%	6.2%	6.0%	8.2%	7.8%	9.6%	8.1%
PE-1993	5.2%	5.9%	7.0%	4.7%	6.4%	7.8%	7.0%	6.7%	6.1%	8.8%	8.5%
RU-1990	13.5%	21.8%	16.3%	19.4%	18.2%	21.3%	17.9%	15.5%	14.5%	16.0%	23.0%
RU-1991	12.7%	15.0%	12.2%	15.7%	15.6%	10.7%	12.1%	12.7%	12.6%	18.1%	14.5%
RU-1992	8.8%	11.7%	8.3%	11.0%	11.8%	9.2%	9.5%	8.9%	10.7%	14.0%	14.2%
RU-1993	5.6%	6.4%	7.0%	5.2%	6.7%	7.6%	6.6%	6.6%	6.3%	9.9%	9.1%
RU-1994	8.9%	8.5%	8.2%	8.3%	10.3%	8.4%	7.9%	7.6%	7.2%	10.1%	21.8%
SP-1990	8.4%	15.6%	11.0%	15.7%	15.0%	14.8%	13.6%	17.4%	13.7%	19.6%	19.5%
SP-1991	6.9%	10.0%	7.0%	9.3%	9.6%	8.2%	7.6%	7.6%	6.5%	11.8%	11.4%
SP-1992	9.0%	9.8%	7.4%	8.9%	10.1%	8.1%	7.6%	9.2%	6.3%	12.7%	12.9%
SP-1993	5.5%	6.5%	7.1%	5.9%	6.7%	8.1%	6.8%	6.6%	6.4%	9.6%	10.3%
SP-1994	7.5%	12.1%	7.7%	10.2%	11.3%	14.1%	9.7%	8.6%	10.7%	16.4%	20.3%
TO-1990	8.6%	14.7%	10.7%	18.2%	17.7%	21.7%	17.9%	13.2%	20.0%	NA	NA
TO-1991	5.1%	8.0%	5.8%	6.4%	7.5%	6.4%	6.9%	6.6%	7.7%	8.3%	8.7%
TO-1992	5.0%	6.6%	5.7%	6.1%	7.7%	6.2%	6.1%	10.0%	5.7%	10.1%	9.3%
TO-1993	5.0%	5.8%	6.9%	4.8%	6.1%	7.9%	6.8%	6.6%	5.9%	8.0%	8.4%

Table III-44. Estimated error in solute yields for the study catchments during the period of 1990 through 1994. The errors were computed by propagating the flux errors for rain, snow and outflow. In the Table the following abbreviations are used: Crystal Lake-CR, Emerald Lake-EM, Lost Lake-LO, Marble Fork-MF, Pear Lake-PE, Ruby Lake-RU, Spuller Lake-SP, Topaz Lake-TP. Sil. = silicate.

SITE/YEAR	H <sup>+</sup>	ANC	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SIL.	HCO <sub>2</sub> <sup>-</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
CR-1990	18.9	16.1	24.1	10.7	23.4	15.4	12.9	13.2	12.4	10.9	18.3	21.2	28.5
CR-1991	5.0	16.0	5.9	7.5	4.9	7.4	11.7	13.1	12.7	11.5	15.2	8.0	8.1
CR-1992	5.0	11.9	6.0	6.3	5.2	5.3	7.7	7.6	9.8	6.0	20.3	8.5	8.0
CR-1993	5.3	11.5	5.8	9.1	4.8	6.6	10.0	10.0	10.7	10.1	10.3	9.0	7.9
EM-1985	5.1	17.9	7.5	7.1	13.0	7.8	14.1	13.3	12.1	10.5	17.6	N	N
EM-1986	5.1	16.6	6.6	7.2	8.6	7.3	12.8	11.3	11.7	9.2	14.2	N	N
EM-1987	4.8	12.9	8.0	6.9	6.0	6.5	9.0	7.4	9.4	9.5	10.8	9.7	10.2
EM-1990	7.0	14.0	11.7	8.9	12.2	9.8	10.8	9.2	10.3	10.6	11.0	N	N
EM-1991	5.8	9.7	7.2	11.9	7.9	5.6	9.6	6.4	8.8	6.6	7.8	9.5	9.7
EM-1992	4.6	8.6	6.0	5.8	5.5	4.7	6.4	5.6	7.0	6.3	14.2	8.6	8.2
EM-1993	5.0	10.1	6.0	6.1	5.1	4.5	7.8	6.0	8.0	12.8	6.3	8.9	8.4
EM-1994	5.3	7.4	6.2	5.0	4.7	4.5	5.7	6.0	6.6	4.7	5.6	11.1	8.3
LO-1990	5.8	22.3	7.4	11.4	7.1	12.8	18.7	16.2	16.9	16.0	20.8	11.9	13.5
LO-1991	8.8	24.2	7.2	11.0	7.4	13.2	19.9	16.4	17.7	17.8	23.6	12.1	10.2
LO-1992	7.8	21.5	7.6	20.2	8.3	14.8	18.6	15.7	21.6	16.0	53.7	10.4	10.1
LO-1993	8.7	17.9	6.7	10.8	8.1	12.5	16.5	16.1	14.4	14.5	19.8	9.9	9.3
MF-1993	6.1	23.0	6.5	18.2	12.3	21.0	22.0	18.7	22.1	19.9	21.4	8.7	8.6
MF-1994	5.6	19.3	6.4	12.0	8.9	21.9	15.8	13.1	15.5	12.8	16.6	11.1	8.2
PE-1990	7.2	26.0	11.7	13.3	18.1	14.0	20.6	17.5	18.9	17.8	25.9	N	N
PE-1991	6.1	28.5	6.8	15.6	12.8	12.3	20.4	16.5	21.2	17.5	27.2	8.4	8.2
PE-1992	5.3	16.7	6.4	9.3	8.4	7.8	13.6	12.3	12.4	11.9	31.8	9.6	8.1
PE-1993	5.7	17.3	7.1	9.9	11.4	10.0	15.1	13.6	13.2	16.5	16.2	8.8	8.5
RU-1990	13.0	16.3	21.5	13.2	15.7	11.9	13.6	12.3	14.6	14.1	16.1	16.0	23.0
RU-1991	11.5	16.9	14.9	11.1	13.4	11.3	14.1	14.1	15.0	15.0	15.4	18.1	14.5
RU-1992	8.5	11.9	11.6	10.4	11.6	8.8	9.8	8.5	10.1	9.7	10.5	14.0	14.2
RU-1993	5.4	12.1	9.8	9.2	15.2	7.9	10.4	9.4	10.7	10.7	10.4	9.9	9.1
RU-1994	8.8	11.4	8.3	8.2	8.7	7.9	10.1	16.0	10.5	12.7	12.9	10.1	21.8
SP-1990	8.1	21.5	15.5	11.4	15.2	16.1	19.7	17.0	16.1	14.2	27.3	19.6	19.5
SP-1991	6.2	13.2	9.9	8.6	9.3	9.4	10.7	10.8	10.8	8.7	11.7	11.8	11.4
SP-1992	8.7	11.0	9.8	8.7	13.7	8.2	9.1	8.0	9.4	5.9	13.9	12.7	12.9
SP-1993	6.2	10.9	6.5	7.6	15.0	8.9	11.0	8.3	8.4	6.5	7.5	9.6	10.3
SP-1994	7.5	87.8	14.2	6.1	18.7	9.6	62.2	56.6	45.5	38.9	22.4	16.4	20.3
TO-1990	8.2	22.0	14.6	12.8	16.6	14.1	19.1	16.5	18.2	16.2	21.9	N	N
TO-1991	5.2	25.3	8.0	19.6	11.9	12.5	20.3	19.6	21.7	21.4	26.5	8.3	8.7
TO-1992	5.0	16.8	8.3	12.5	10.6	8.4	17.2	15.2	14.3	10.4	43.1	10.1	9.3
TO-1993	5.0	17.2	7.0	12.9	21.7	11.3	18.7	17.0	15.5	18.3	17.2	8.0	8.4

Table III-45. Effect of sampling frequency on the determination of annual solute export from the Emerald Lake watershed during water years 1993 and 1994. In this analysis the annual export of solutes calculated from chemical samples collected ca. daily during snowmelt is compared to annual export with snowmelt sampling frequencies of approximately weekly (~7 days), biweekly (~14 days), monthly (~28 days) and bimonthly (~56 days). Annual exports obtained with these sampling intervals are expressed as a percentage of annual exports calculated from daily samples:

$$((A - D) / D) * 100$$

where:

A = the annual flux of solute calculated from less than daily sample interval, and  
D = the annual flux of solute calculated from daily sample interval.

If the percentage for a solute is positive than the annual export for this solute at that particular sampling frequency is too high; if it is negative then it is too low. The average percent-difference is calculated from the absolute value of the differences for each ion. Ammonium was not included in these analyses because it cannot be reliably measured during much of the year due to low concentrations.

Year/Interval	H <sup>+</sup>	ANC	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	STL.	AVG
1993 1 Day	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1994 1 Day	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1993 7 Day	-13.2%	3.1%	0.1%	4.2%	0.5%	3.0%	1.7%	2.1%	3.7%	2.6%	3.5%
1994 7 Day	-5.8%	-0.7%	4.0%	2.2%	1.5%	2.7%	3.8%	2.2%	4.1%	1.7%	2.9%
1993 14 Day	-17.1%	10.5%	1.2%	4.6%	1.7%	6.0%	4.1%	4.9%	4.0%	5.5%	5.9%
1994 14 Day	-5.6%	-2.1%	2.7%	1.4%	2.0%	4.1%	5.7%	4.9%	6.1%	3.6%	3.8%
1993 28 Day	-20.2%	26.3%	8.8%	11.2%	2.8%	14.0%	10.5%	10.9%	18.0%	9.2%	13.2%
1994 28 Day	3.6%	9.2%	11.7%	4.3%	2.6%	10.1%	12.5%	10.3%	13.0%	11.3%	8.9%
1993 56 Day	21.2%	55.5%	21.1%	7.0%	5.8%	29.7%	21.8%	22.5%	44.3%	16.3%	20.3%
1994 56 Day	5.7%	17.1%	14.7%	-10.3%	3.6%	12.6%	20.0%	9.9%	14.3%	11.2%	11.9%

Table III-46. Solute balance of selected ions during the rise and fall of snowmelt 1993 at Emerald Lake. Predicted flux is the amount of outflow flux of solute assuming that snowmelt equaled outflow discharge during the period and that this melted snow was not altered by watershed processes. Bulk snow chemistry was used for Predicted flux. Actual flux is the amount of solute lost from the basin via the outflow and is calculated from daily measurement of outflow discharge and chemistry. Total solute storage is the amount of solute contained in the snowpack in the basin at maximum accumulation plus any additional snow which fell after the spring snow-survey and minus solutes lost from snowmelt (Predicted). Units are equivalents for fluxes and thousands of cubic meters for discharge. DIN is dissolved inorganic nitrogen and is the sum of ammonium and nitrate.

Period/Solute	Predicted From Melted Snow	Actual Outflow Flux	Total Storage in Snow Pack	Outflow Discharge for Period	Period
Rising-Hydrogen	3,887	483	13,631	747	1-April to 15-June
Falling-Hydrogen	5,430	814	9,744	1,044	16-June to 30-September
Rising-Chloride	2,093	1,743	7,340	747	1-April to 15-June
Falling-Chloride	2,924	1,899	5,247	1,044	16-June to 30-September
Rising-Nitrate	1,345	4,882	4,718	747	1-April to 15-June
Falling-Nitrate	1,879	3,852	3,373	1,044	16-June to 30-September
Rising-Sulfate	1,794	4,983	6,291	747	1-April to 15-June
Falling-Sulfate	2,506	5,783	4,497	1,044	16-June to 30-September
Rising-Calcium	673	16,043	2,359	747	1-April to 15-June
Falling-Calcium	940	13,734	1,686	1,044	16-June to 30-September
Rising-DIN	2,990	5,076	10,485	747	1-April to 15-June
Falling-DIN	4,177	4,469	7,495	1,044	16-June to 30-September

Table III-47. Solute balance of selected solutes during the rise and fall of snowmelt 1986 at Emerald Lake. Predicted flux is the amount of outflow flux of solute assuming that snowmelt equaled outflow discharge during the period and that this melted snow was not altered by watershed processes. Bulk snow chemistry was used for Predicted flux. Actual flux is the amount of solute lost from the basin via the outflow and is calculated from daily measurement of outflow discharge and from weekly to biweekly samples of outflow chemistry. Total solute storage is the amount of solute contained in the snowpack in the basin at maximum accumulation plus any additional snow which fell after the spring snow-survey and minus solutes lost from snowmelt (Predicted). Units are equivalents for fluxes and thousands of cubic meters for discharge. DIN is dissolved inorganic nitrogen and is the sum of ammonium and nitrate.

Period/Solute	Predicted From Melted Snow	Actual Outflow Flux	Total Storage in Snow Pack	Outflow Discharge for Period	Period
Rising-Hydrogen	4,301	1,510	13,184	935	1-April to 15-June
Falling-Hydrogen	4,733	1,085	8,883	1,029	16-June to 30-September
Rising-Chloride	2,899	3,682	8,885	935	1-April to 15-June
Falling-Chloride	3,190	2,192	5,986	1,029	16-June to 30-September
Rising-Nitrate	1,683	6,411	5,159	935	1-April to 15-June
Falling-Nitrate	1,852	3,046	3,476	1,029	16-June to 30-September
Rising-Sulfate	1,496	5,382	4,586	935	1-April to 15-June
Falling-Sulfate	1,646	4,722	3,090	1,029	16-June to 30-September
Rising-Calcium	561	21,663	1,720	935	1-April to 15-June
Falling-Calcium	617	16,139	1,159	1,029	16-June to 30-September
Rising-DIN	2,992	6,462	9,171	935	1-April to 15-June
Falling-DIN	3,293	3,157	6,179	1,029	16-June to 30-September

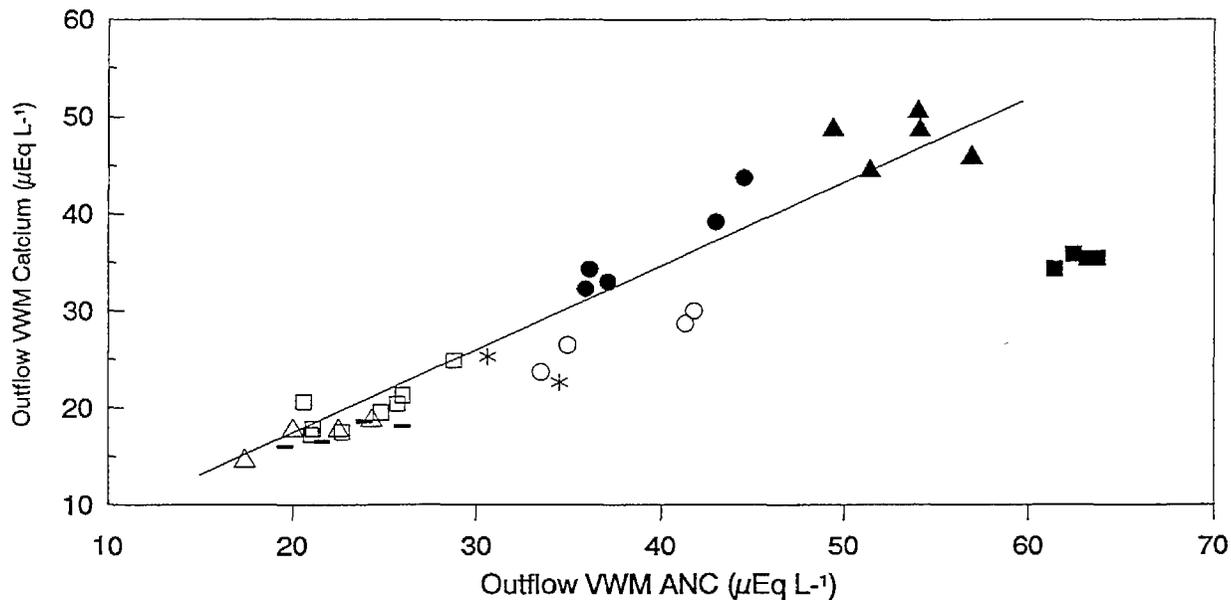
## Figure Captions

- Figure III-1. Relationship between VWM ANC and VWM calcium (top panel) and VWM sum of base cations (bottom panel) in outflow from the eight study sites. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-2. Scatterplot of annual loading to annual catchment yield of hydrogen-ion for the eight study catchments from 1985 through 1994.
- Figure III-3. Scatterplot of annual loading to annual catchment yield of hydrogen-ion for the Emerald Lake catchment from 1985 through 1994.
- Figure III-4. Scatterplot of annual loading to annual catchment yield of chloride (top panel) and sulfate (bottom panel) for the eight study catchments from 1985 through 1994.
- Figure III-5. Scatterplot of annual loading to annual catchment yield of chloride (top panel) and sulfate (bottom panel) for the Emerald Lake catchment from 1985 through 1994.
- Figure III-6. Scatterplot of annual loading to annual catchment yield of calcium (top panel) and sodium (bottom panel) for the eight study catchments from 1985 through 1994.
- Figure III-7. Scatterplot of annual loading to annual catchment yield of magnesium (top panel) and potassium (bottom panel) for the eight study catchments from 1985 through 1994.
- Figure III-8. Scatterplot of annual loading to annual catchment yield of calcium (top panel) and sodium (bottom panel) for the Emerald Lake catchment from 1985 through 1994.
- Figure III-9. Scatterplot of annual loading to annual catchment yield of magnesium (top panel) and potassium (bottom panel) for the Emerald Lake catchment from 1985 through 1994.
- Figure III-10. Scatterplot of annual loading to annual catchment yield of ammonium (top panel) and nitrate (bottom panel) for the eight study catchments from 1985 through 1994.
- Figure III-11. Scatterplot of annual loading to annual catchment yield of ammonium (top panel) and nitrate (bottom panel) for the Emerald Lake catchment from 1985 through 1994.
- Figure III-12. Scatterplot of annual loading to annual catchment yield of dissolved inorganic nitrogen (DIN) for the eight study catchments (top panel) and the Emerald Lake catchment (bottom panel) from 1985 through 1994.
- Figure III-13. Effect of sampling frequency on the determination of annual export of base cations, chloride and silicate during water years 1993 and 1994 at Emerald Lake. In the analysis the daily chemical record was degraded to simulate weekly, biweekly, monthly and monthly sampling regimes.

- Figure III-14. Effect of sampling frequency on the determination of annual export of hydrogen-ion, ANC, nitrate and sulfate during water years 1993 (top panel) and 1994 (bottom panel) at Emerald Lake. In the analysis the daily chemical record was degraded to simulate weekly, biweekly, monthly and monthly sampling regimes.
- Figure III-15. Effect of sampling frequency on the determination of ANC and hydrogen-ion export during water year 1993 at Emerald Lake. In the analysis the daily chemical record was degraded to simulate weekly, biweekly, monthly and monthly sampling regimes. Data are plotted as cumulative export during snowmelt (May through September).
- Figure III-16. Effect of sampling frequency on the determination of ANC and calcium export during water year 1994 at Emerald Lake. In the analysis the daily chemical record was degraded to simulate weekly, biweekly, monthly and monthly sampling regimes. Data are plotted as cumulative export during snowmelt (May through September).
- Figure III-17. Scatterplot of snow-water equivalence vs. winter loading of ammonium (top panel) and nitrate (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-18. Scatterplot of snow-water equivalence vs. winter loading of hydrogen-ion (top panel) and sulfate (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-19. Scatterplot of snow-water equivalence vs. winter loading of chloride (top panel) and sodium (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-20. Scatterplot of snow-water equivalence vs. winter loading of calcium (top panel) and magnesium (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-21. Scatterplot of snow-water equivalence vs. winter loading of potassium for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-22. Scatterplot of snow-water equivalence vs. winter loading of acetate (top panel) and formate (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-23. Scatterplot of annual runoff vs. annual export of ANC (top panel) and hydrogen-ion (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.

- Figure III-24. Scatterplot of annual runoff vs. annual export of ANC (top panel) and hydrogen-ion (bottom panel) for the Emerald Lake catchment from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated for Emerald Lake and the other study sites as well.
- Figure III-25. Scatterplot of annual runoff vs. annual export of nitrate (top panel) and sulfate (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-26. Scatterplot of annual runoff vs. annual export of nitrate (top panel) and sulfate (bottom panel) for the Emerald Lake catchment from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated for Emerald Lake and the other study sites as well.
- Figure III-27. Scatterplot of annual runoff vs. annual export of chloride (top panel) and sodium (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-28. Scatterplot of annual runoff vs. annual export of chloride (top panel) and sodium (bottom panel) for the Emerald Lake catchment from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-29. Scatterplot of annual runoff vs. annual export of calcium (top panel) and silicate (bottom panel) for the eight study catchments from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-30. Scatterplot of annual runoff vs. annual export of calcium (top panel) and silicate (bottom panel) for the Emerald Lake catchment from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated for Emerald Lake and the other study sites as well.
- Figure III-31. Scatterplot of annual runoff vs. annual export of magnesium (top panel) and potassium (bottom panel) for the Emerald Lake catchment from 1985 through 1994. Equations and correlation statistics for the best-fit lines are indicated.
- Figure III-32. Times series of discharge and ANC (top panel) and pH (bottom panel) in the Marble Fork river during a series of autumn rain and snow storms in 1994. The timing of the precipitation events is indicated with arrows. Individual chemicals samples are indicated by open circles.
- Figure III-33. Times series of discharge and nitrate (top panel) and sulfate (bottom panel) in the Marble Fork river during a series of autumn rain and snow storms in 1994. The timing of the precipitation events is indicated with arrows. Individual chemicals samples are indicated by open circles.
- Figure III-34. Times series of discharge and sum of base cations (top panel) and silicate (bottom panel) in the Marble Fork river during a series of autumn rain and snow storms in 1994. The timing of the precipitation events is indicated with arrows. Individual chemicals samples are indicated by open circles.

