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CONTROLS ON SURFACE WATER CHEMISTRY IN THE UPPER MERCED RIVER BASIN, YOSEMITE NATIONAL PARK, CALIFORNIA

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ABSTRACT

Surface water draining granitic bedrock in Yosemite National Park exhibits considerable variability in chemical composition, despite the relative homogeneity of bedrock chemistry. Other geological factors, including the jointing and distribution of glacial till, appear to exert strong controls on water composition.

Chemical data from three surface water surveys in the upper Merced River basin conducted in August 1981, June 1988 and August 1991 were analysed and compared with mapped geological, hydrological and topographic features to identify the solute sources and processes that control water chemistry within the basin during baseflow.

Water at most of the sampling sites was dilute, with alkalinities ranging from 26 to 77 μequiv. l^{-1}. Alkalinity was much higher in two subcatchments, however, ranging from 51 to 302 μequiv. l^{-1}. Base cations and silica were also significantly higher in these two catchments than in the rest of the watershed. Concentrations of weathering products in surface water were correlated to the fraction of each subcatchment underlain by surficial material, which is mostly glacial till. Silicate mineral weathering is the dominant control on concentrations of alkalinity, silica and base cations, and ratios of these constituents in surface water reflect the composition of local bedrock.

Chloride concentrations in surface water samples varied widely, ranging from <1 to 96 μequiv. l^{-1}. The annual volume-weighted mean chloride concentration in the Merced River at the Happy Isles gauge from 1968 to 1990 was 26 μequiv. l^{-1}, which was five times higher than in atmospheric deposition (4–5 μequiv. l^{-1}), suggesting that a source of chloride exists within the watershed. Saline groundwater springs, whose locations are probably controlled by vertical jointing in the bedrock, are the most likely source of the chloride.

Sulphate concentrations varied much less than most other solutes, ranging from 3 to 14 μequiv. l^{-1}. Concentrations of sulphate in quarterly samples collected at the watershed outlet also showed relatively little variation, suggesting that sulphate may be regulated to some extent by a within-watershed process, such as sulphate adsorption.

KEY WORDS surface water chemistry; granitic bedrock; Yosemite

INTRODUCTION

Lakes in the Sierra Nevada are among the most dilute surface waters encountered in the USA based on data collected during the Western Lake Survey, with over 65% of target population lakes having alkalinities less than 100 μequiv. l^{-1} (Eilers *et al.*, 1987; Landers *et al.*, 1987; Melack and Stoddard, 1991). This makes aquatic resources in the Sierra Nevada particularly sensitive to the effects of anthropogenic disturbances such as acid deposition, changes in land use and increased nutrient loadings. Weathering processes are the main source of alkalinity and base cations to most surface waters in the Sierra Nevada (Stoddard, 1987), but the combination of unreactive bedrock and the thin and patchy nature of soils limit alkalinity production. To gain a better understanding of weathering processes controlling surface water composition in the central Sierra Nevada, we have carried out an investigation of the spatial variability in major ion chemistry during baseflow in an alpine/subalpine basin in Yosemite National Park.

Bedrock geology in Yosemite National Park is dominated by granitic intrusive rock with a relatively uniform composition, and there have been no large-scale metamorphic events to alter the rock since it

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was intruded (Huber, 1987; Bateman, 1992). Despite the relatively uniform bedrock composition, a series of regional water sampling surveys have identified considerable variation in water chemistry (Feth *et al.*, 1964; Garrels and Mackenzie, 1967; Hoffman *et al.*, 1976; Sorenson and Hoffman, 1981; Melack *et al.*, 1985; Landers *et al.*, 1987).

Two of the previous water chemistry studies focused on identification of the sources of the rock-derived dissolved constituents in natural waters (Feth *et al.*, 1964; Garrels and Mackenzie, 1967). In a study of spring water in the granitic terrane of the Sierra Nevada, Feth *et al.* (1964) noted that most of the cations, alkalinity and silica in the water could be attributed to the weathering of silicate minerals. Garrels and Mackenzie (1967) took the analysis of the same spring water data set one step further, quantifying the relative contributions of the important silicate minerals. They concluded that approximately 80% of the weathering products (base cations, alkalinity and silica) in ephemeral spring water were derived from the breakdown of plagioclase. These studies provided an important insight into the types of weathering reactions that control the ratios of weathering products in natural waters. However, little work has been done in the Yosemite area in determining the reasons for the broad ranges seen in solute concentrations or for the large variations in anion ratios.