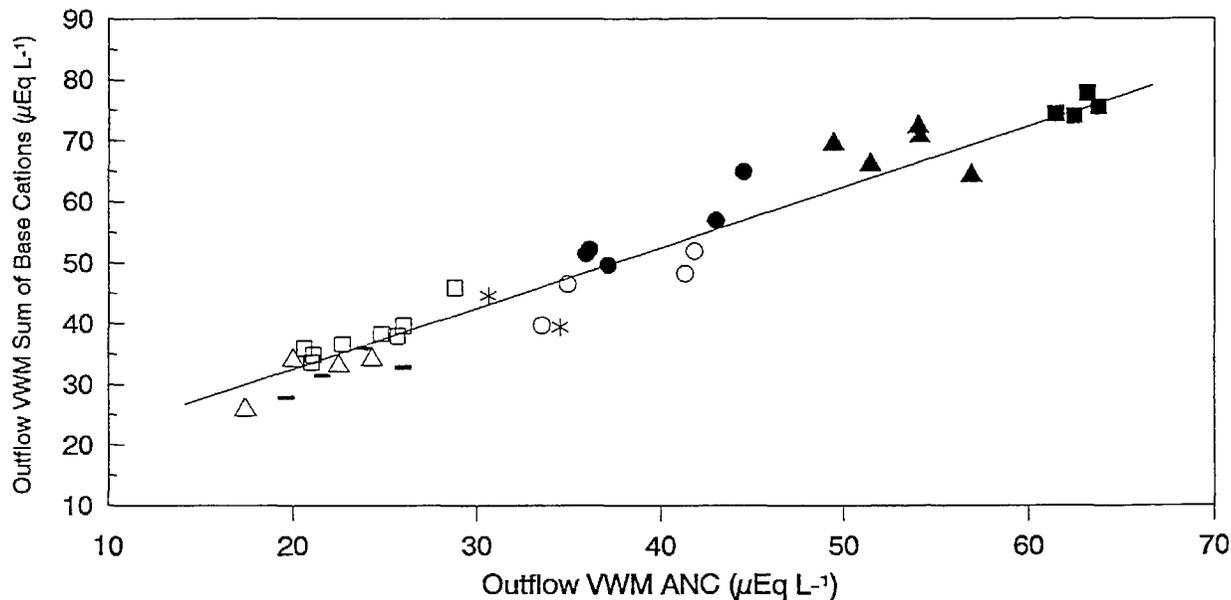
ANC vs Calcium  
Annual VWM Outflow Chemistry



Emerald   Pear   Topaz   Marble   Crystal   Ruby   Spuller   Lost  
 □   △   ○   \*   ■   ▲   ●   -

$Y = 0.92(X) - 2.96, r^2=0.92$  (without Crystal Lake)

ANC vs Sum of Base Cations  
Annual VWM Outflow Chemistry



Emerald   Pear   Topaz   Marble   Crystal   Ruby   Spuller   Lost  
 □   △   ○   \*   ■   ▲   ●   -

$Y = 1.06(X) + 10.4, r^2=0.95$

Figure III-1

WATERSHED SOLUTE BALANCE  
1985-1994: HYDROGEN

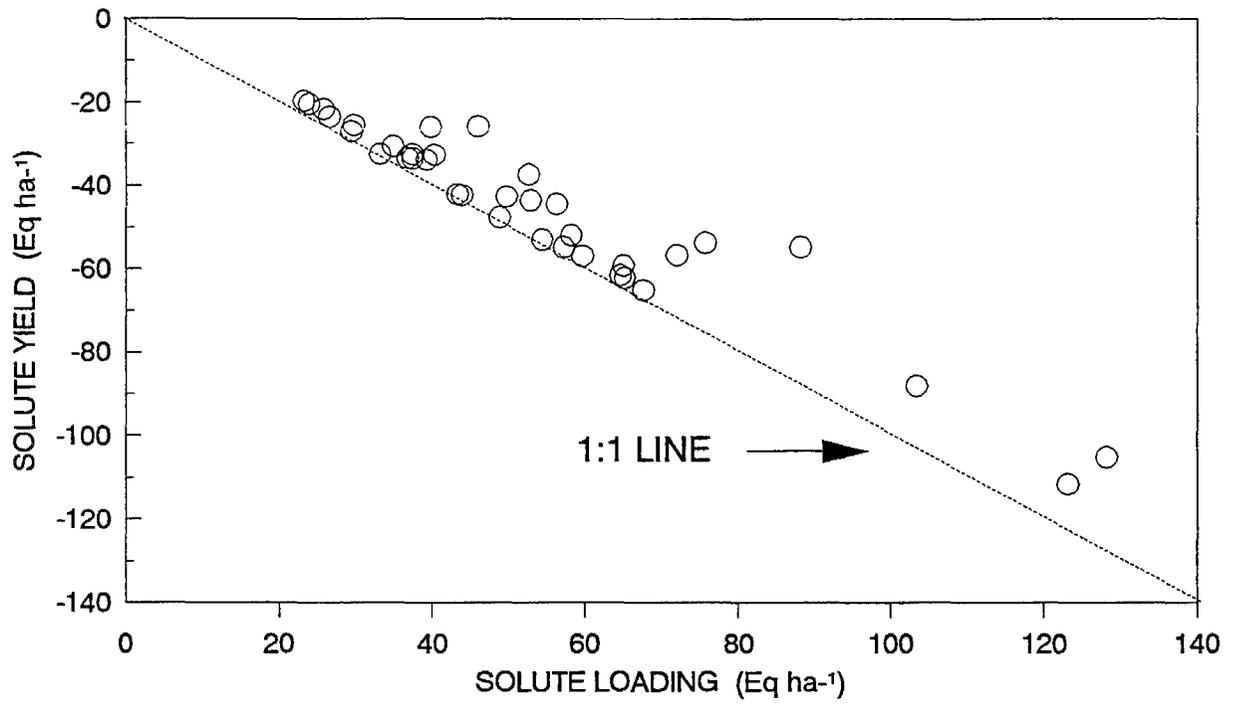


Figure III-2

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: HYDROGEN

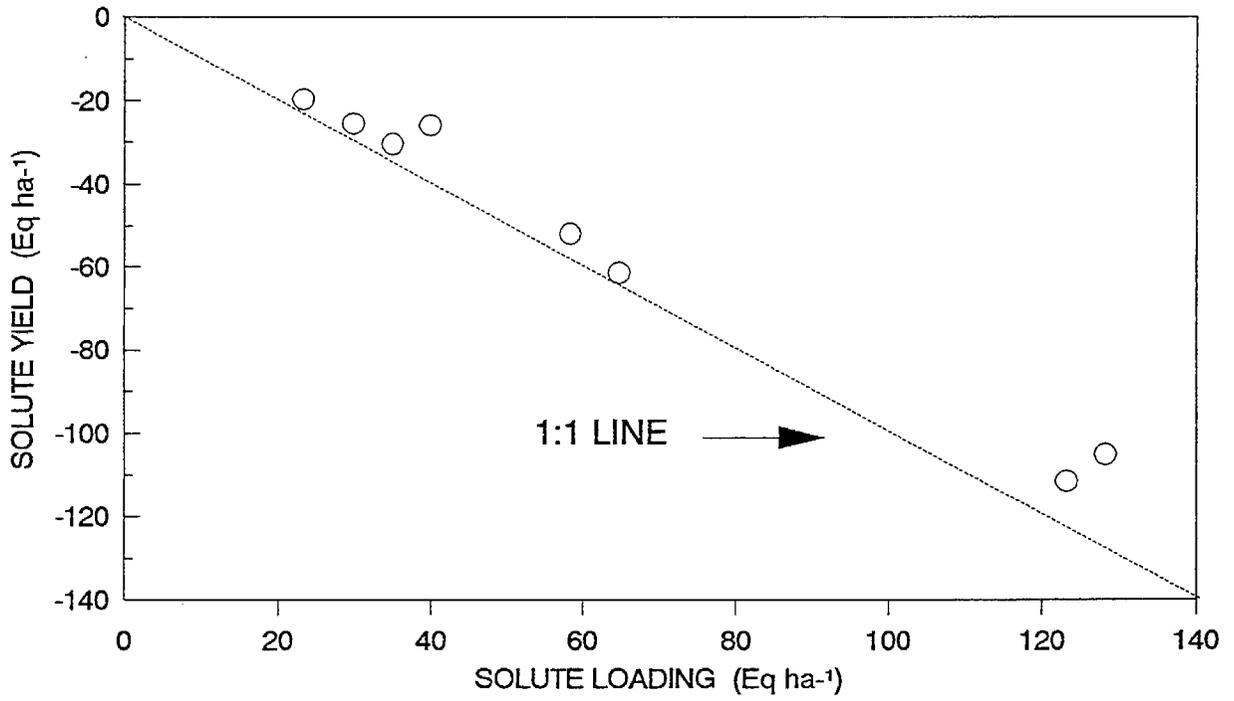
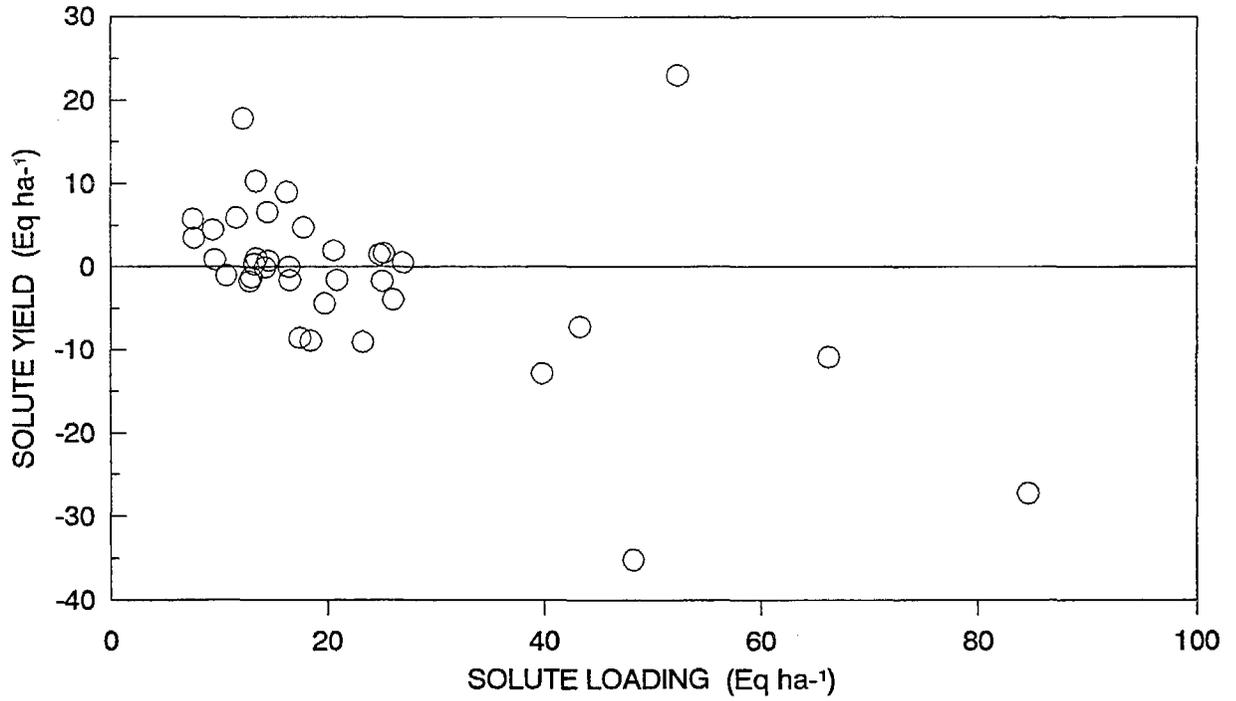


Figure III-3

WATERSHED SOLUTE BALANCE  
1985-1994: CHLORIDE



WATERSHED SOLUTE BALANCE  
1985-1994: SULFATE

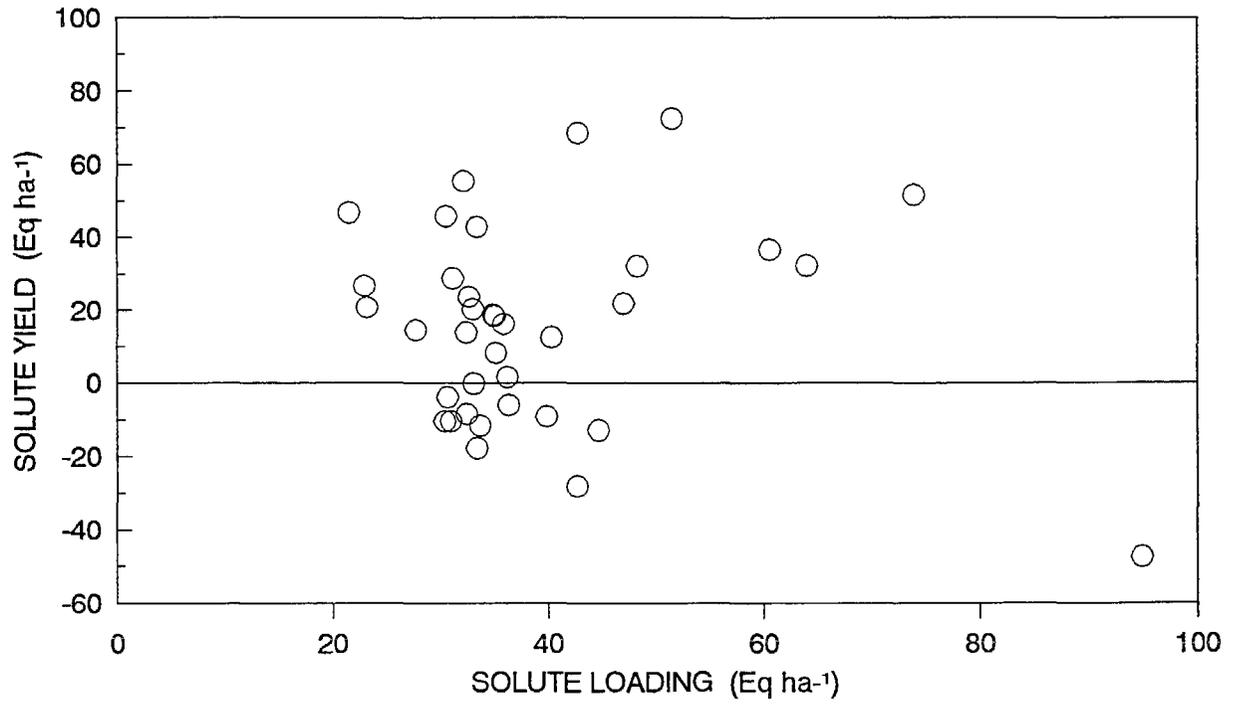
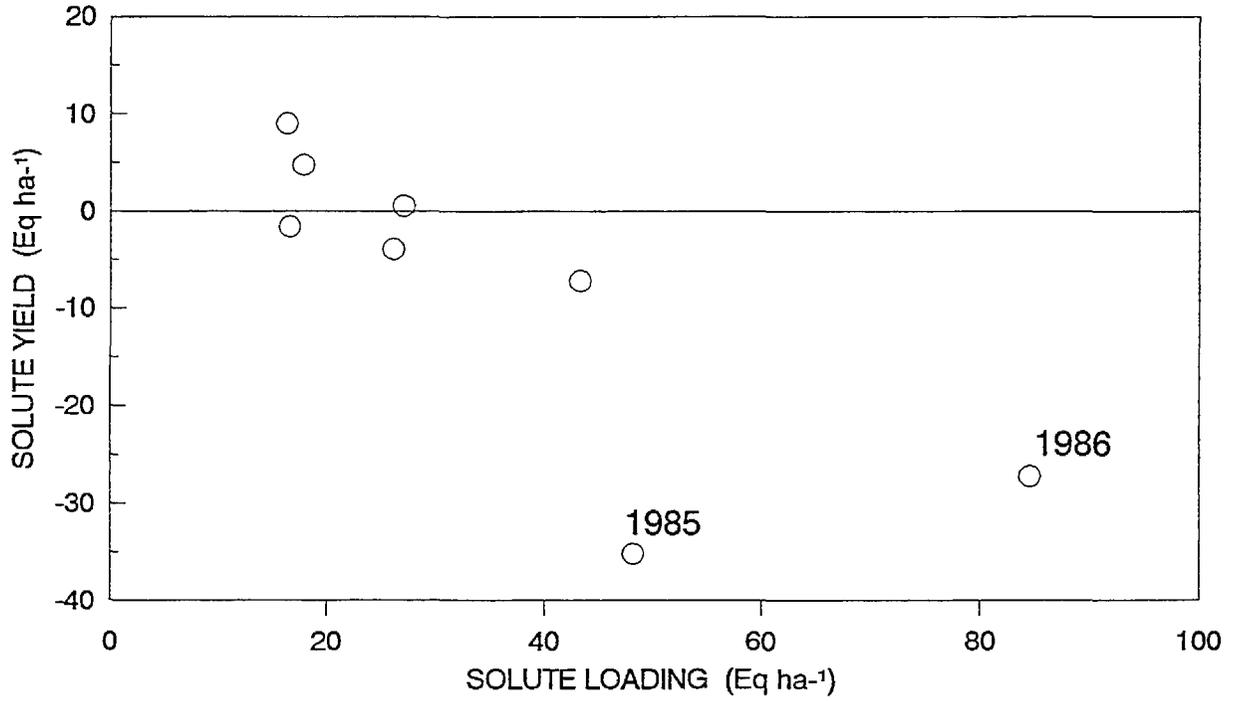


Figure III-4

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: CHLORIDE



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: SULFATE

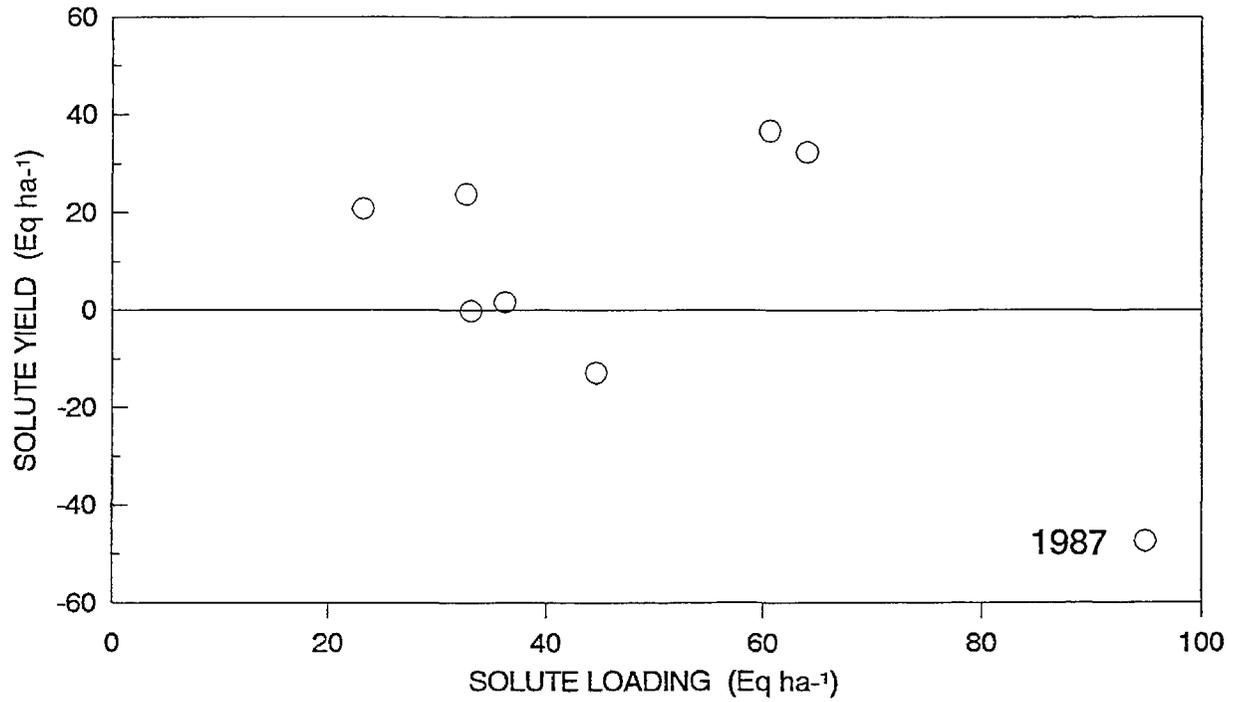


Figure III-5

WATERSHED SOLUTE BALANCE  
1985-1994: CALCIUM



WATERSHED SOLUTE BALANCE  
1985-1994: SODIUM

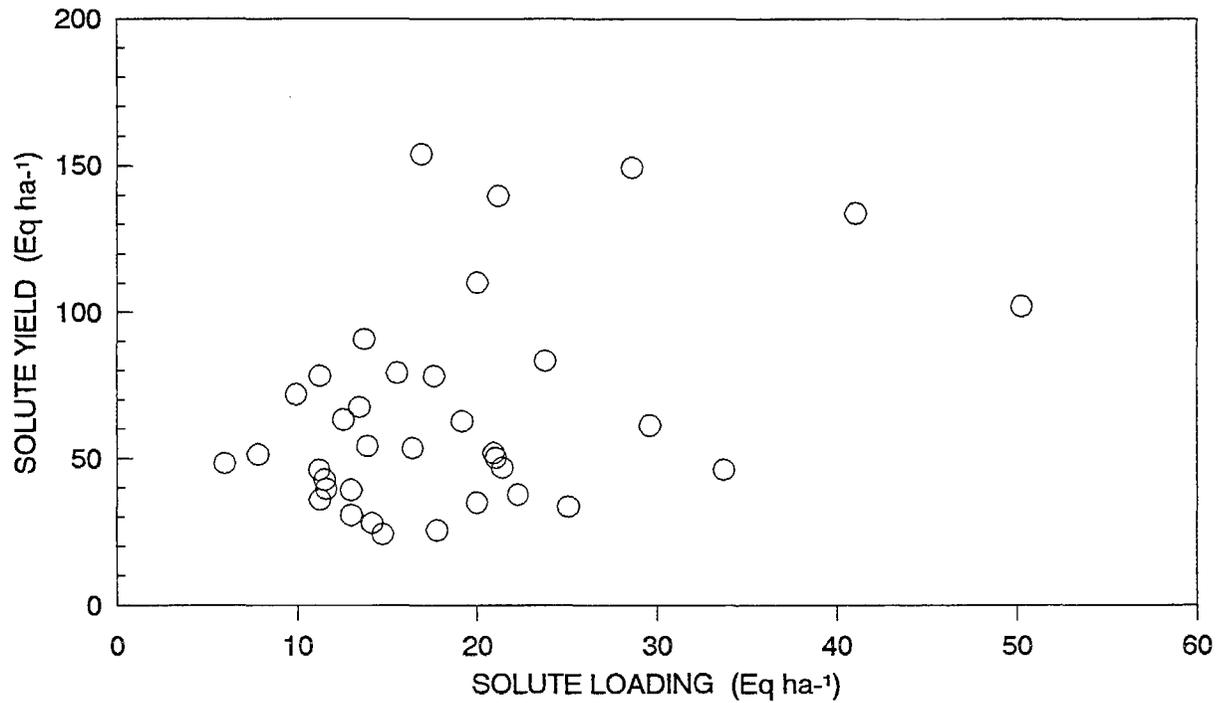


Figure III-6

WATERSHED SOLUTE BALANCE  
1985-1994: MAGNESIUM



WATERSHED SOLUTE BALANCE  
1985-1994: POTASSIUM

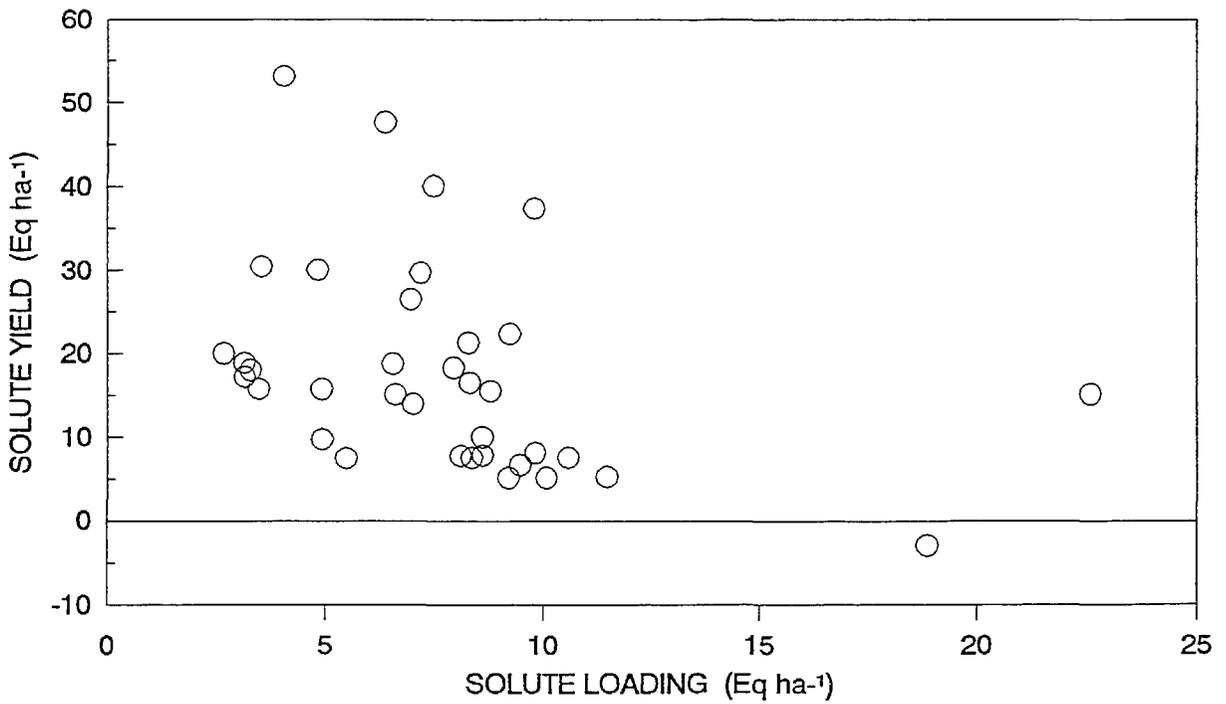
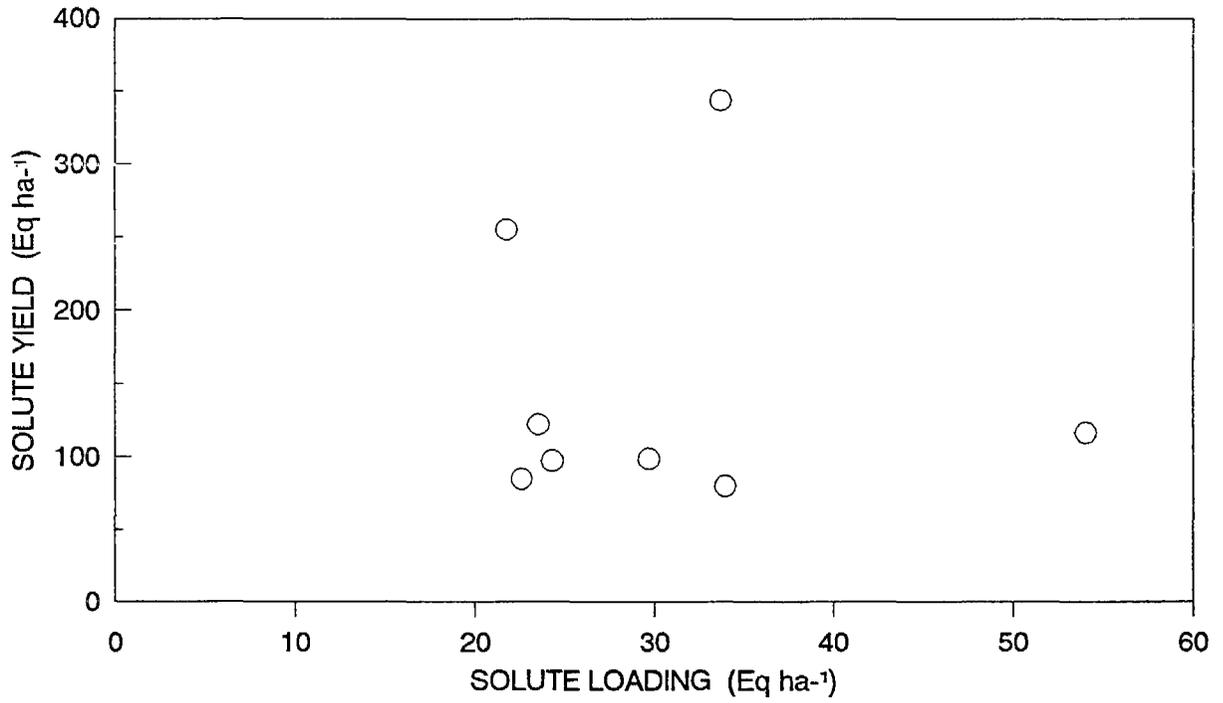


Figure III-7

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: CALCIUM



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: SODIUM

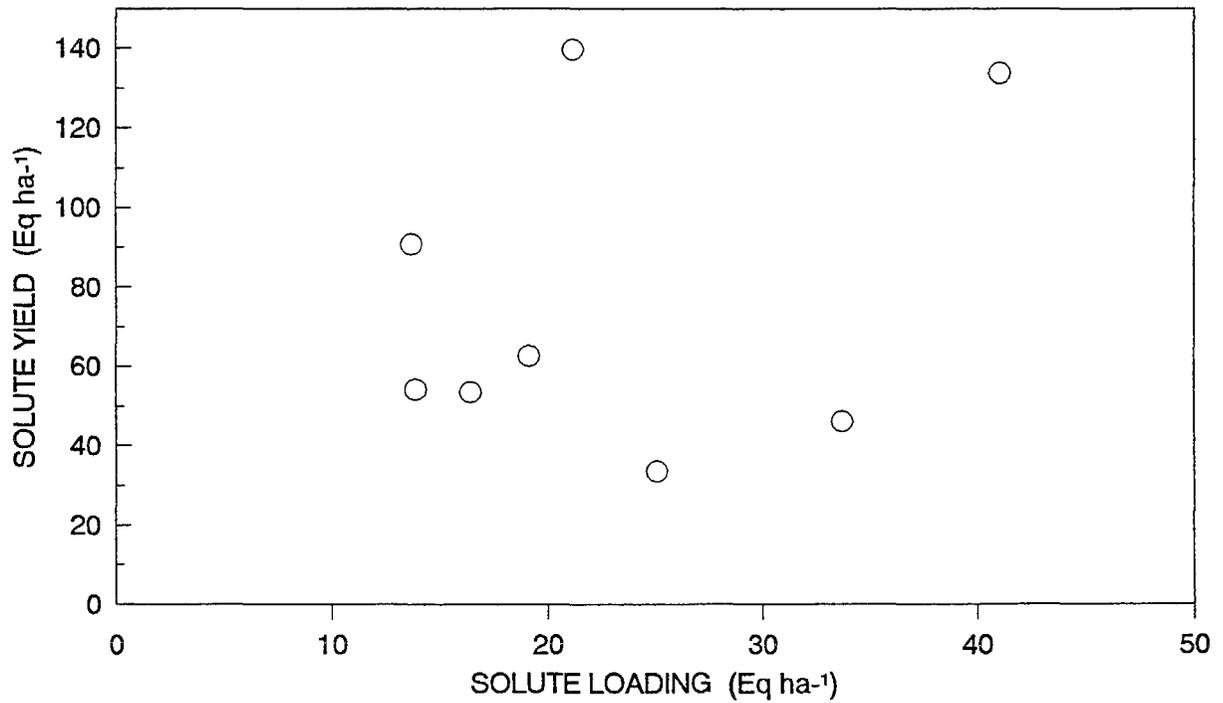
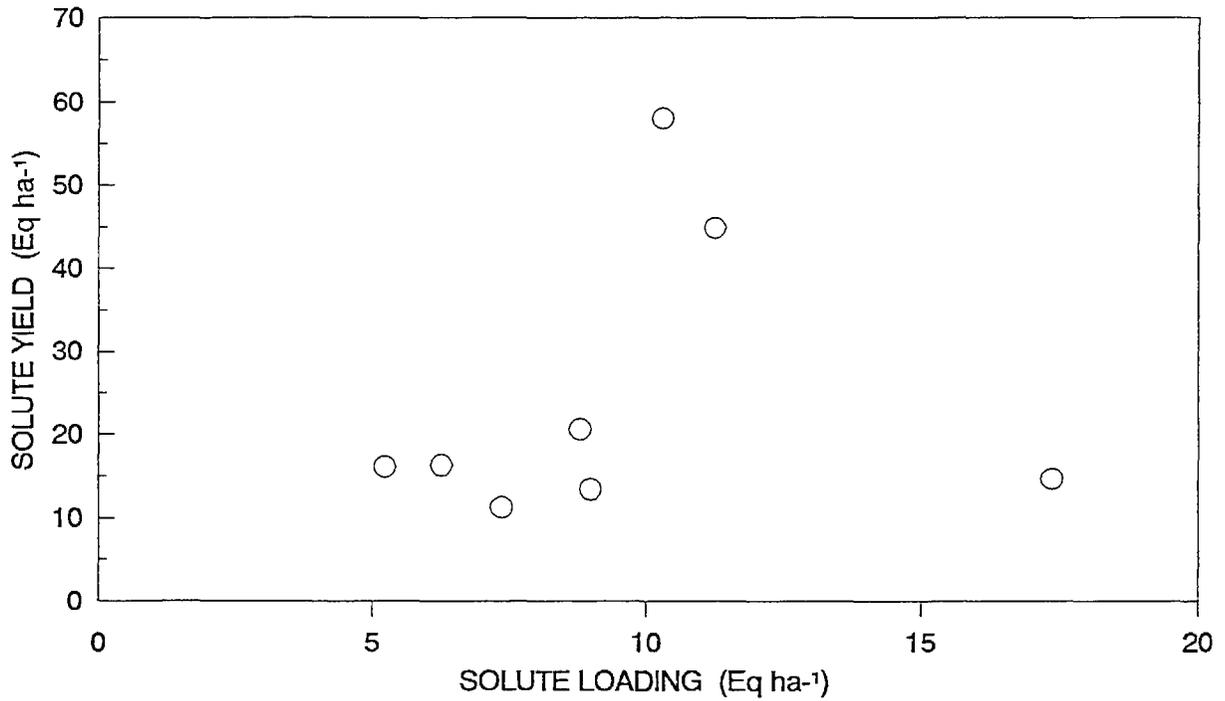


Figure III-8

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: MAGNESIUM



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: POTASSIUM

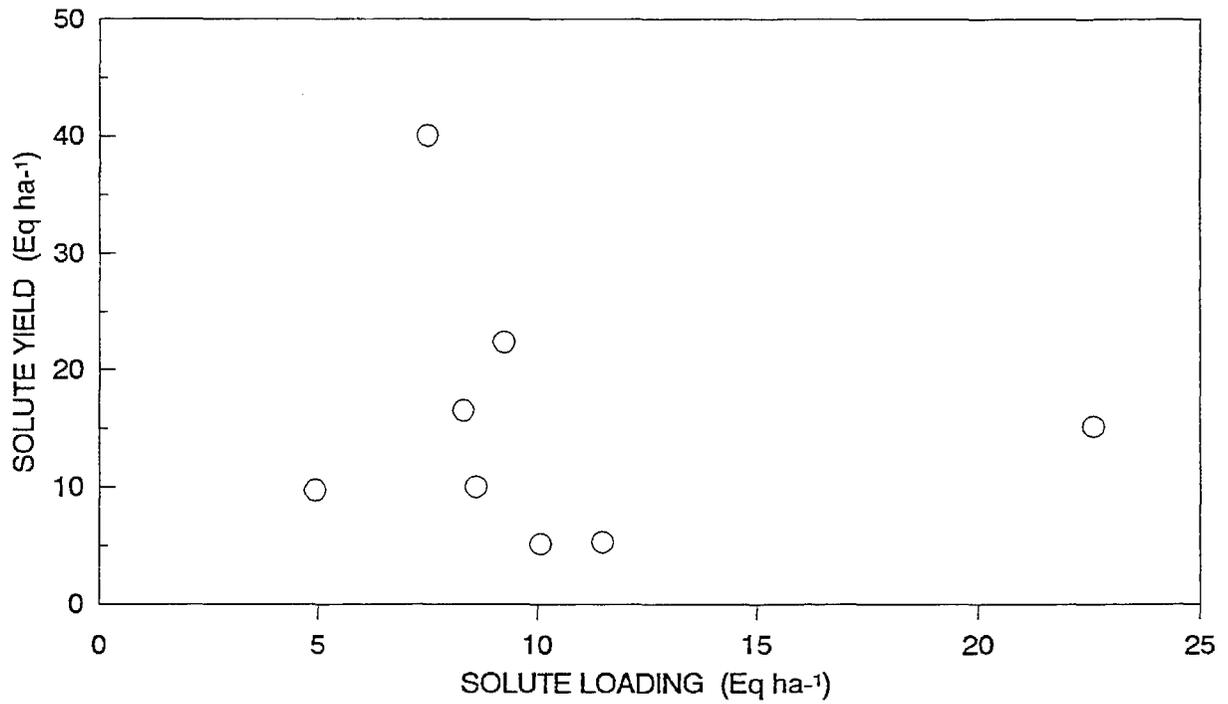
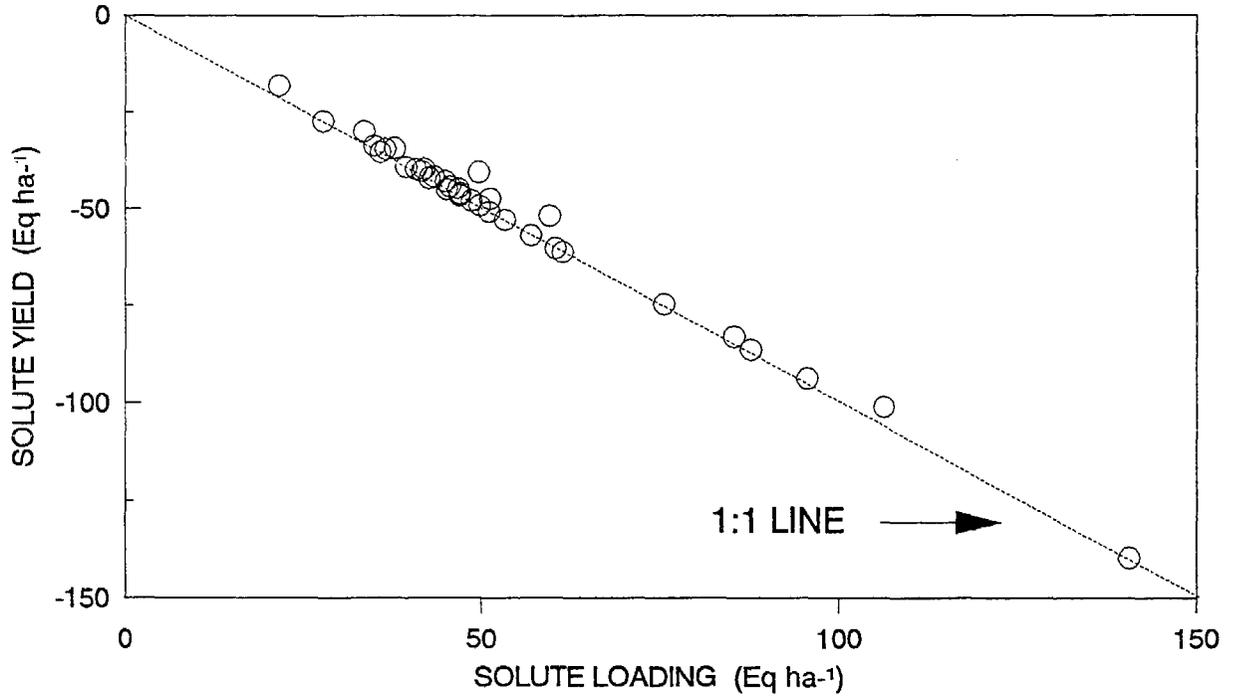


Figure III-9

WATERSHED SOLUTE BALANCE  
1985-1994: AMMONIUM



WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE

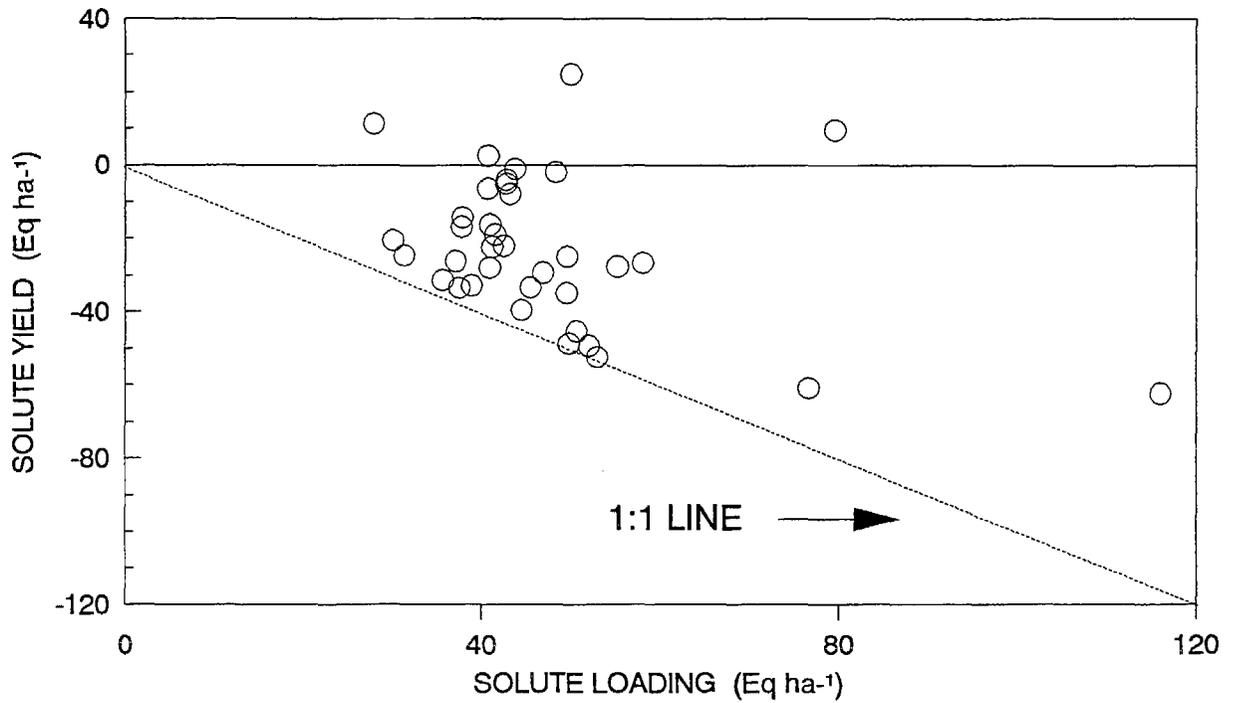
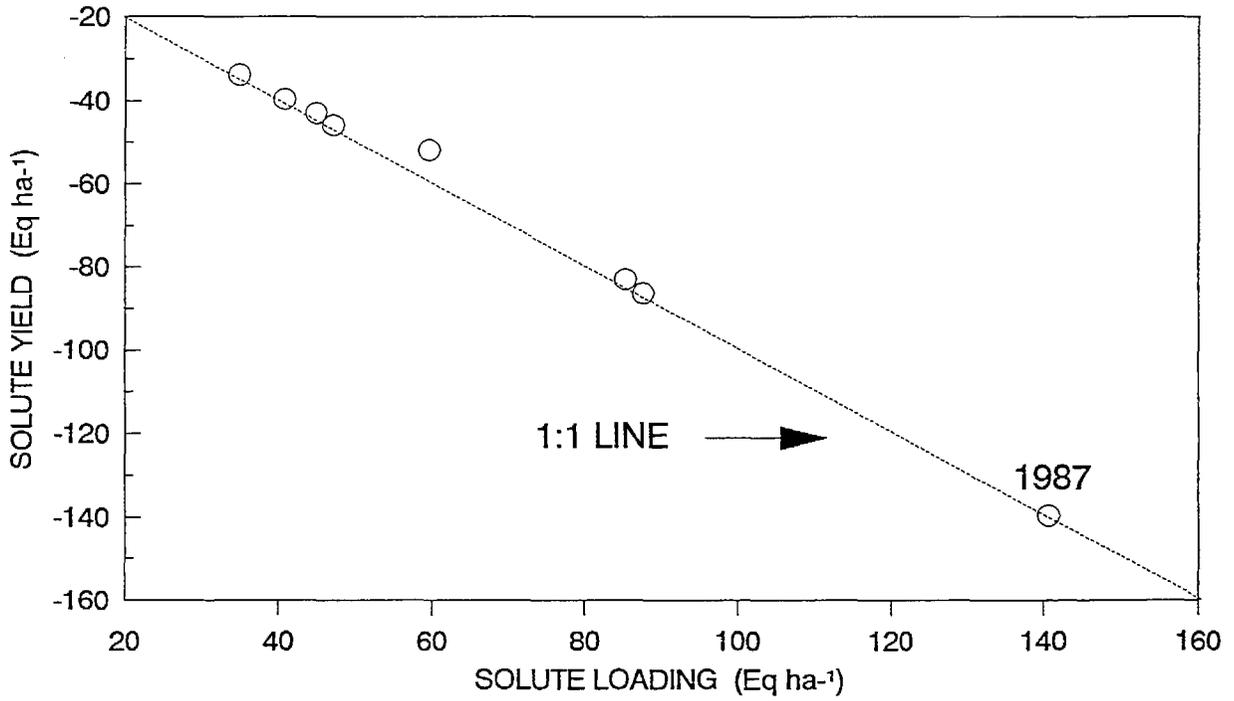


Figure III-10

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: AMMONIUM



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE

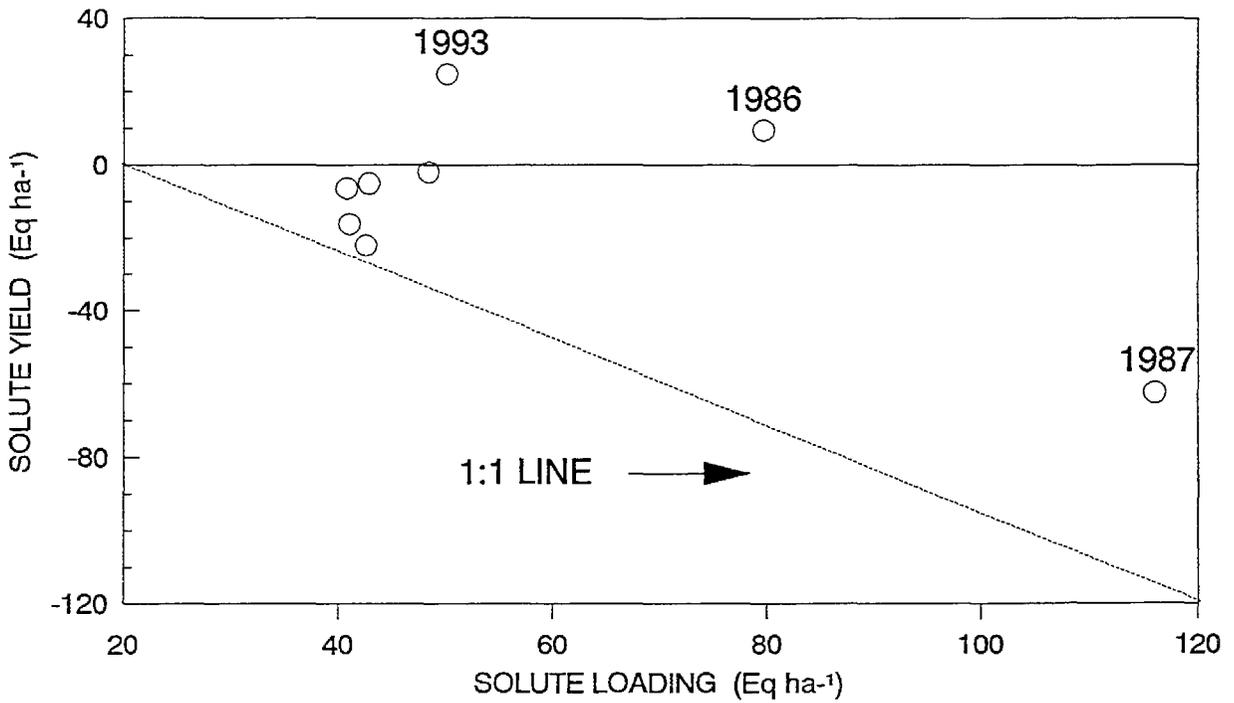
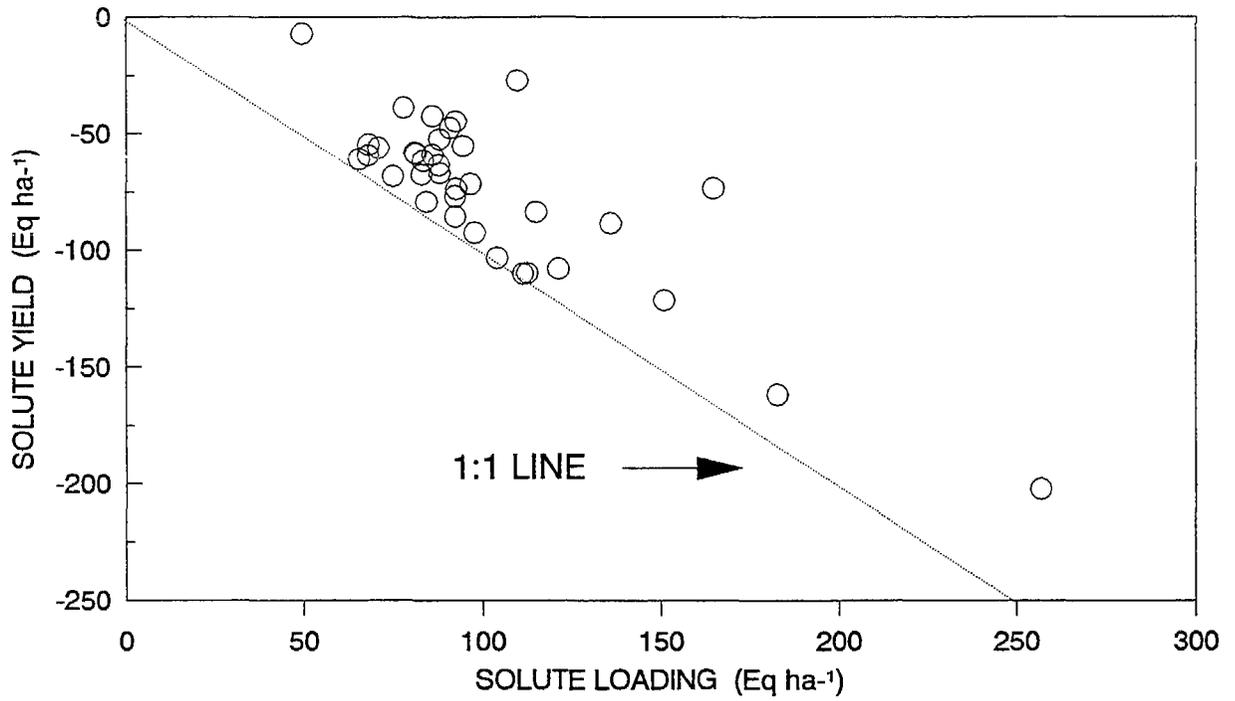