The purpose of this study is to determine the causes of variations in surface water chemistry identified in three surface water synoptic studies of the upper Merced River basin which were conducted in August 1981, June 1988 and August 1991. In addition, this information will be useful for documenting baseline water quality conditions in the park, and for guiding resource managers in identifying suitable strategies for monitoring ecologically sensitive areas. Both of the synoptic samplings in August were carried out during periods of very low flow, and the June sampling occurred near the end of snowmelt. Thus our conclusions will apply only to sources or processes that dominate during base flow conditions or near the end of snowmelt.

Drainage basin characteristics

The upper Merced River watershed is on the western slope of the Sierra Nevada Mountains in Yosemite National Park (Figure 1). The drainage basin is 465 km^2 and ranges in elevation from 1220 m at the Happy Isles Bridge to 3997 m at Mount Lyell. The watershed contains over 100 lakes and ponds, most of which are located in headwater cirques. Large faces of exposed granite are common along the steep valley walls, and forested areas tend to develop on ridge-top benches and along the valley floors. Vegetation covers approximately 45% of the basin and includes a red fir forest that grades into a mixed subalpine forest above 2750 m (Rundel *et al.*, 1977). Above the timberline (~3200 m), the vegetation consists of low-lying tundra plants and alpine meadow vegetation. There are no roads in the upper Merced River watershed, but three large campgrounds (capacity > 50 people per night) are located in the watershed. Tourist and pack animal traffic is high in these areas during the summer months.

The upper Merced River watershed is one of 57 drainage basins in the US Geological Survey Hydrologic Benchmark (HBM) Network. The HBM Network was initiated in 1967 to provide long-term data on water quality and discharge for small undeveloped watersheds nationwide (Cobb and Biesecker, 1971; Lawrence, 1987). A gauging station (Happy Isles gauge, Figure 1) is operated by the HBM Network at Happy Isles Bridge approximately 3 km upstream from Yosemite Village. Discharge has been measured at the Happy Isles gauge since 1915 and water quality measurements have been made semi-monthly to quarterly since 1968. Average annual runoff measured at the Happy Isle gauge is 64 cm. Runoff in the 1981, 1988 and 1991 water years was 44, 40 and 44 cm, respectively, reflecting the relatively small amounts of precipitation that occurred during those years. A monitoring station for the collection of precipitation volume and chemistry has been operating since 1981 near the Crane Flat Ranger Station (elevation 1800 m) as part of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). Average precipitation at the NADP station (Figure 1) was 110 cm yr^{-1} between 1982 and 1991. Average annual precipitation in Yosemite Valley (elevation 1200 m) is 95 cm and increases to 127 cm near Tuolumne Meadows at an elevation of 2650 m (M. Butler, NPS, pers. comm.). The annual hydrograph is driven by snowmelt, with peak flows occurring in May and June and minimum flows in September and October. Usually over 95% of the precipitation occurs in the form of snow between October and April (Cobb and Biesecker,