Figure III-11

WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE + AMMONIUM



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE + AMMONIUM

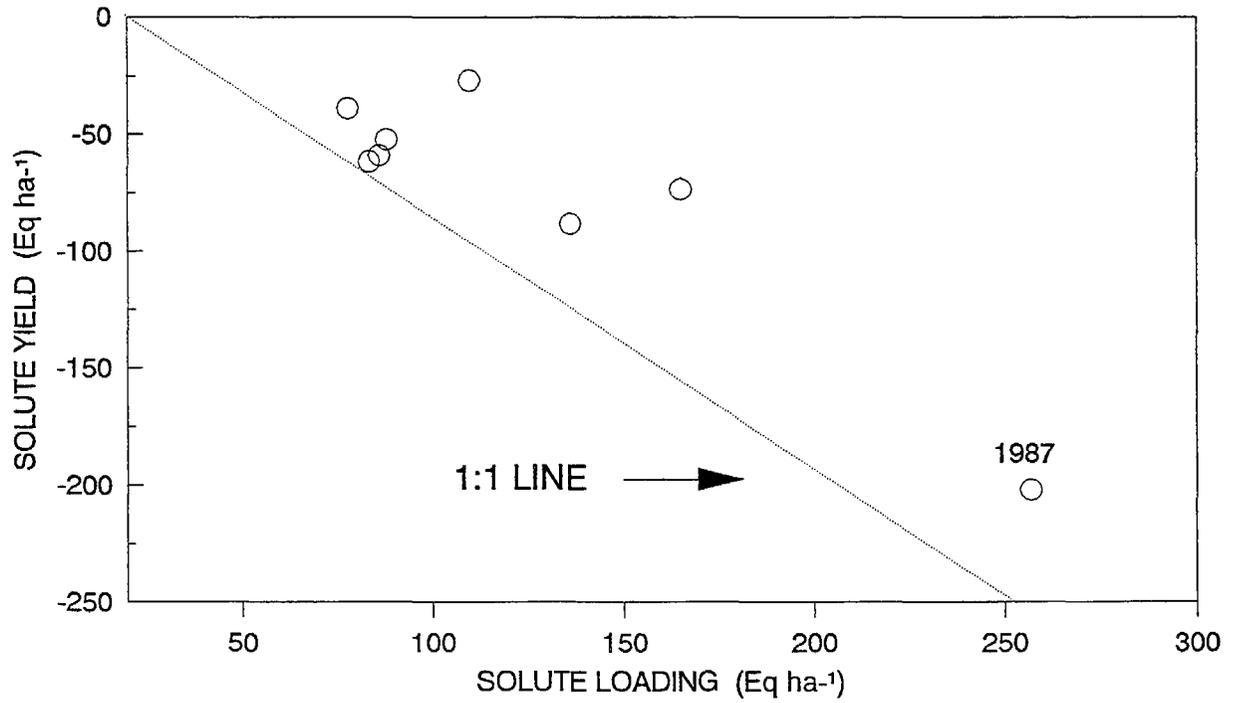
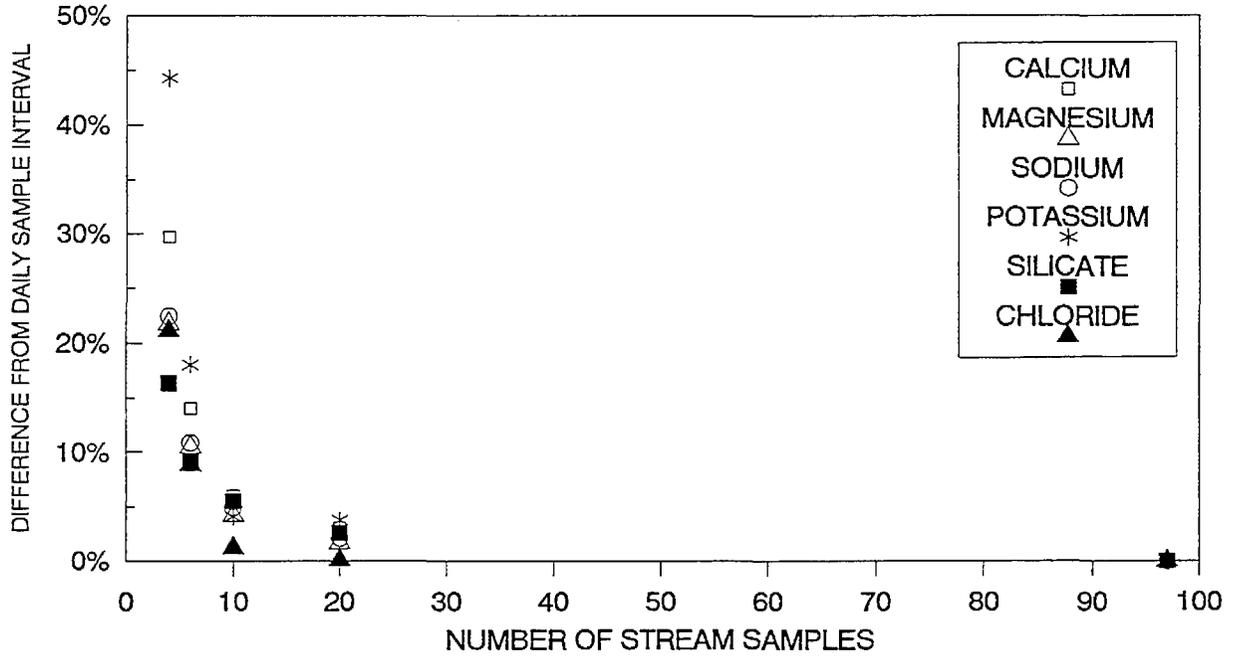


Figure III-12

EFFECT OF SAMPLING FREQUENCY ON  
THE DETERMINATION OF ANNUAL SOLUTE EXPORT  
WATER YEAR 1993



EFFECT OF SAMPLING FREQUENCY ON  
THE DETERMINATION OF ANNUAL SOLUTE EXPORT  
WATER YEAR 1994

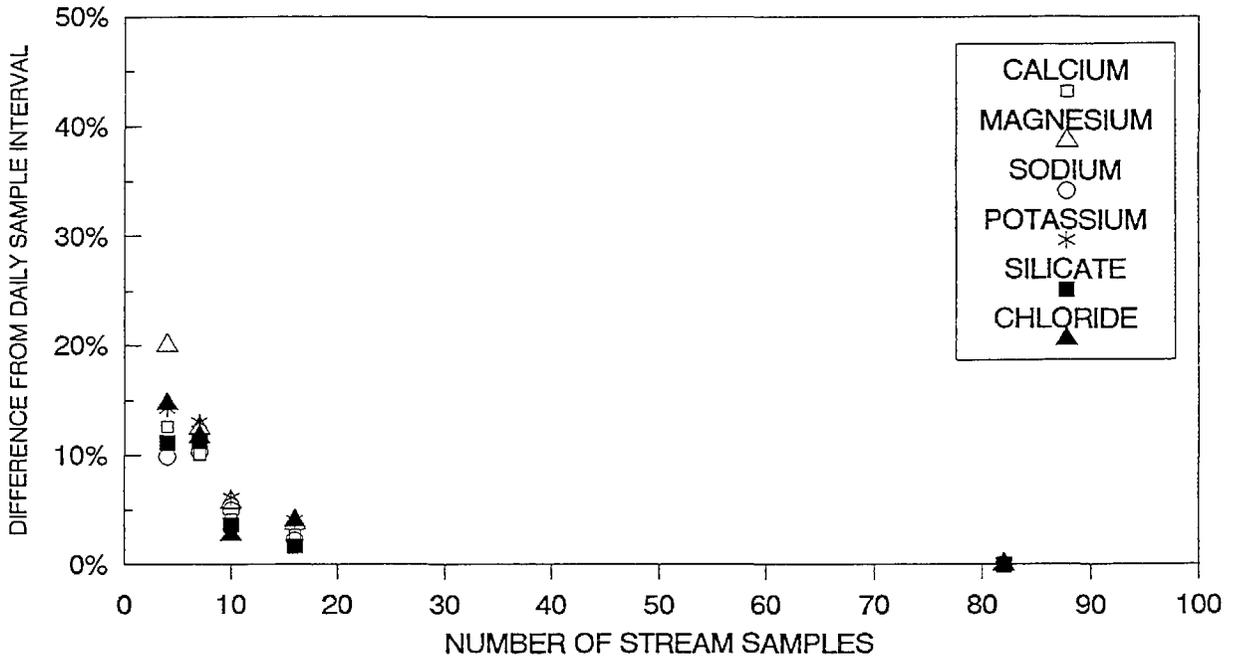
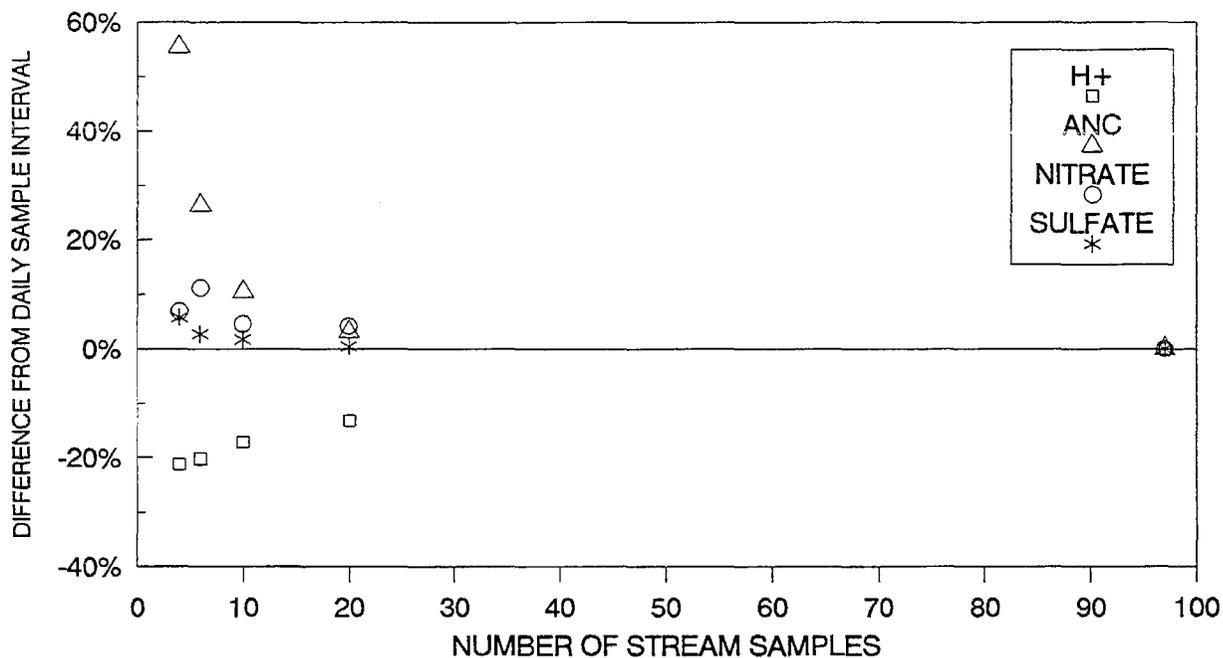


Figure III-13

EFFECT OF SAMPLING FREQUENCY ON  
THE DETERMINATION OF ANNUAL SOLUTE EXPORT  
WATER YEAR 1993



EFFECT OF SAMPLING FREQUENCY ON  
THE DETERMINATION OF ANNUAL SOLUTE EXPORT  
WATER YEAR 1994

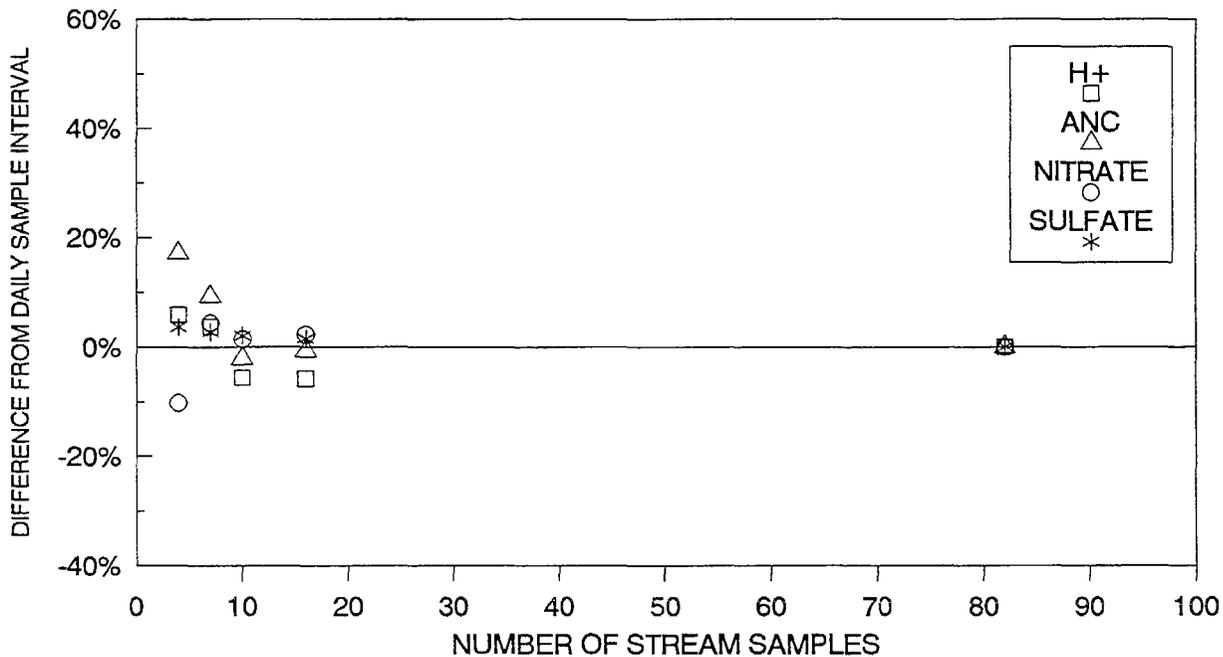
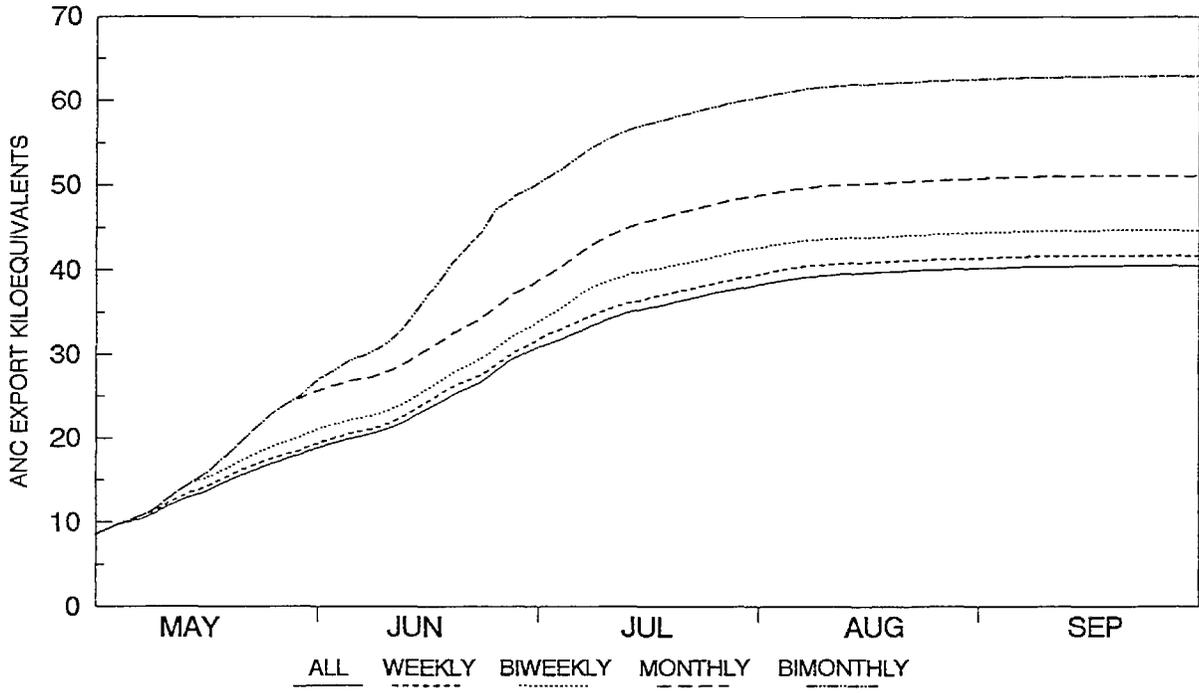


Figure III-14

EFFECT OF SAMPLING FREQUENCY ON ANC EXPORT  
EMERALD LAKE WATERSHED, WATER YEAR 1993



EFFECT OF SAMPLING FREQUENCY ON H+ EXPORT  
EMERALD LAKE WATERSHED, WATER YEAR 1993

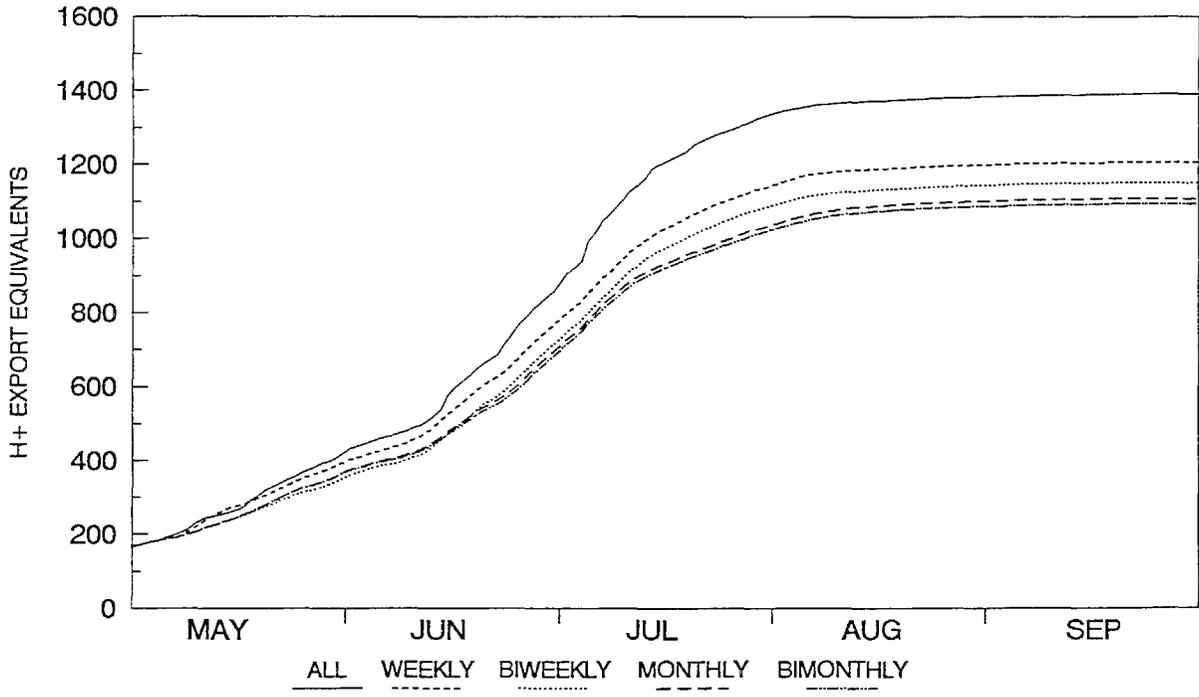
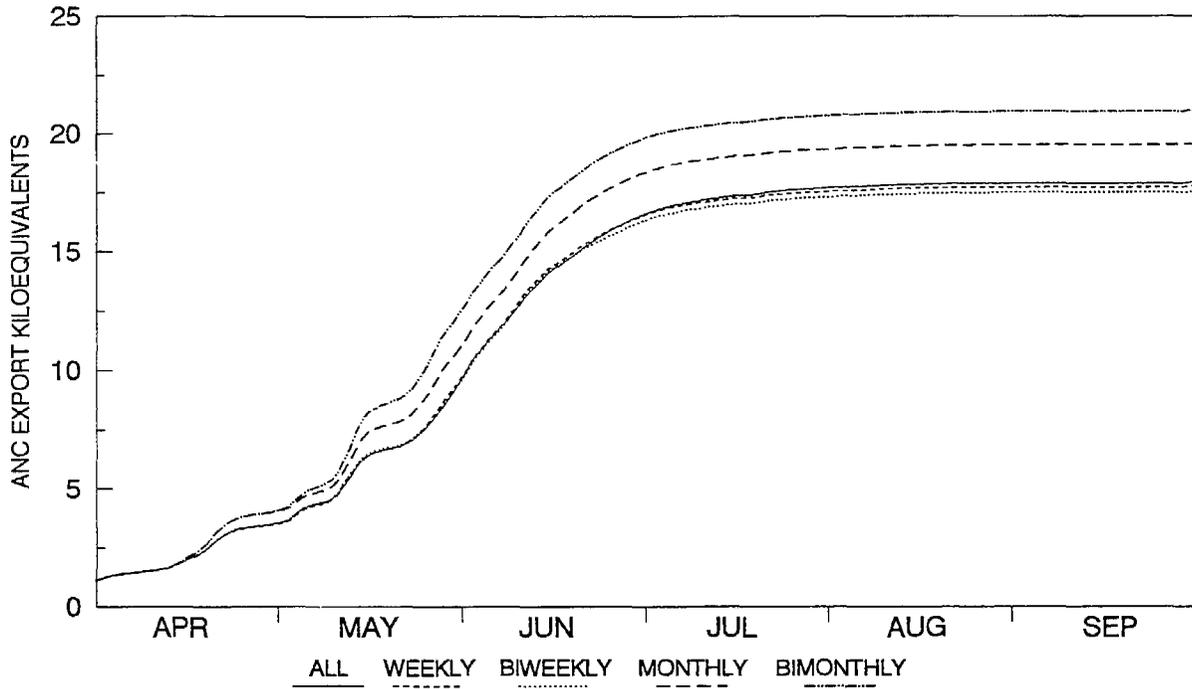


Figure III-15

EFFECT OF SAMPLING FREQUENCY ON ANC EXPORT  
EMERALD LAKE WATERSHED WATER YEAR 1994



EFFECT OF SAMPLING FREQUENCY ON CALCIUM EXPORT  
EMERALD LAKE WATERSHED WATER YEAR 1994

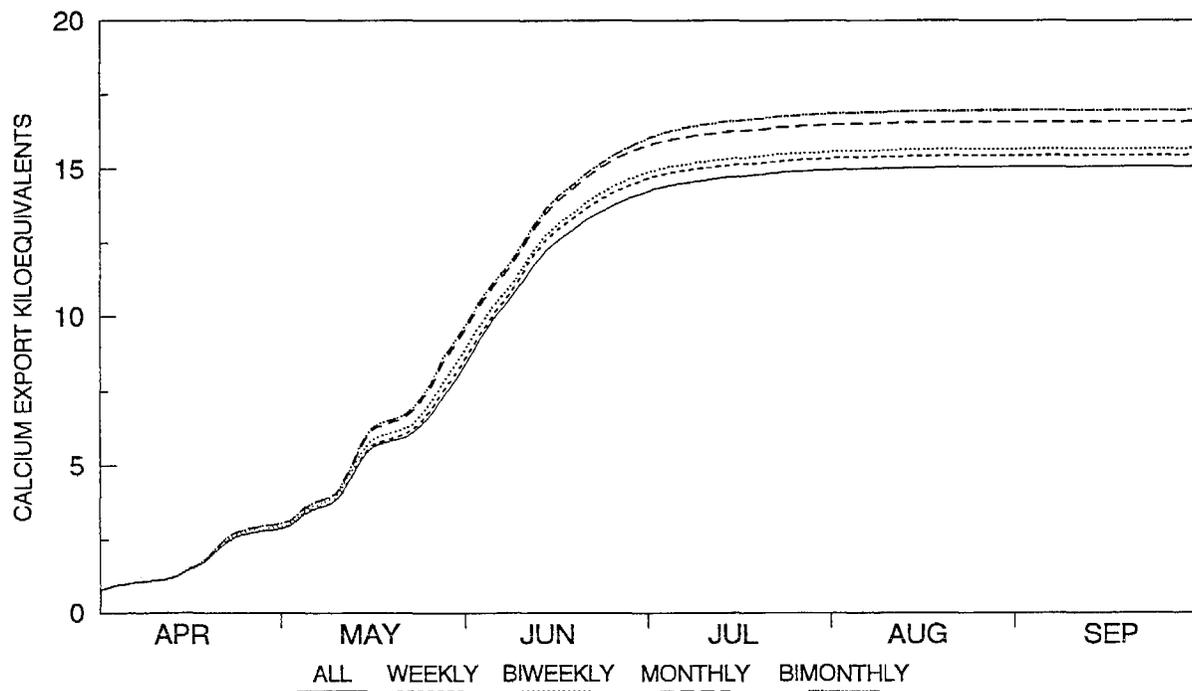
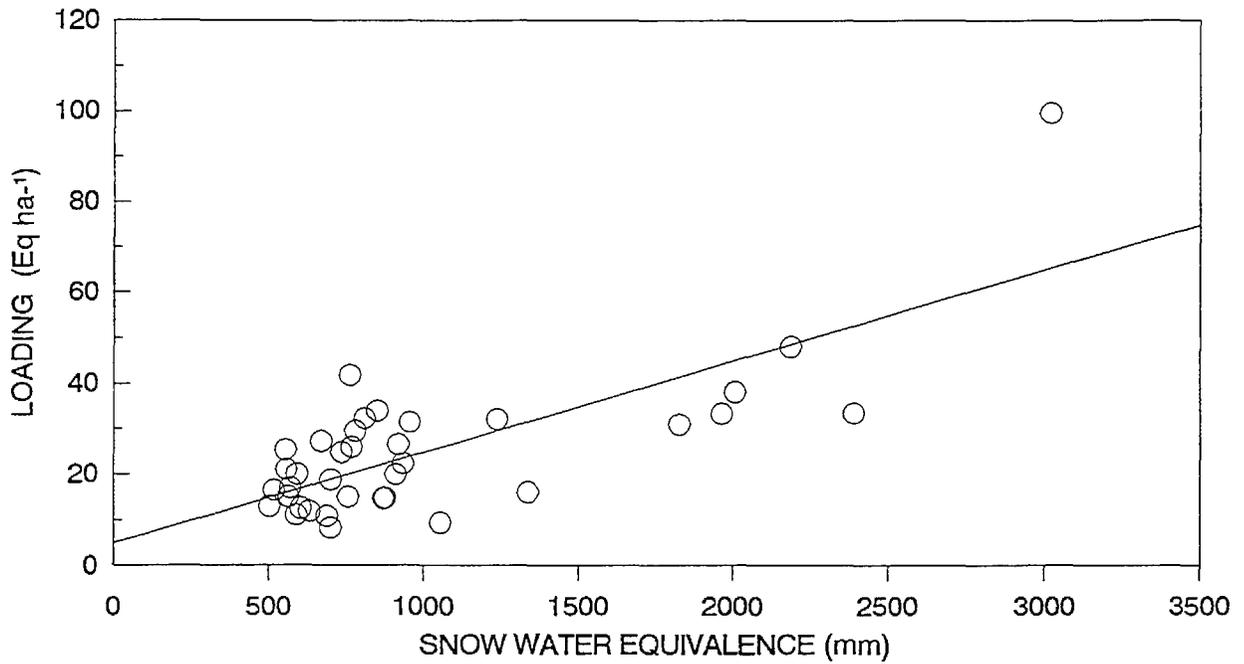