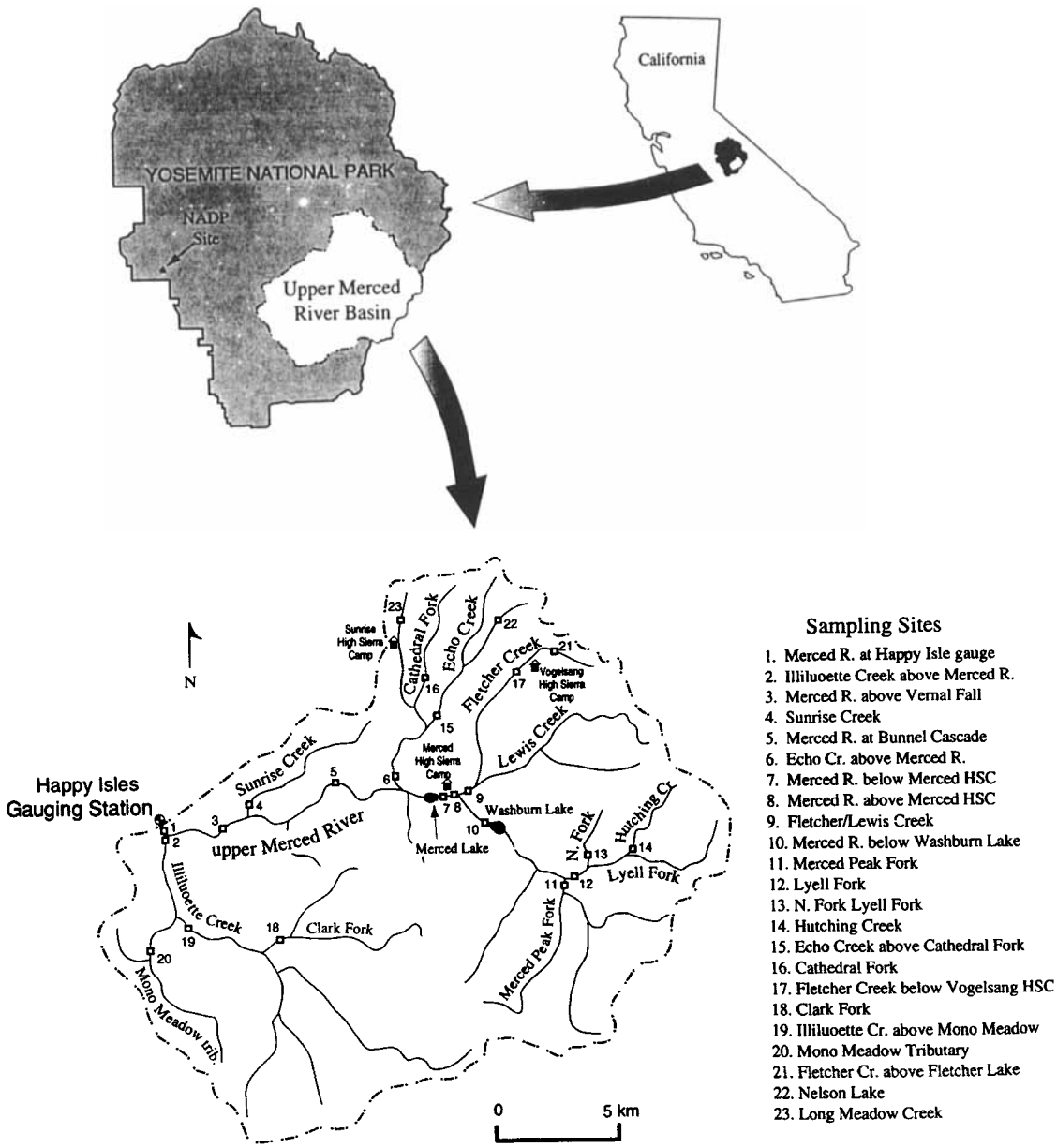

Figure 1. Map showing the upper Merced River basin and locations of sampling sites

1971). On average, approximately 40% of the annual precipitation is lost to evapotranspiration. Groundwater outflow from the basin is minimal.

Geology

Most of the Sierra Nevada mountain range is underlain by granitic rocks of the Sierra Nevada batholith. Because of excellent geological exposures, the Sierra Nevada batholith is one of the most intensively studied and well-mapped plutonic bodies in the USA. Bateman (1992) and Huber (1987) give excellent descriptions of the geology of Yosemite, and most of the following section is derived from their work. Most of the rocks in the upper Merced basin are part of the Tuolumne Intrusive Suite, a group of four concentrically arranged

plutonic bodies. The rocks within the Tuolumne Suite are all granites and granodiorites, but composition and texture differs across the suite. The oldest and most mafic unit forms the margin of the suite and is present along the south-west boundary of the watershed in the Illilouette subdrainage basin. These dark, fine-grained rocks are composed predominately of plagioclase, biotite and hornblende. The rocks are progressively younger and more felsic towards the core of the suite, which underlies the watershed near the northern boundary. The rocks in the core are lighter coloured and coarser grained than rocks near the margin and are composed primarily of plagioclase, quartz and K-feldspar. In addition to changes in mineral abundances across the suite, the average calcium : sodium ratio of the plagioclase decreases inward from 0.67 near the margin to less than 0·25 in the core.

Other important rock units in the basin include granites and granodiorites belonging to the intrusive suites of Washburn Lake, Buena Vista Crest and Yosemite Valley. In general, the granites in these suites contain plagioclase, quartz, K-feldspar and biotite, and the granodiorites contain plagioclase, quartz, biotite and hornblende. Relatively small outcrops of hornfels and other metavolcanic rocks, which were probably derived from pyroclastic rocks (tuff and tuff breccia), occur in the south-east part of the watershed. Limited exposures of metasedimentary rocks and diorite occur along the eastern margin of the basin.