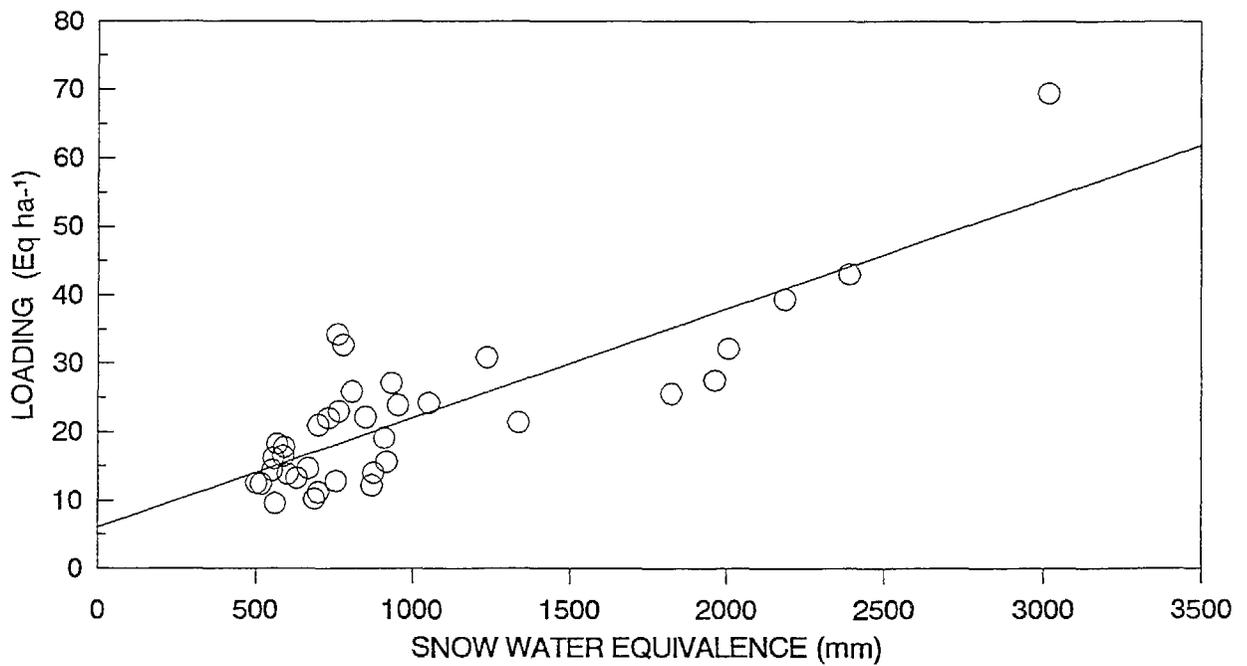
Figure III-16

WATERSHED LOADING  
1985-1994: AMMONIUM



$Y = 0.0200(X) + 4.95; R^2 = 0.59$

WATERSHED LOADING  
1985-1994: NITRATE



$Y = 0.0159(X) + 6.08; R^2 = 0.71$

Figure III-17

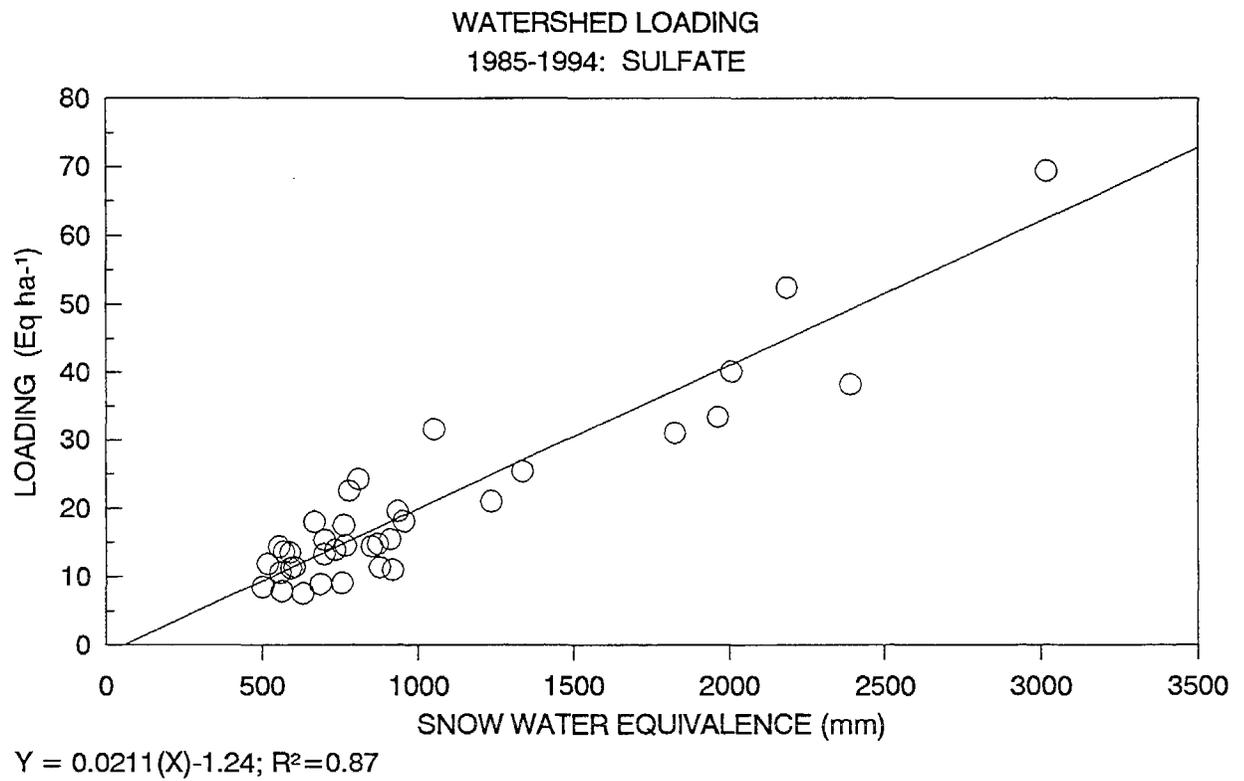
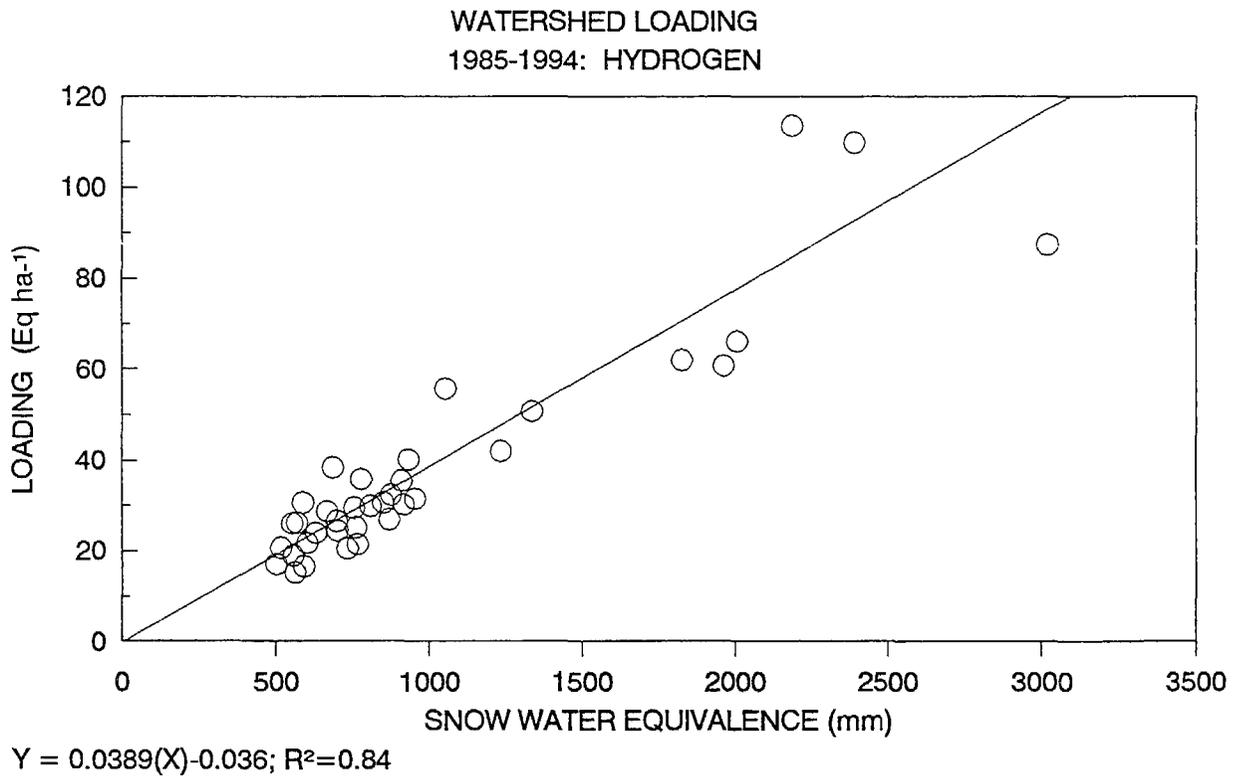
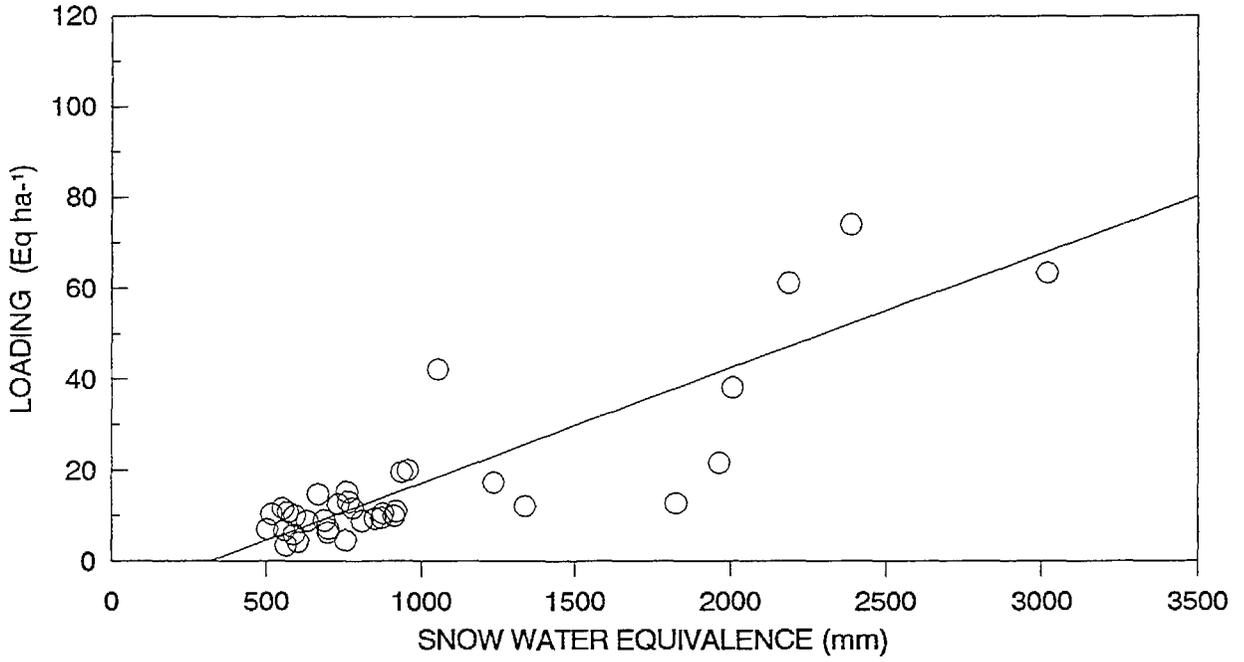


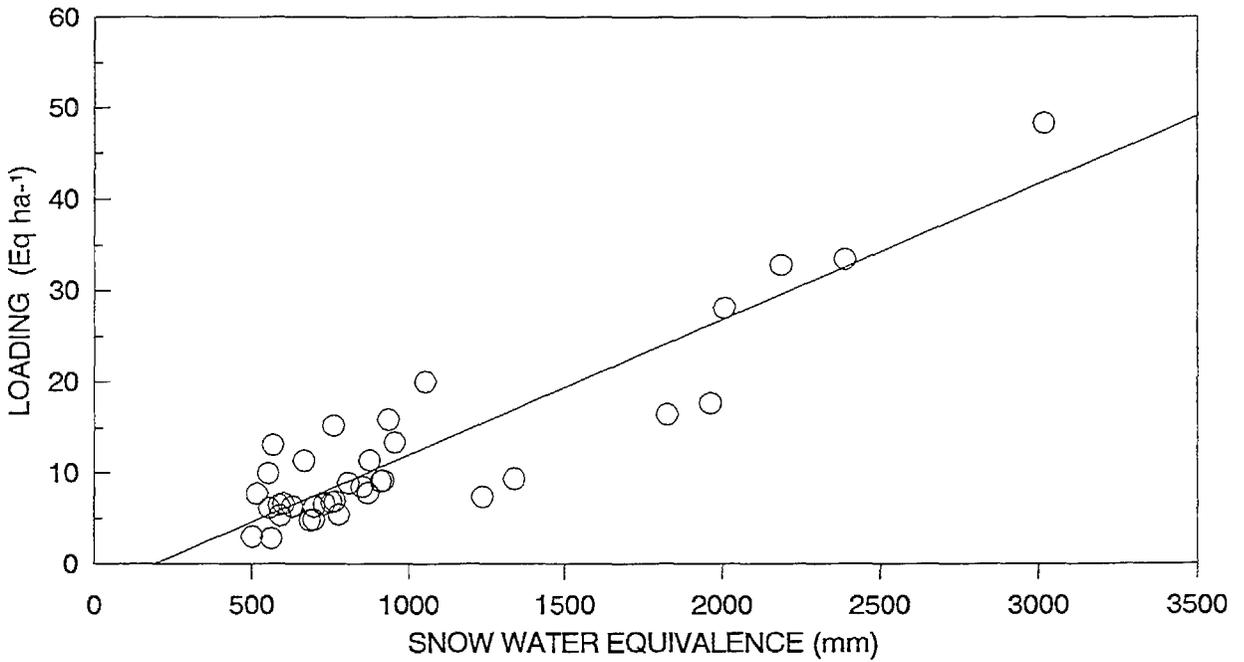
Figure III-18

WATERSHED LOADING  
1985-1994: CHLORIDE



$Y = 0.0252(X) - 7.99; R^2 = 0.75$

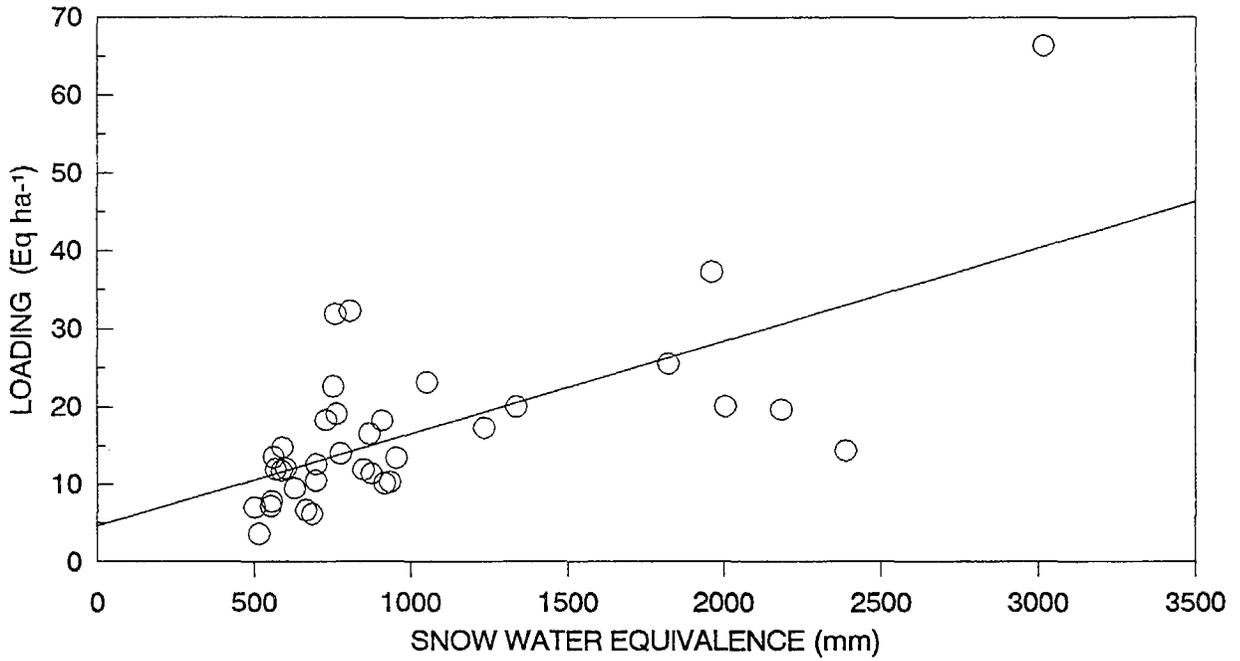
WATERSHED LOADING  
1985-1994: SODIUM



$Y = 0.0148(X) - 2.84; R^2 = 0.84$

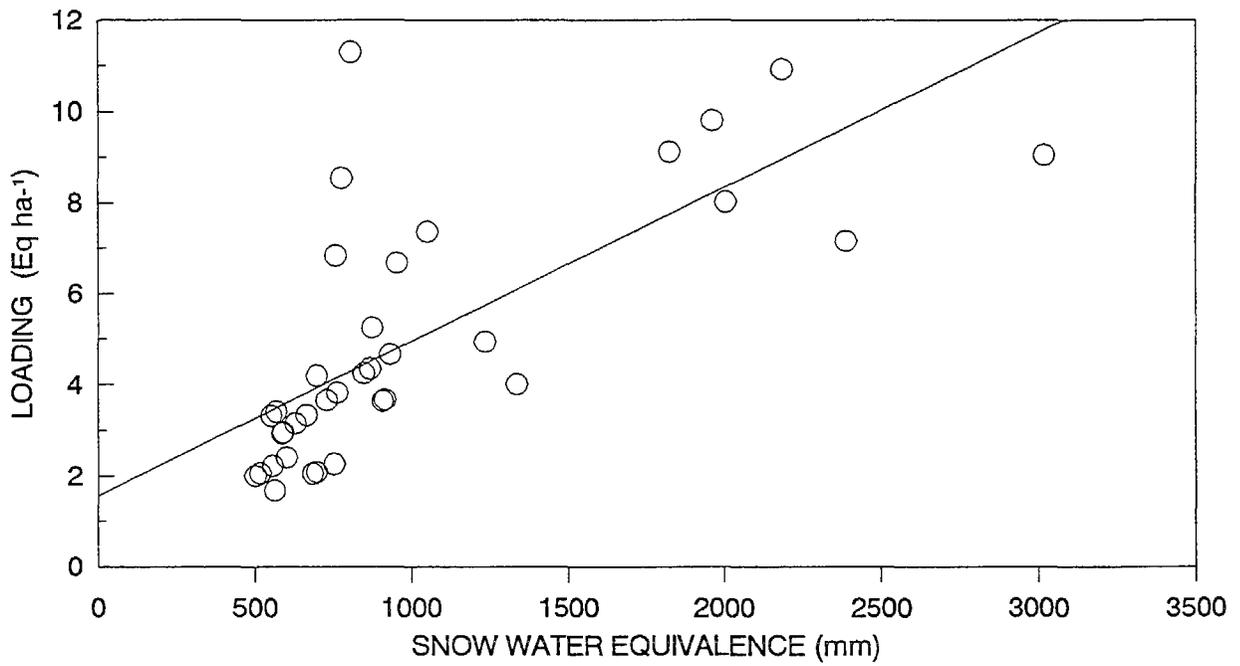
Figure III-19

WATERSHED LOADING  
1985-1994: CALCIUM



$Y = 0.0119(X) + 4.58; R^2 = 0.44$

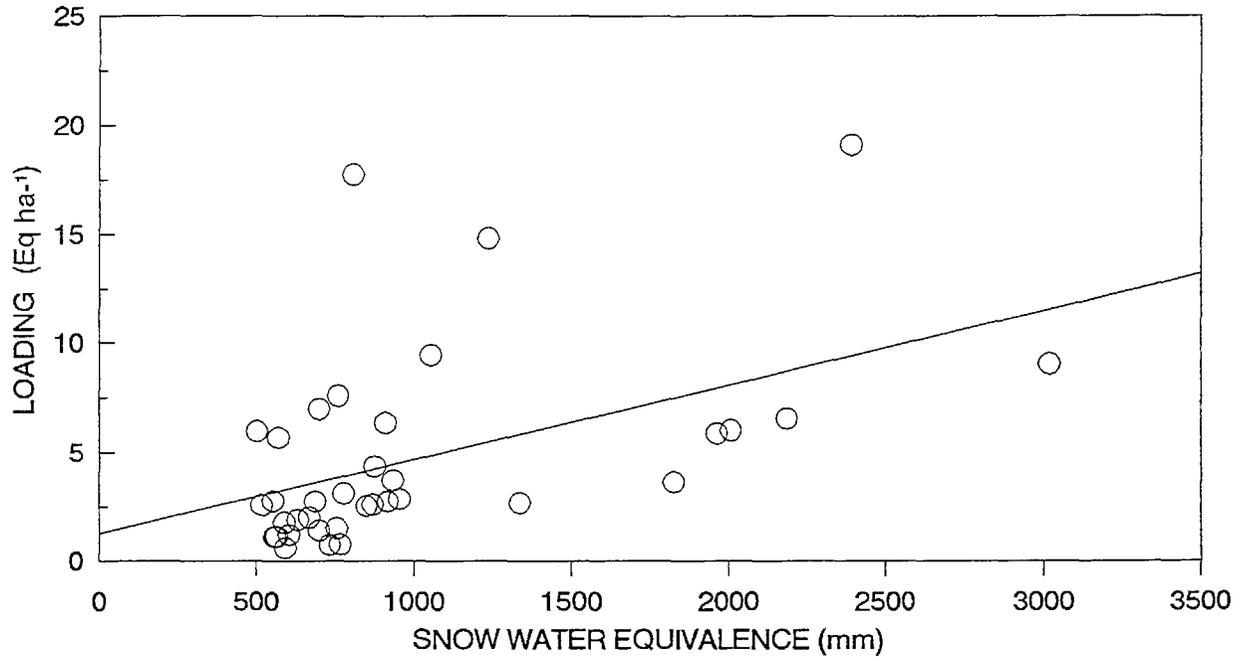
WATERSHED LOADING  
1985-1994: MAGNESIUM