Approximately 20% of the upper Merced River basin is underlain by surficial deposits. These surficial deposits are primarily glacial tills that occur in valley bottoms as lateral and recessional moraines. Till is particularly extensive in the Illilouette and Sunrise subdrainage basins, where it covers about one-third of the land surface. The till has a mineralogy similar to the granitic bedrock present at higher elevations to the east, and thus was probably derived from it.

METHODS

Water samples were collected from sites along the main channel and major tributary streams in the basin during June 1988 and August 1991. Three subsamples were retained from each site for chemical analysis, including an unfiltered sample for alkalinity, a filtered sample for anion analyses and a filtered, acidified (0·4% nitric acid) sample for cation and silica determinations. Filtration was performed within 12 hours of collection using a rinsed 0·45 μm polycarbonate membrane filter. The pH was measured within 12 hours on an unfiltered sample using a combination electrode designed for low ionic strength waters. The electrode was standardized with pH 4 and 7 buffers and checked against a dilute sulphuric acid standard (pH 4·85) and distilled water. All samples were analysed for major element chemistry at the US Geological Survey National Water Quality Laboratory (NWQL) in Arvada, Colorado using low-level methods described in detail by Fishman and Friedman (1989). Anions were determined by ion chromatography and alkalinity was measured by second-derivative titration. The reporting limits for anions and alkalinity are 1·0 and 10 μequiv. l^{-1}, respectively. Major cations and silica were determined by inductively coupled plasma atomic emission spectrometry. Reporting limits for calcium, magnesium, potassium and silica are equal to or less than 1.0 μequiv. l^{-1}, and sodium is 8 μequiv. l^{-1}. Quality assurance procedures included the analysis of field blanks and duplicate samples (10%) and calculation of charge balance. For the 1988 and 1991 samples, all but two samples had charge imbalances between +1 and +12%, calculated as the difference between the cations and anions divided by the sum of the cations and anions.

In addition to the samples collected in 1988 and 1991, data were used from a survey of lakes and streams in Yosemite National Park conducted by the US Geological Survey during the summer 1981. The purpose of this survey was to provide the National Park Service with baseline water quality data for the upper Merced and Tuolumne River basins (S. K. Sorenson, USGS, pers. comm.). Collection and measurement procedures are outlined by Hoffman *et al.* (1976; 1978) and Sorenson and Hoffman (1981). All samples were analysed at the NWQL in Arvada, Colorado; however, this was before the establishment of their low ionic strength facility. Reporting limits for these samples were all less than 5 μequiv. l^{-1}, except sulphate and alkalinity, which had reporting limits of 20 μequiv. l^{-1}. Data are stored in the US Geological Survey's Water Data and Storage Retrieval Information System (WATSTORE).

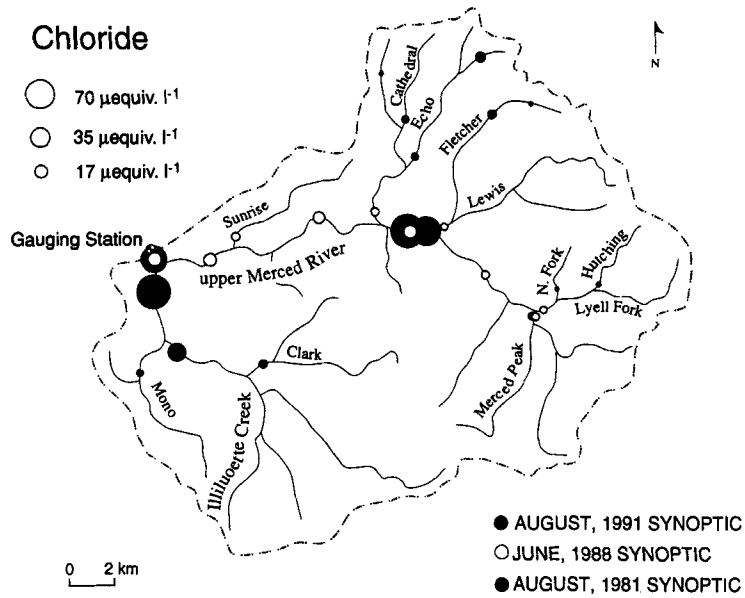

Figure 2. Bubble plot showing chloride concentrations in surface water samples collected during August 1981, June 1988 and August 1991 synoptics. Area of bubble is proportional to concentration

RESULTS AND DISCUSSION

Chloride

Chloride concentrations in samples collected during the three surface water synoptics are illustrated in Figure 2 and are listed in Table I. Concentrations in samples collected during the 1981 and 1991 surface water synoptics were highly variable, ranging from <1 to 96 μequiv. l^{-1}, but concentrations in samples taken during the 1988 synoptic varied much less, ranging from 4 to 16 μequiv. l^{-1}.