$Y = 0.0034(X) + 1.56; R^2 = 0.54$

Figure III-20

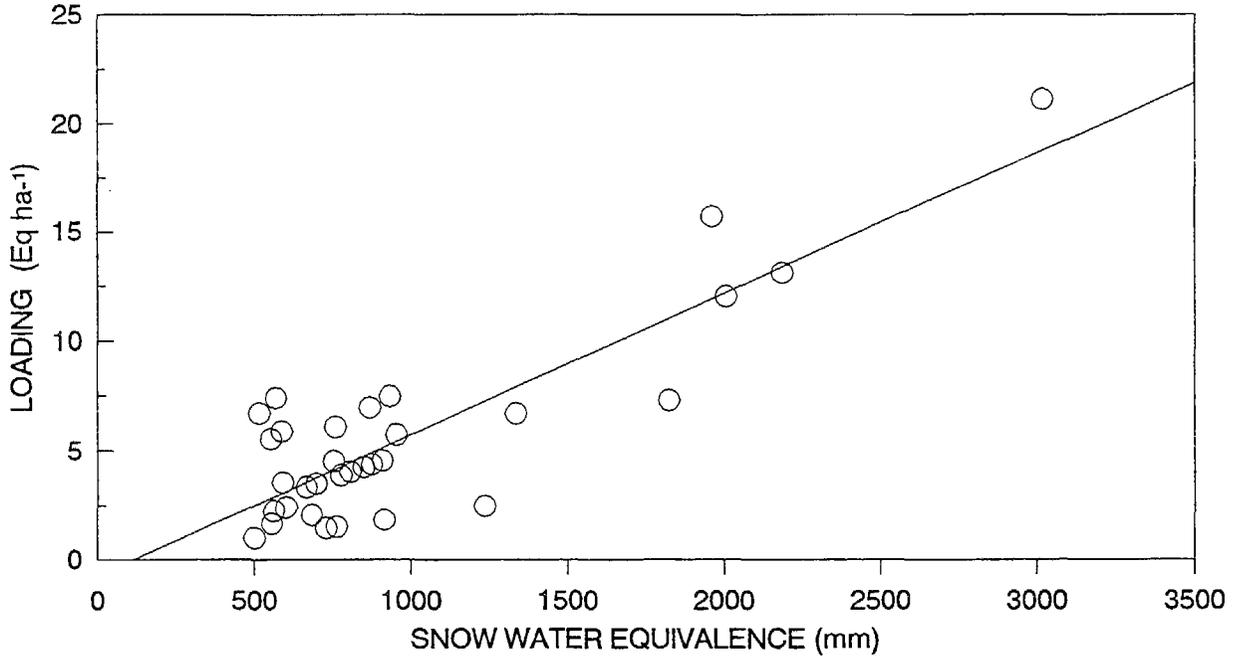
WATERSHED LOADING  
1985-1994: POTASSIUM



$Y = 0.0034(X) + 1.28; R^2 = 0.23$

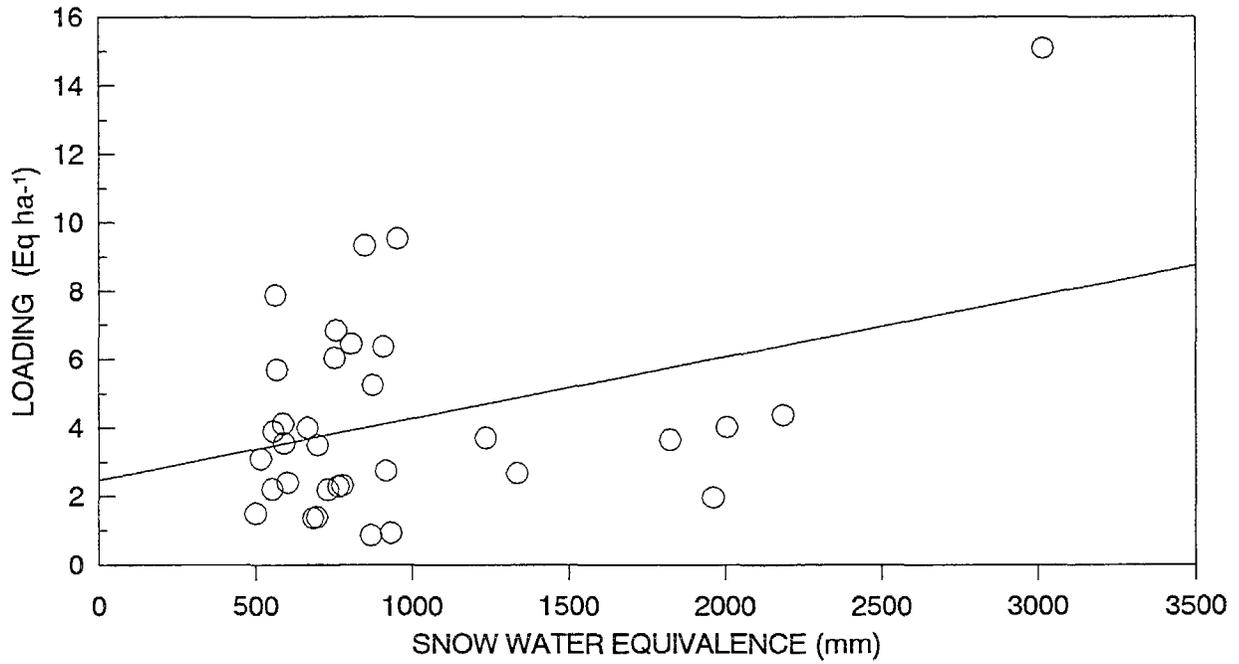
Figure III-21

WATERSHED LOADING  
1985-1994: ACETATE



$Y = 0.0065(X) - 0.75; R^2 = 0.77$

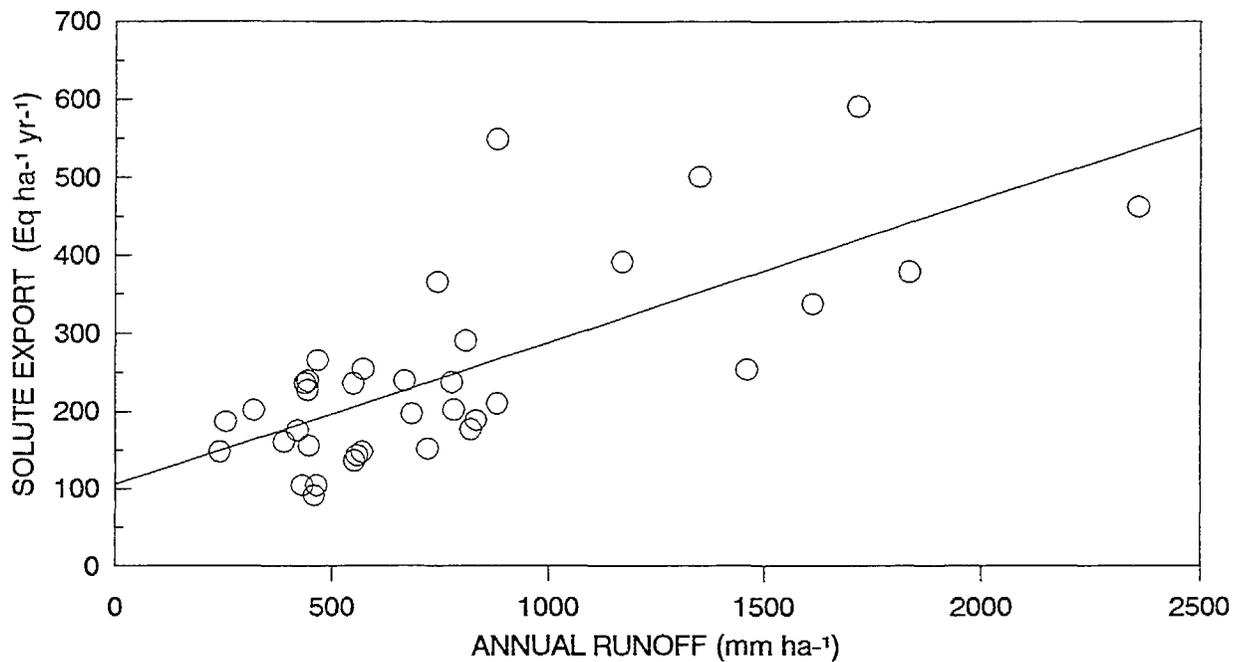
WATERSHED LOADING  
1985-1994: FORMATE



$Y = 0.0018(X) + 2.46; R^2 = 0.14$

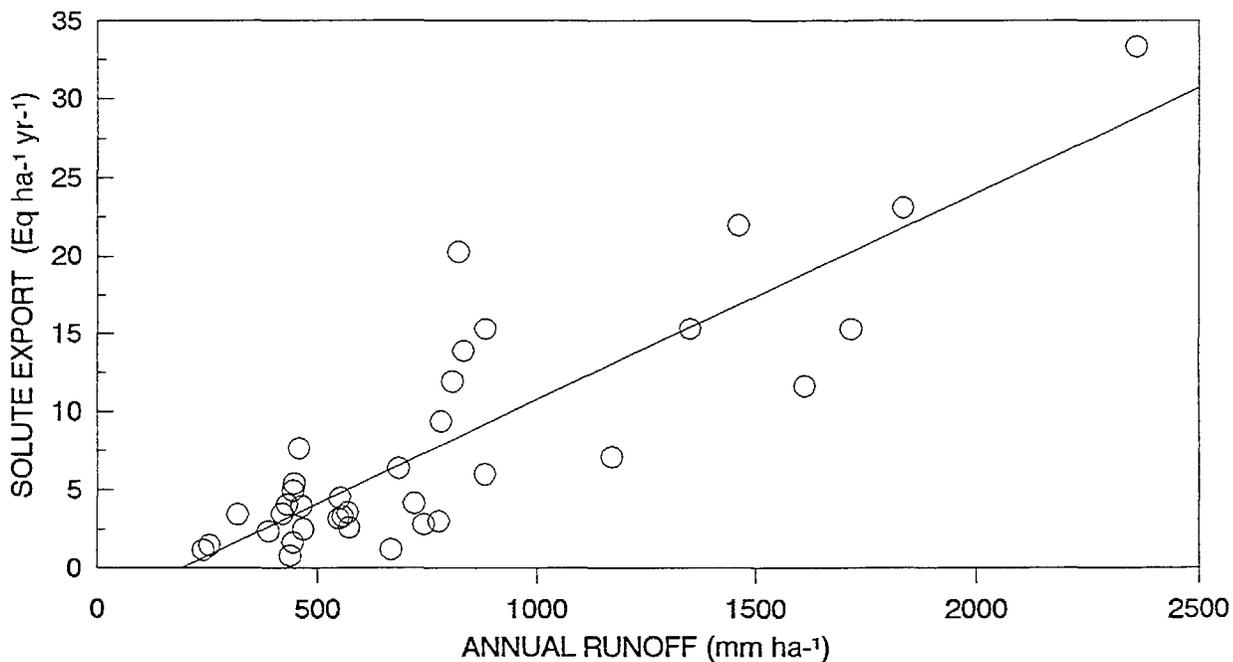
Figure III-22

WATERSHED SOLUTE BALANCE  
1985-1994: ANC



$Y = 0.183(X) + 106; r^2 = 0.52$

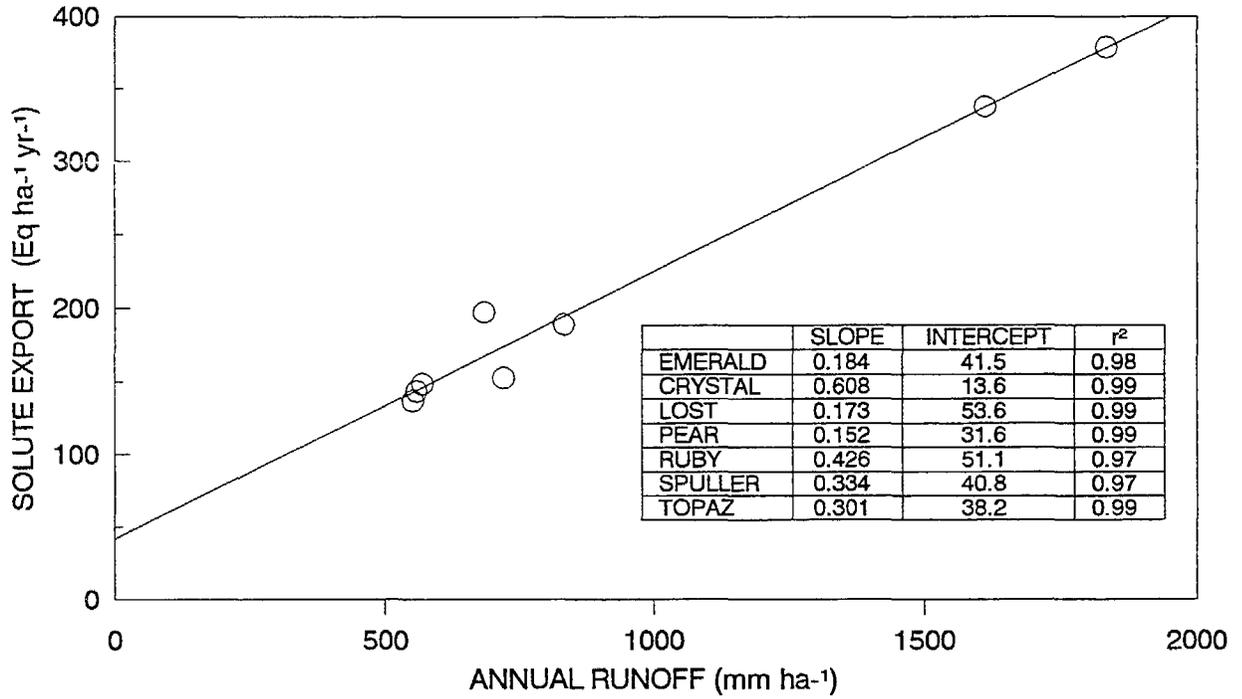
WATERSHED SOLUTE BALANCE  
1985-1994: HYDROGEN-ION



$Y = 0.013(X) - 2.55; r^2 = 0.74$

Figure III-23

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: ANC



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: HYDROGEN-ION

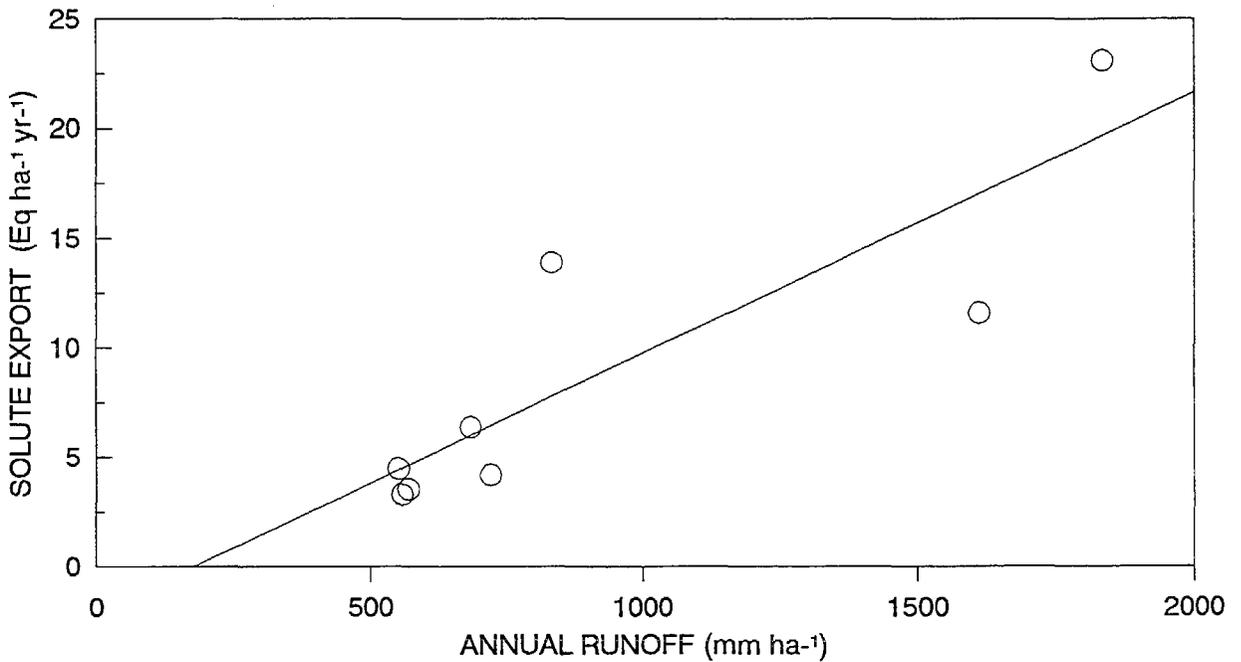
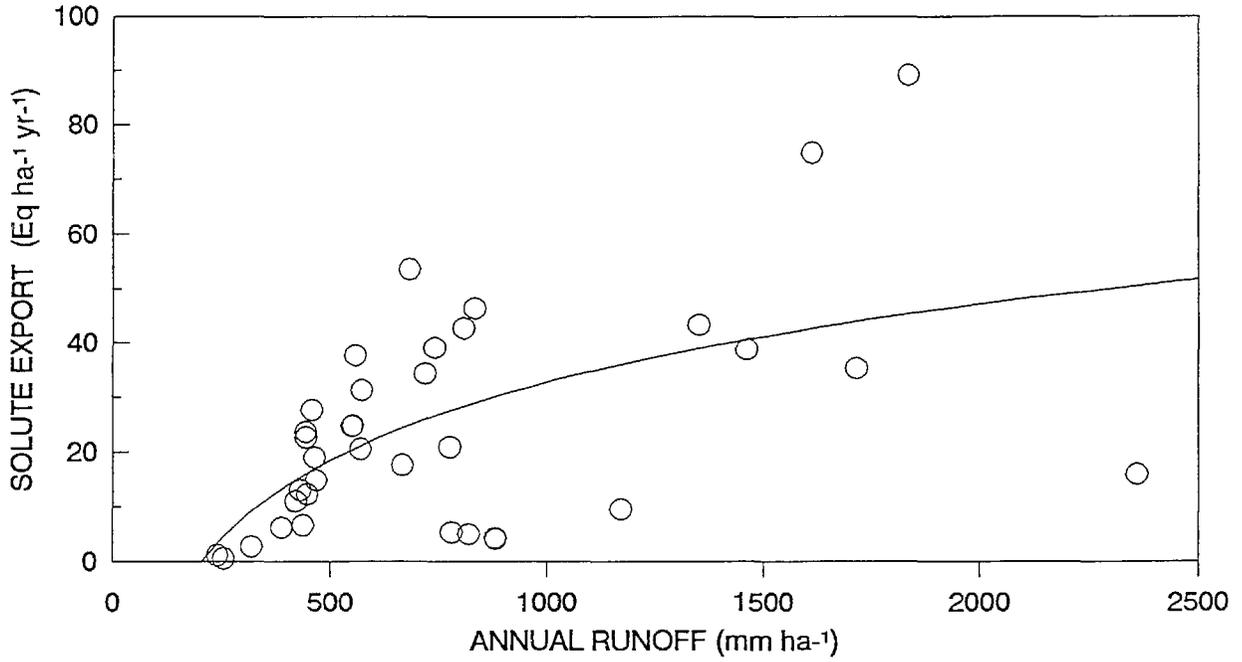


Figure III-24

WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE



WATERSHED SOLUTE BALANCE  
1985-1994: SULFATE

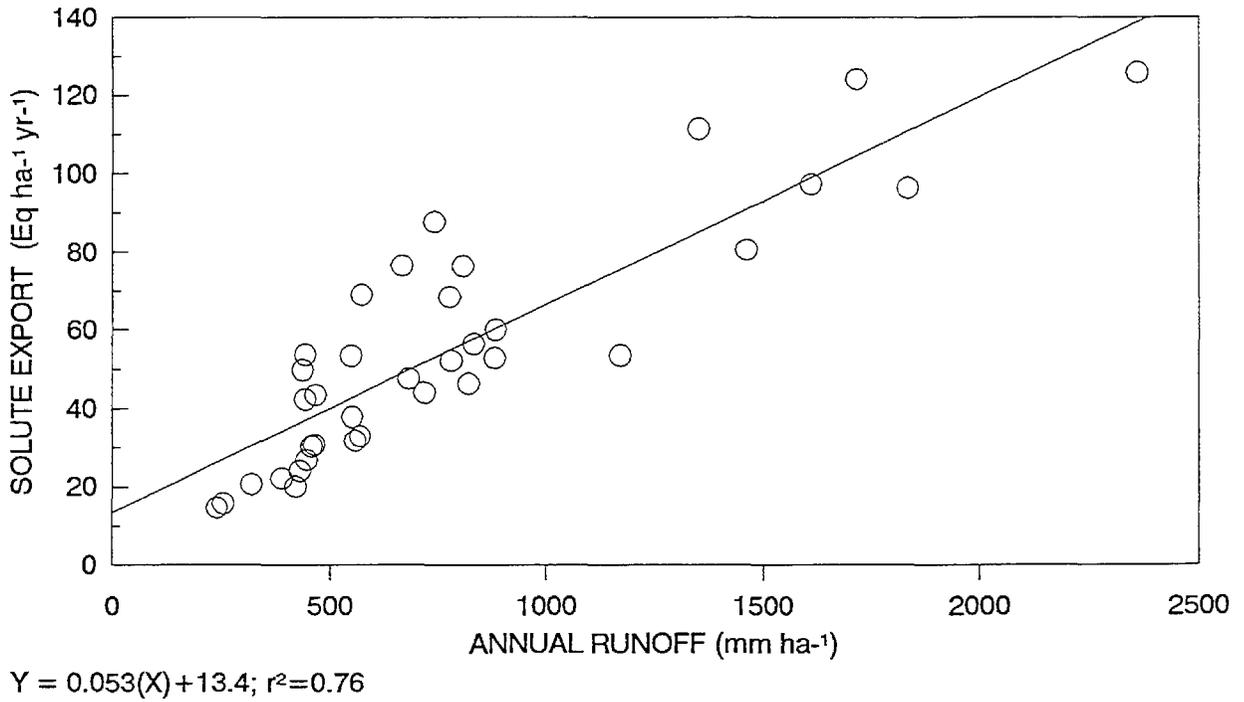
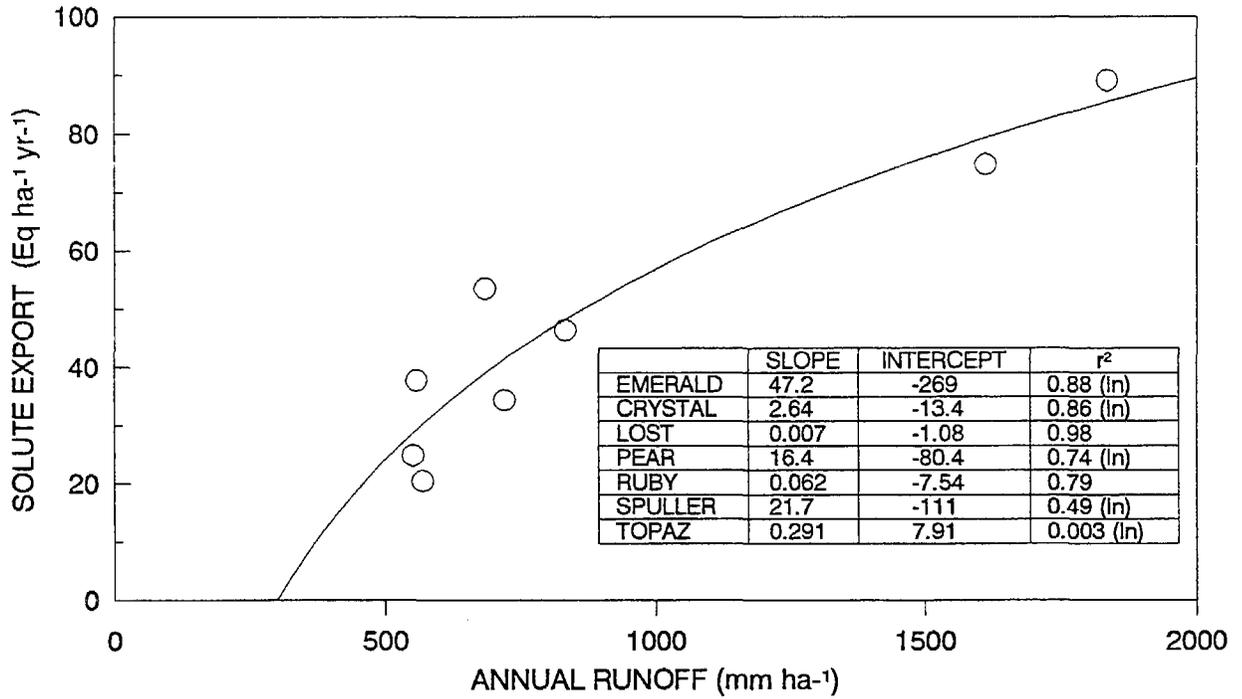


Figure III-25

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: NITRATE



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: SULFATE

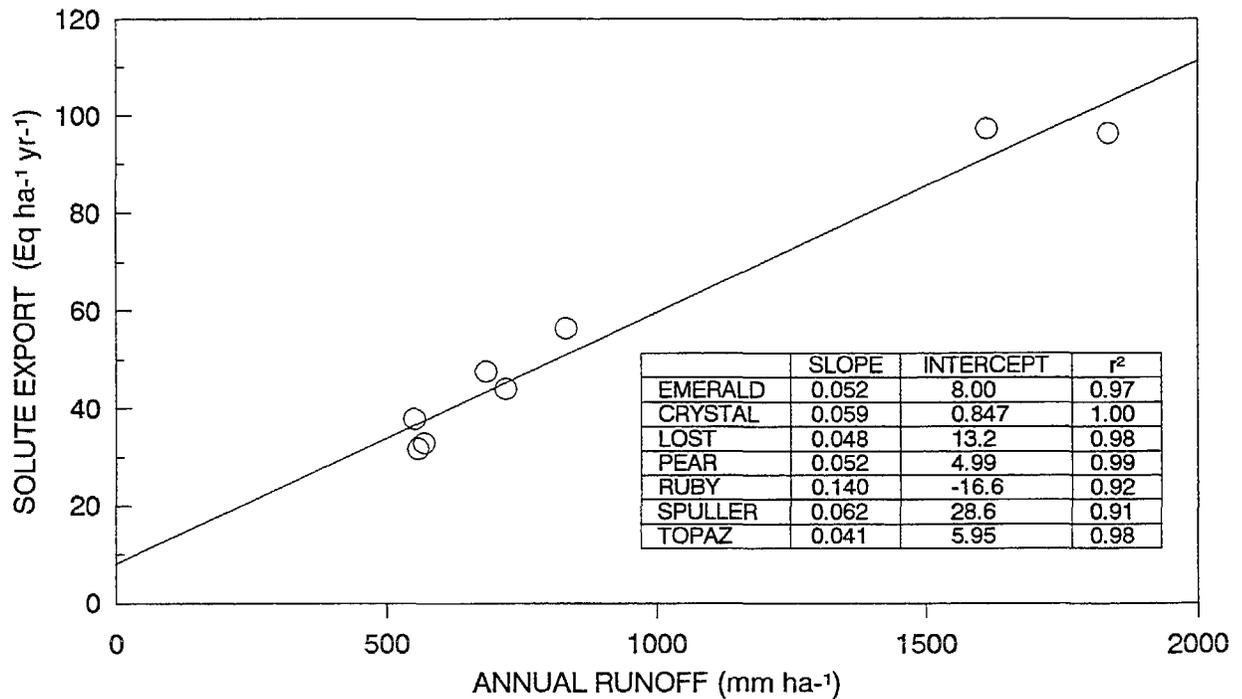
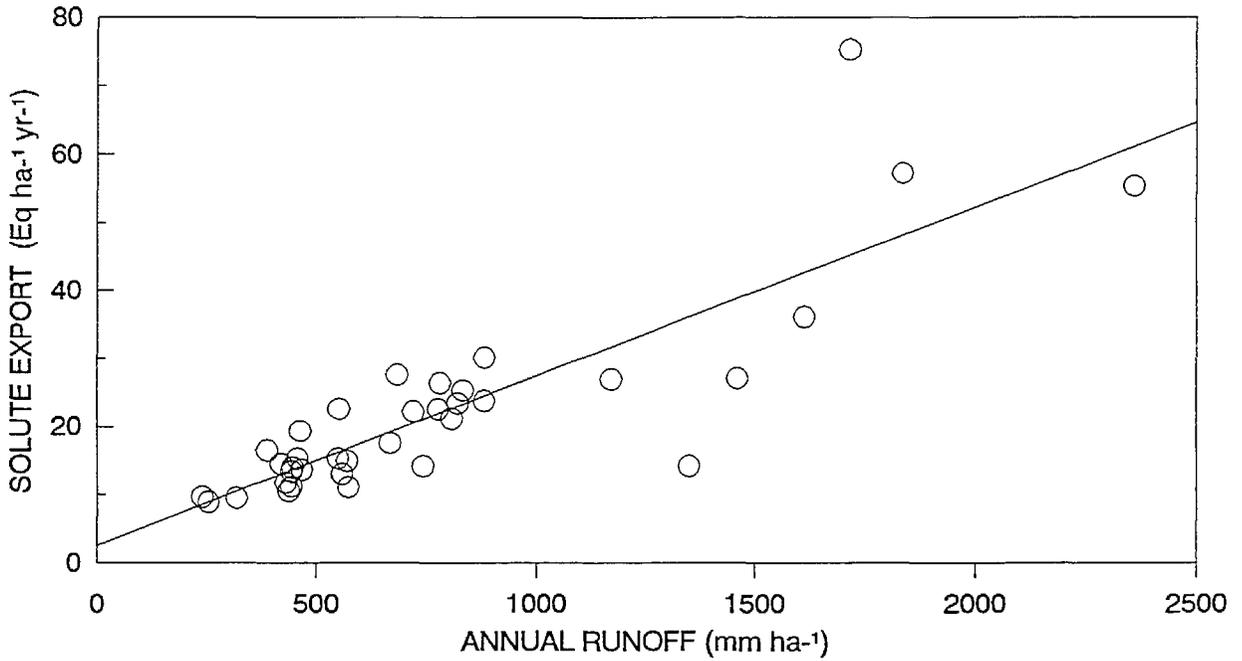


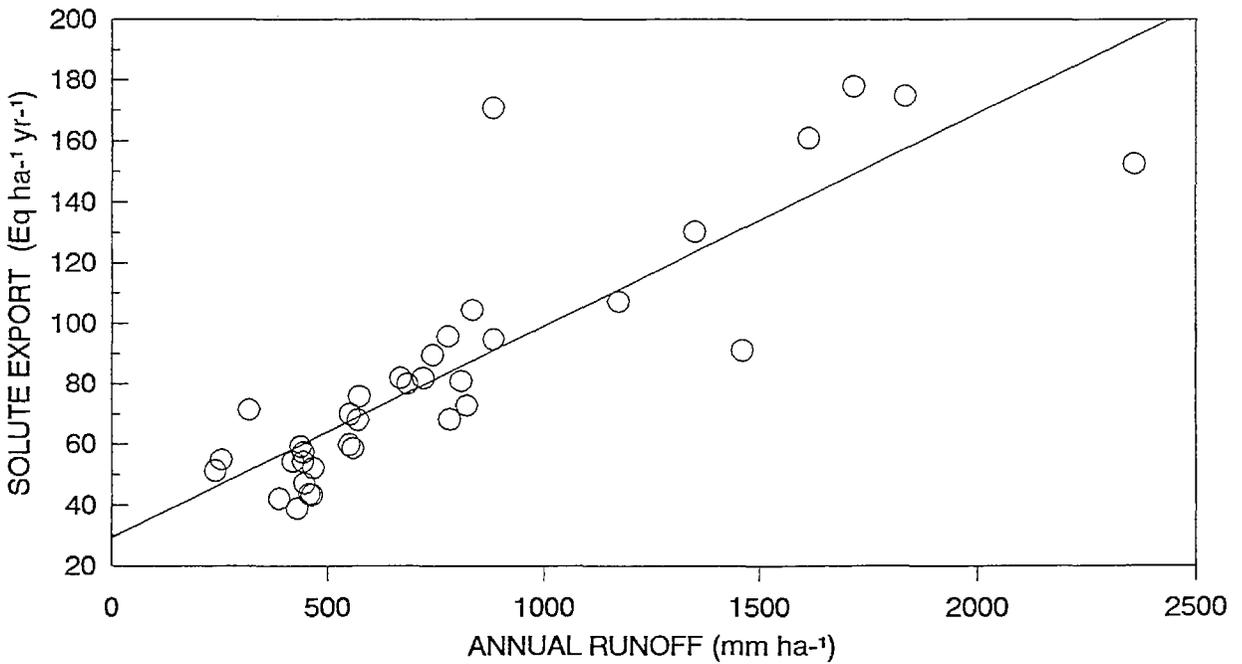
Figure III-26

WATERSHED SOLUTE BALANCE  
1985-1994: CHLORIDE



$Y = 0.025(X) + 2.58; r^2 = 0.72$

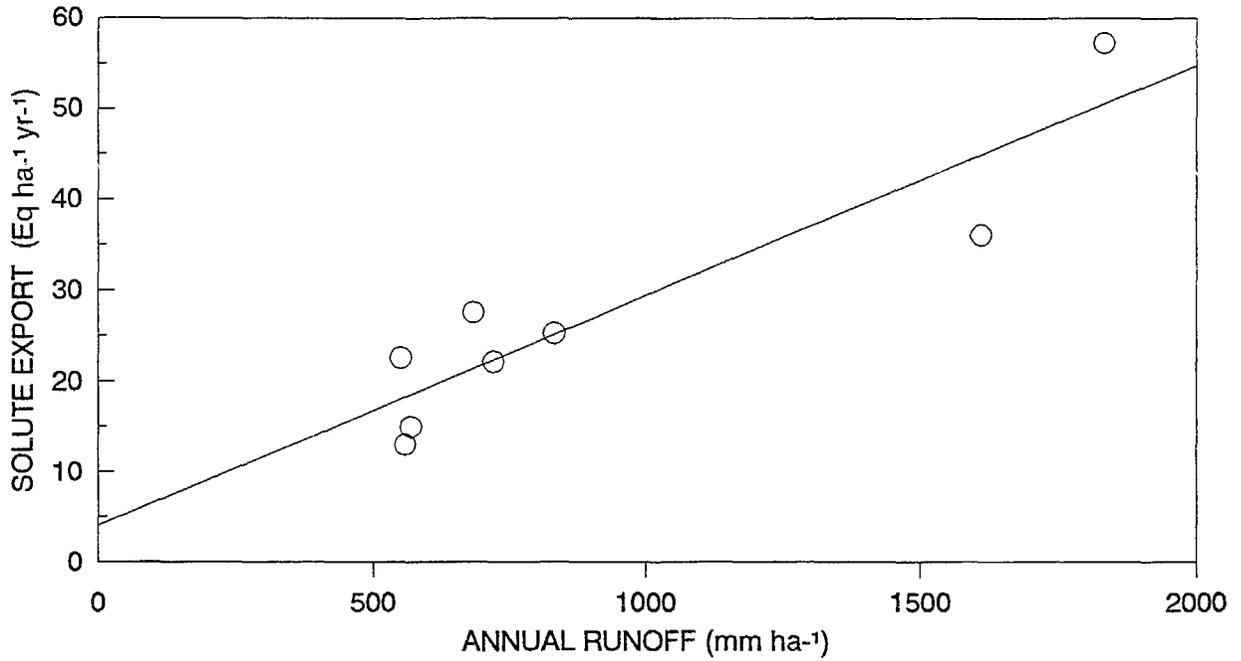
WATERSHED SOLUTE BALANCE  
1985-1994: SODIUM



$Y = 0.070(X) + 29.3; r^2 = 0.74$

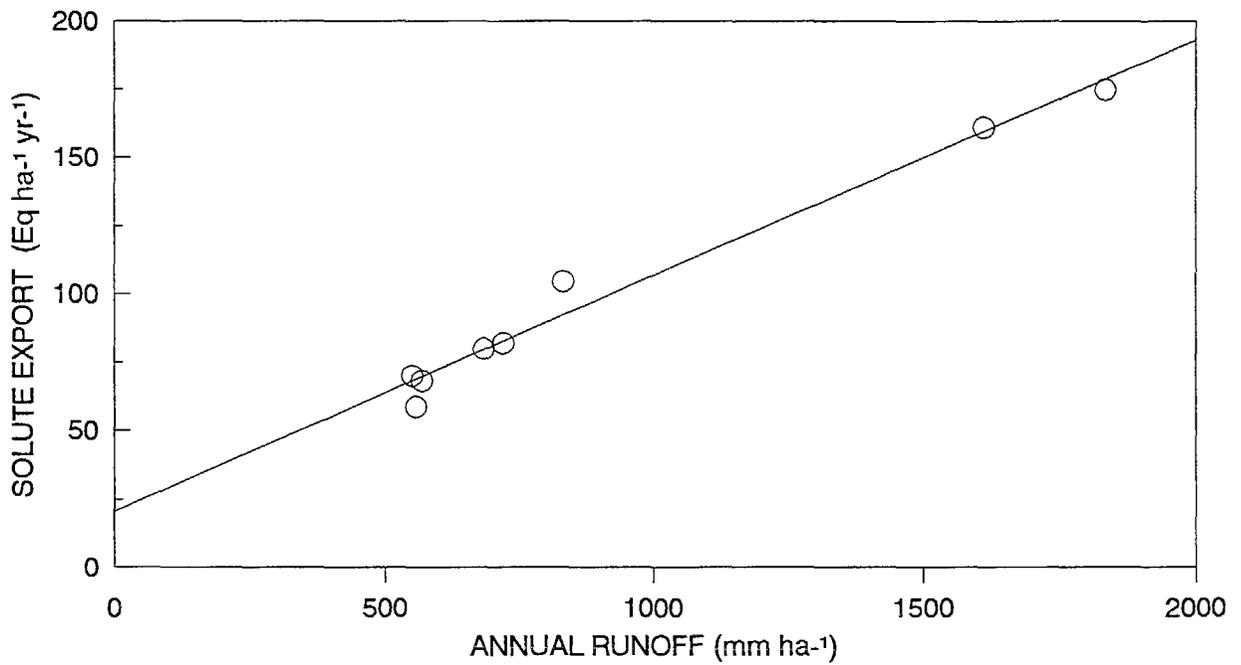
Figure III-27

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: CHLORIDE



$Y = 0.025(X) + 4.01; r^2 = 0.84$

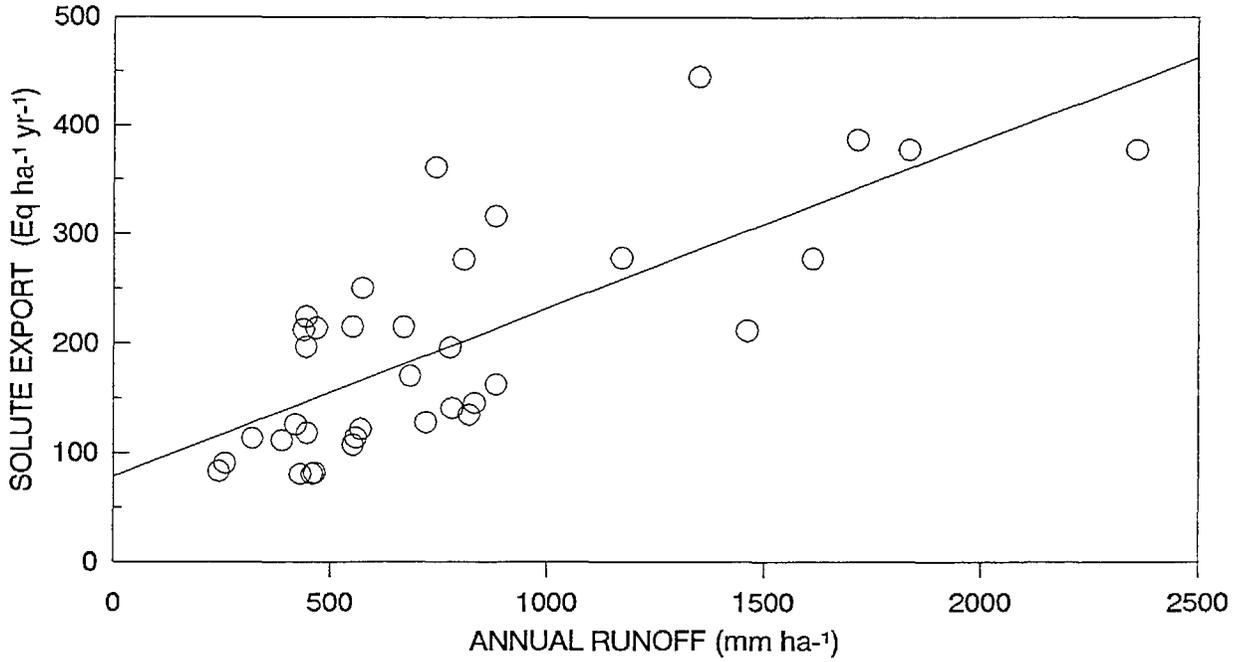
EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: SODIUM



$Y = 0.086(X) + 20.6; r^2 = 0.98$

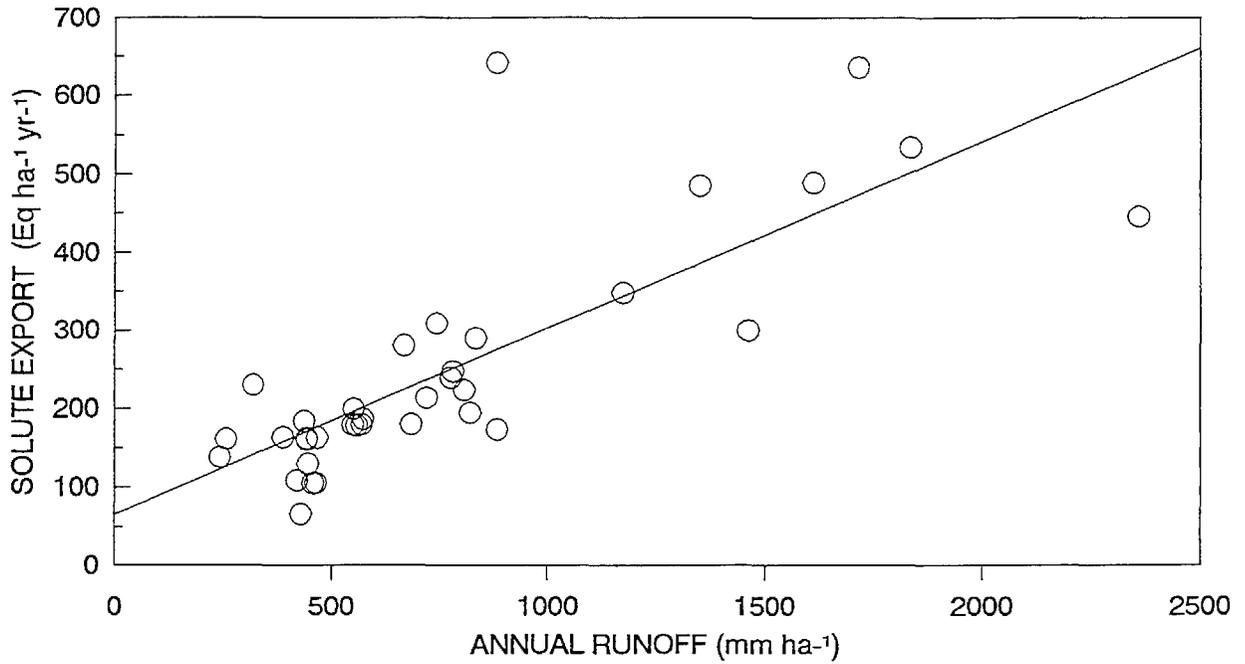
Figure III-28

WATERSHED SOLUTE BALANCE  
1985-1994: CALCIUM



$Y = 0.154(X) + 78.3; r^2 = 0.55$

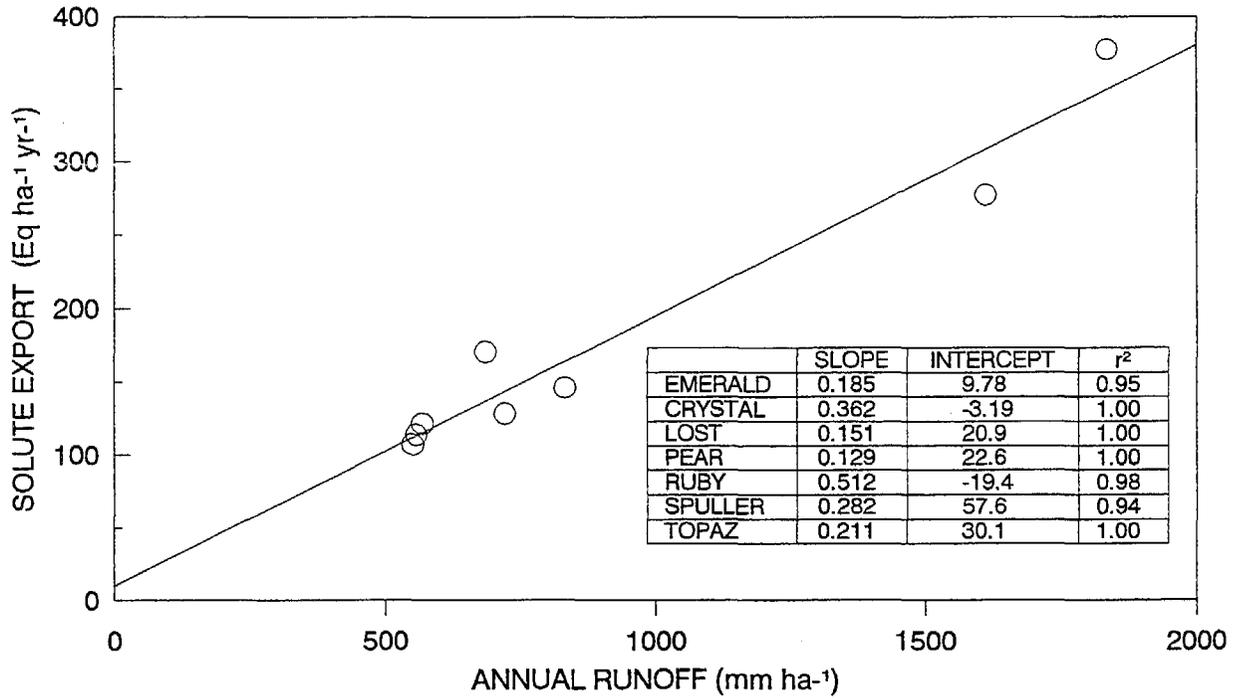
WATERSHED SOLUTE BALANCE  
1985-1994: SILICATE



$Y = 0.238(X) + 65.0; r^2 = 0.63$

Figure III-29

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: CALCIUM



EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: SILICATE

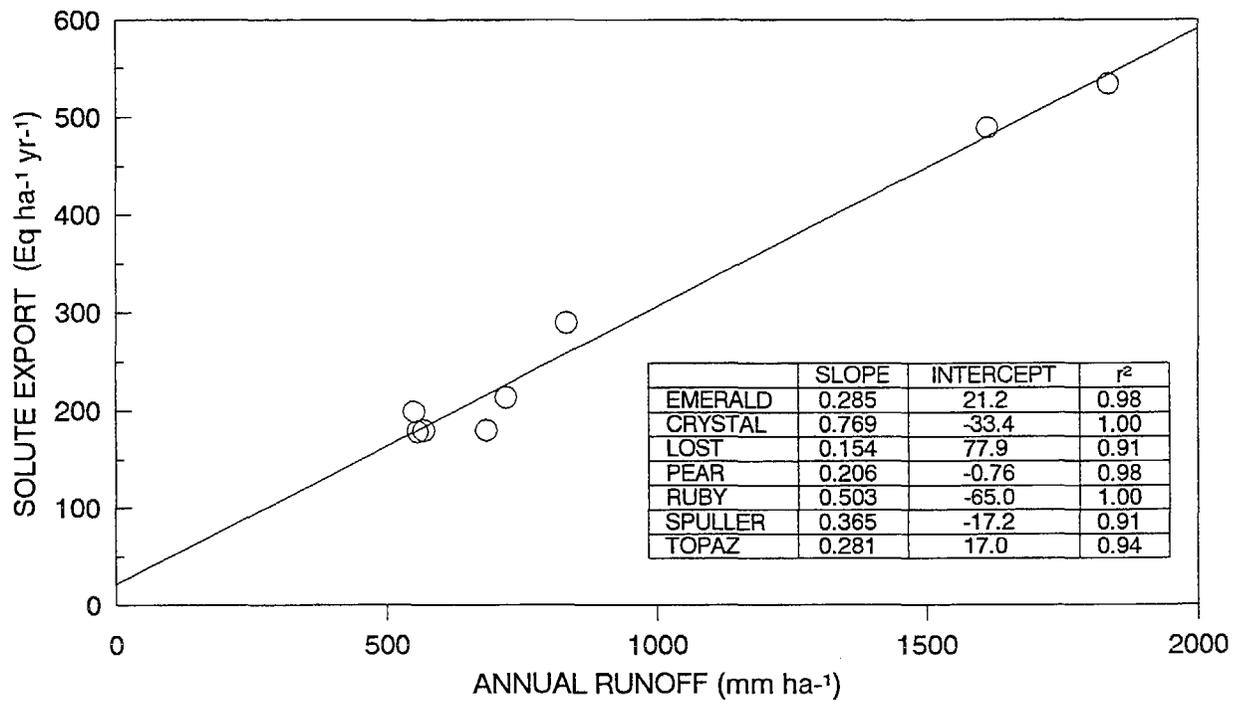
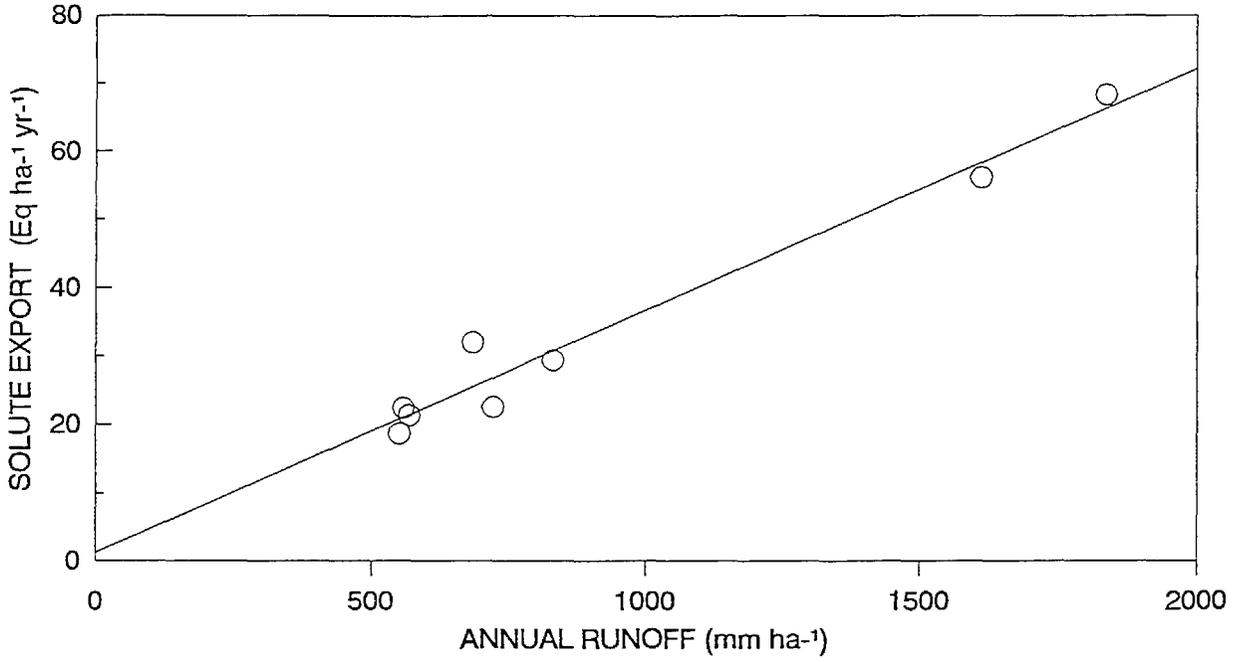


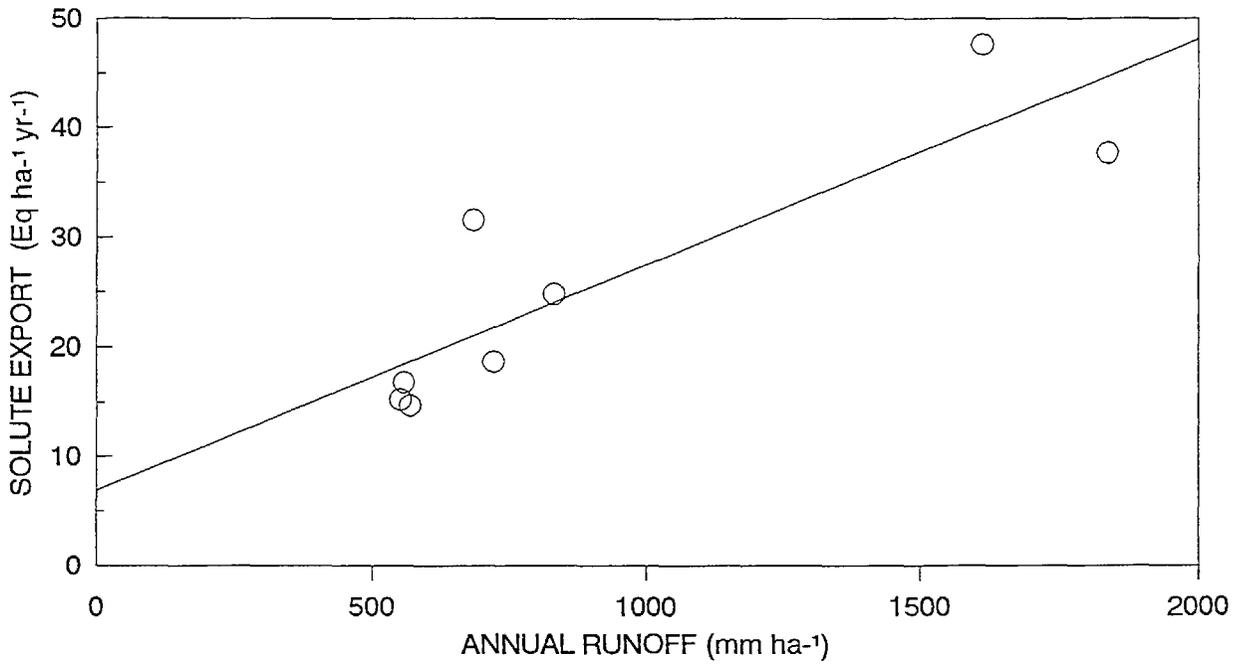
Figure III-30

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: MAGNESIUM



$Y = 0.036(X) + 1.21; r^2 = 0.97$

EMERALD WATERSHED SOLUTE BALANCE  
1985-1994: POTASSIUM



$Y = 0.021(X) + 6.92; r^2 = 0.75$

Figure III-31

MARBLE FORK OF KAWEAH  
 SEPTEMBER AND OCTOBER 1994

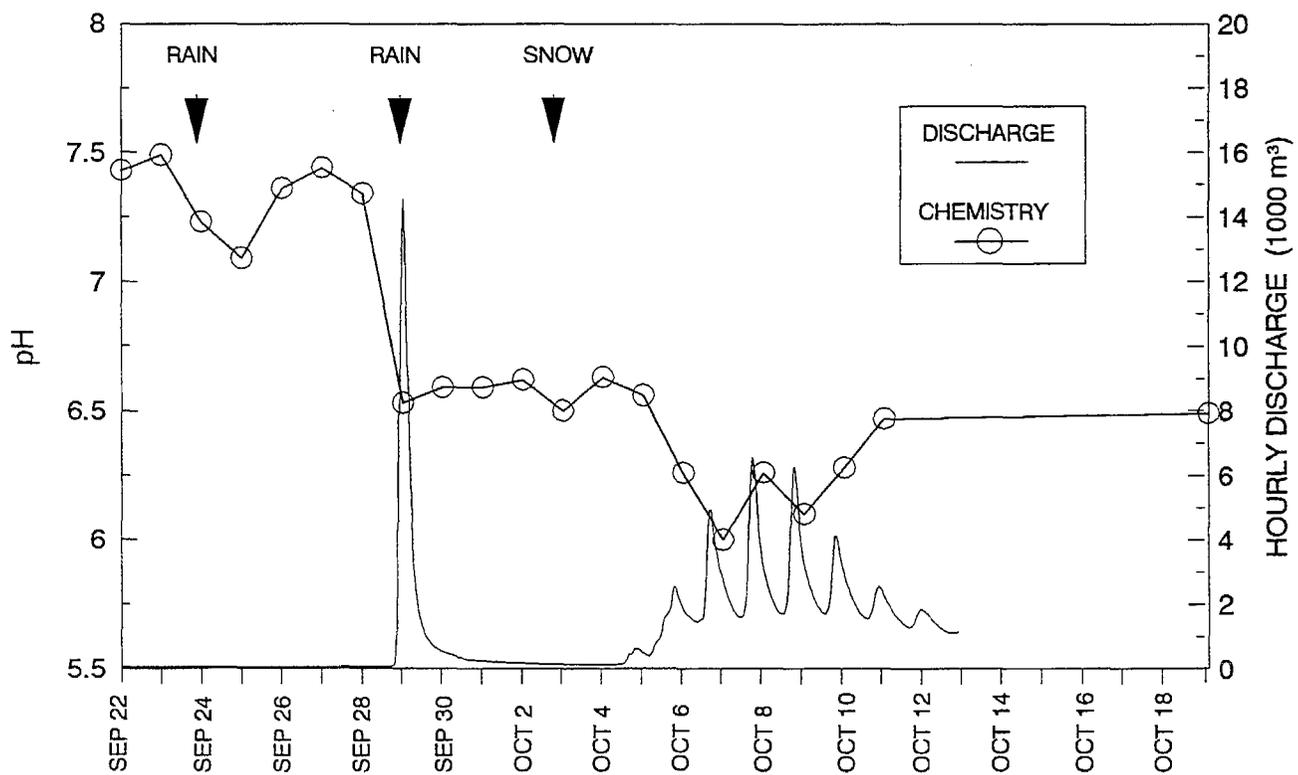
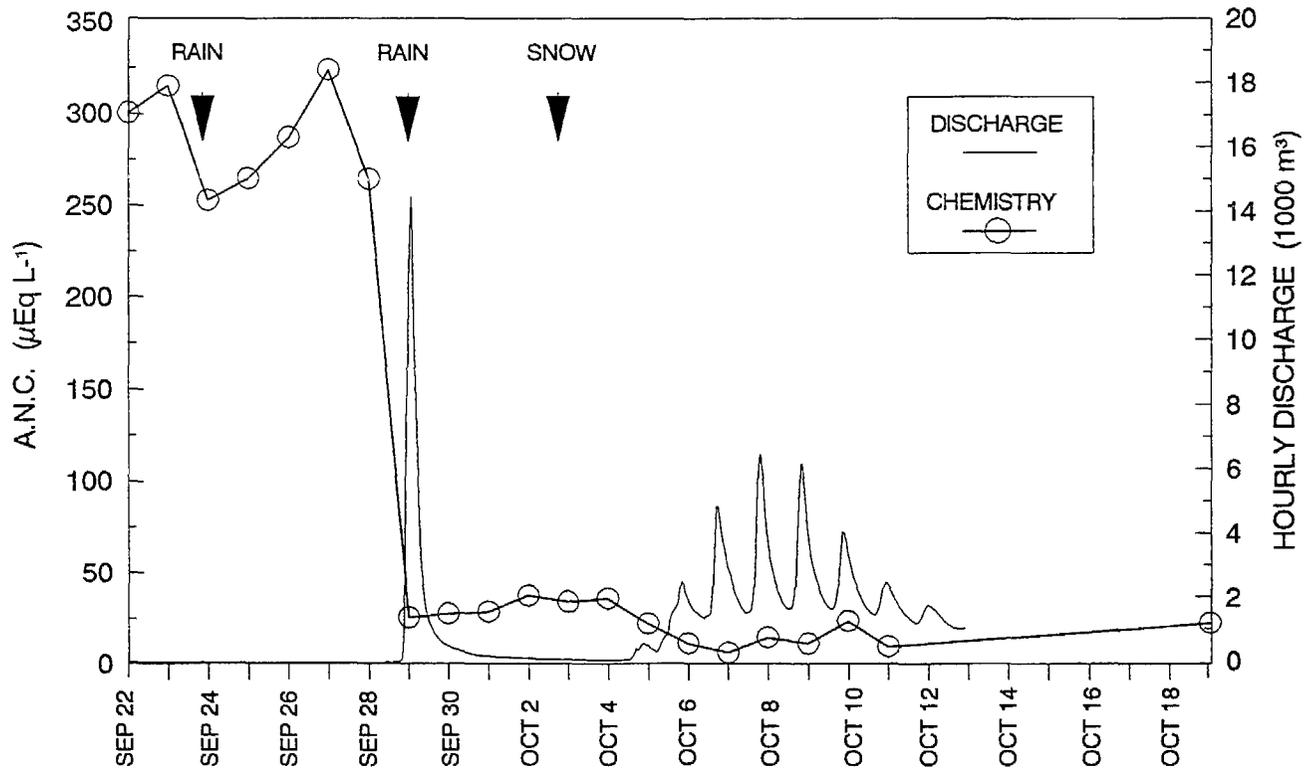


Figure III-32

MARBLE FORK OF KAWEAH  
 SEPTEMBER AND OCTOBER 1994

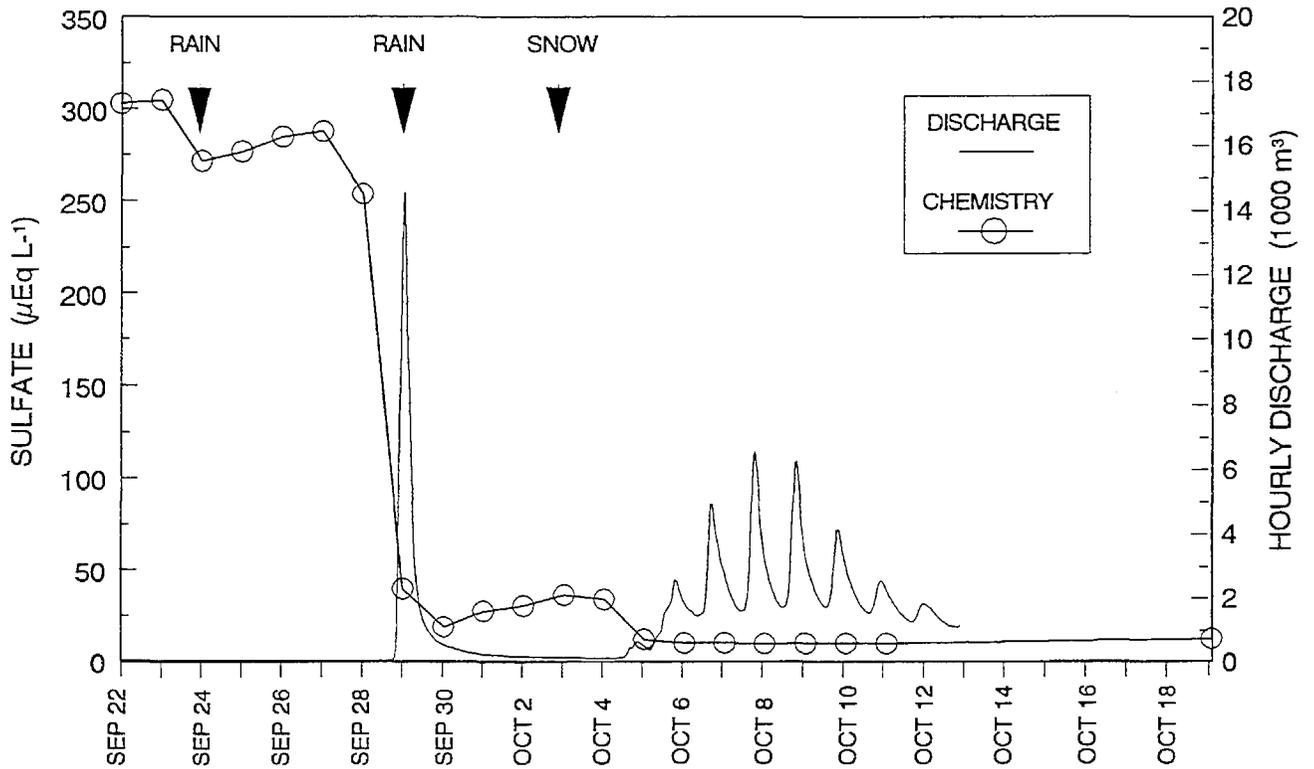
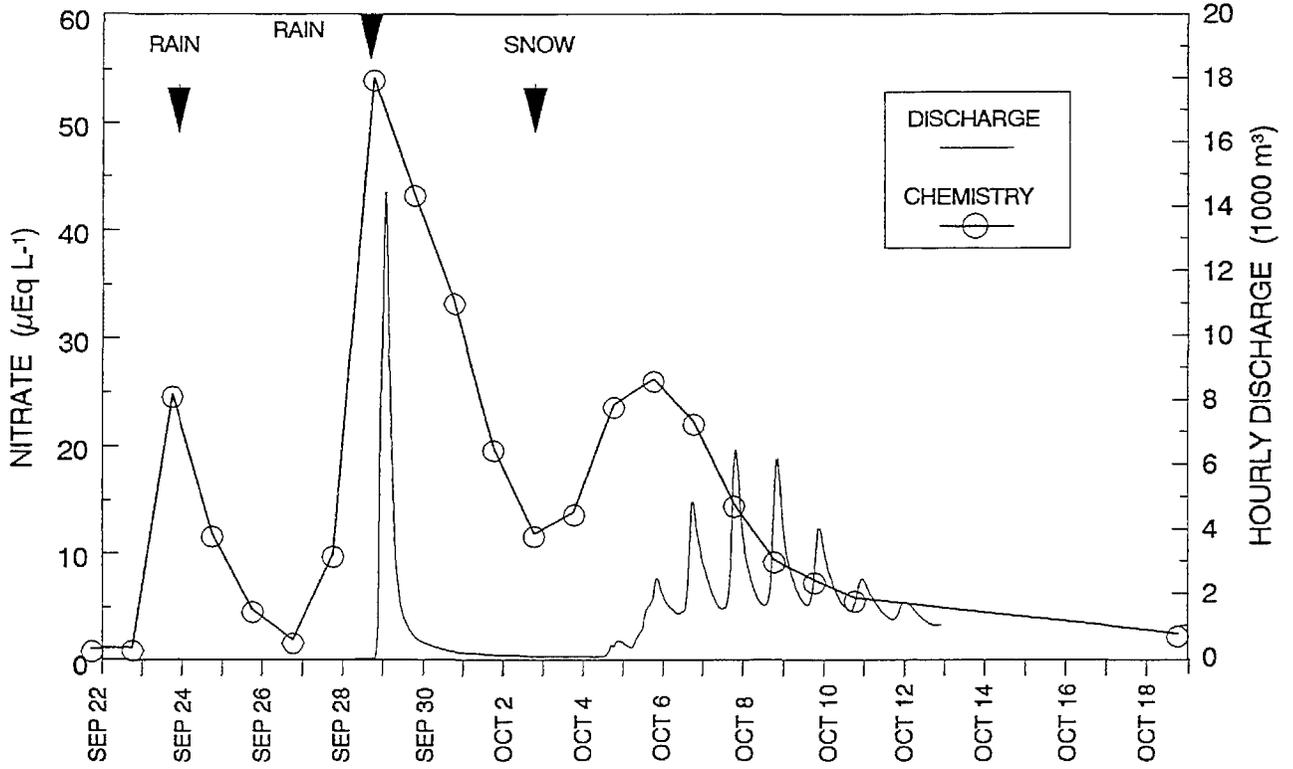


Figure III-33

MARBLE FORK OF KAWEAH  
 SEPTEMBER AND OCTOBER 1994

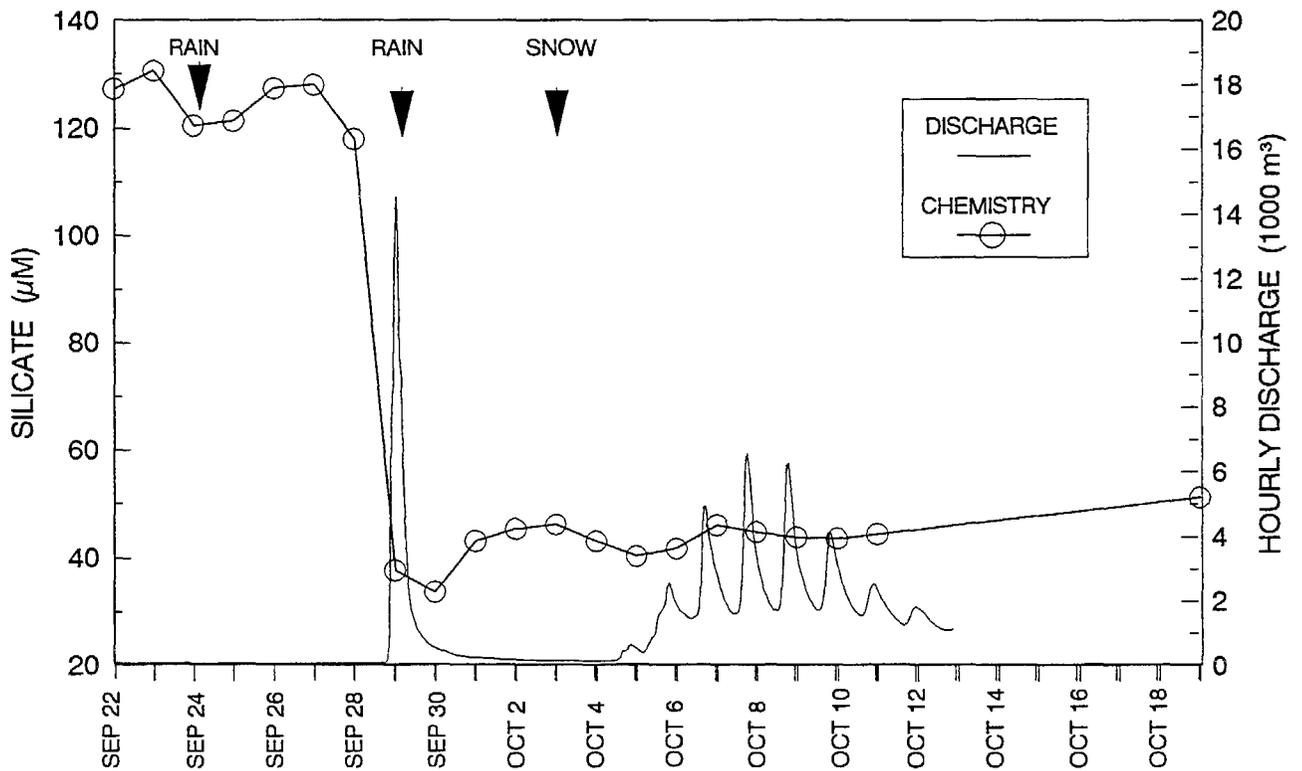
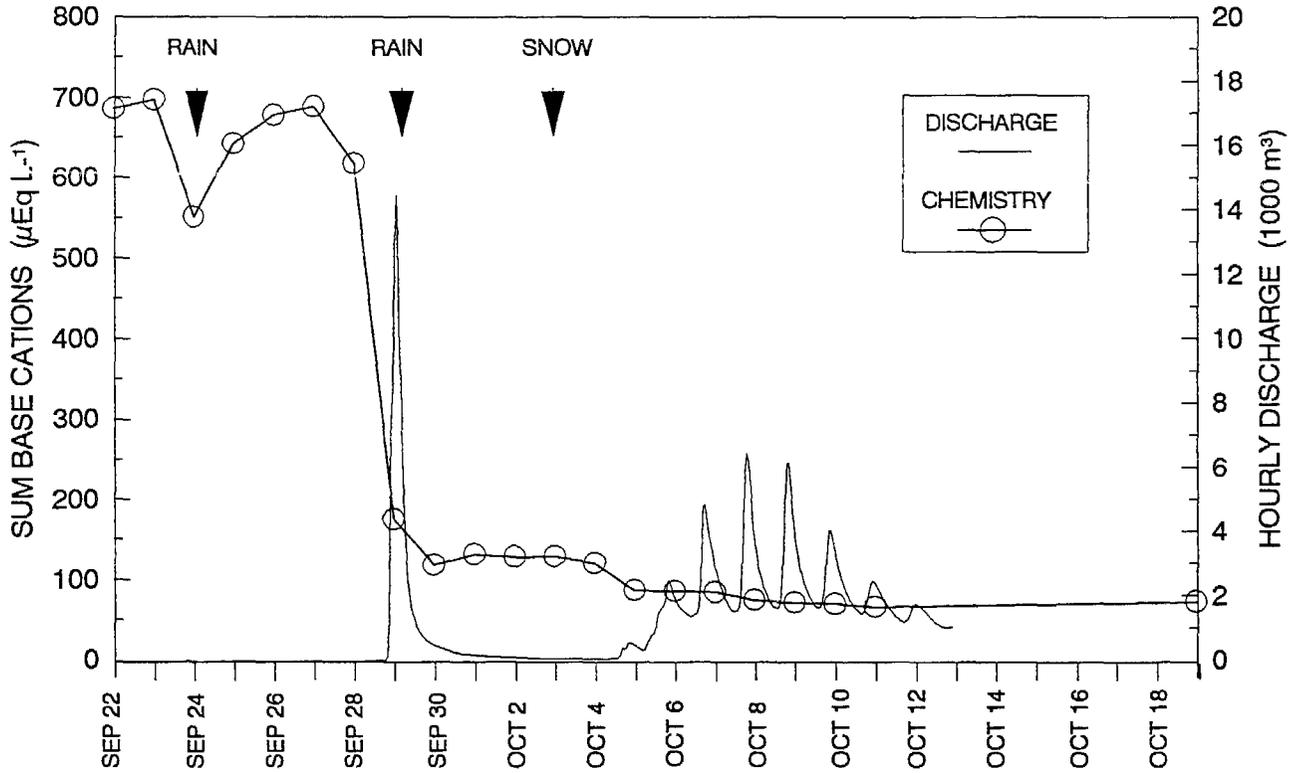


Figure III-34