The differences in concentrations between the synoptics are related to different flow conditions in the basin during sampling. Discharge at the Happy Isles gauge was 14·2 m^3 s^{-1} during the June 1988 synoptic, 1·8 m^3 s^{-1} during the August 1991 synoptic and 0·4 m^3 s^{-1} during the August 1981 synoptic. Chloride concentrations in samples taken from the Merced River above Merced Lake in order of decreasing flow were 14, 62 and 90 μequiv. l^{-1} during the 1988, 1991 and 1981 synoptics, respectively. This inverse relation between chloride and discharge is also apparent in the HBM network data collected at the Happy Isles gauge, where chloride shows a strong inverse relationship with flow, as do alkalinity, silica and base cations (Figure 3), and is consistent with a hydrological system where relatively concentrated groundwater is diluted by snowmelt during the springtime.

In addition to variations in chloride with flow, considerable spatial variability was observed between sampling sites. For example, chloride concentrations in samples collected from the main stem of the Merced River in 1981 and 1991 ranged from 57 to 90 μequiv. l^{-1} whereas in most tributaries, chloride ranged from <1 to 6 μequiv. l^{-1}. The only tributary to the Merced River that had chloride concentrations significantly above chloride levels in precipitation was Illilouette Creek, which joins the main stem of the Merced River just above the Happy Isles gauge. In the 1991 synoptic, chloride in Illilouette Creek 5 km above the confluence with the Merced River was 25 μequiv. l^{-1}. In the 1981 synoptic, chloride in Illilouette Creek just above the confluence with the Merced River was 90 μequiv. l^{-1} (Figure 2). Surface water samples collected during several previous studies also showed high chloride concentrations along the main stem and low concentrations in most tributaries (Sorenson and Hoffman, 1981). Analysis of the HBM data collected at the Happy Isles gauge indicates that high chloride concentrations are not uncommon for the upper reach of the Merced River. Chloride concentrations at the Happy Isles gauge between 1968 and 1990 ranged from <1 to 280 μequiv. l^{-1}.

Table I. Major ion chemistry and discharge for samples collected during the 1991, 1988 and 1981 sampling synoptics. Discharge is given in $m^3 s^{-1}$ and all chemical constituents are expressed in units of μequiv. l^{-1}, except for SiO_2 in $\mu mol l^{-1}$. Site numbers correspond to sampling locations on Figure 1

Site No.	Sampling site	Q	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	SiO_2
1991 Synoptic												
1	Merced R. at Happy Isles gauge	1·77	7·08	89·8	14·8	65·2	7·2	56·5	2·1	10·6		70·0
7	Merced R. below Merced HSC	1·56	6·92	79·8	9·1	52·2	4·3	62·1	2·1	12·1	59·4	36·7
8	Merced R. above Merced HSC	1·56	6·65	79·8	5·8	56·5	7·9	67·8	2·1	11·9	65·0	36·7
13	North Fork Lyell Creek	0·027	6·95	23·0	4·9	26·1	3·1	1·4	<1·0	4·2	38·2	83·3
11	Merced Peak Fork		6·53	30·4	4·9	13·0	2·6	4·8	2·9	10·2	25·6	25·0
14	Hutching Creek	0·099	6·82	36·4	8·2	17·4	3·6	1·7	7·1	10·0	33·2	31·7
16	Cathedral Fork	0·014	6·68	54·9	8·2	52·2	4·3	4·5	<1·0	14·4	77·4	90·0
15	Echo Creek above Cathedral Fork	0·023	7·12	33·9	11·5	39·1	4·1	25·4	<1·0	5·8		85·0
19	Illilouette Creek above Mono Meadow	0·218	7·61	139·7	29·6	91·3	12·3	25·4	<1·0	10·0	226·0	183·3
18	Clark Fork	0·003	6·11	43·4	10·7	21·7	4·1	5·9	3·6	4·0	51·0	61·7
20	Mono Meadow Tributary	0·022	7·11	164·7	38·7	113·0	14·8	3·7	<1·0	3·1	302·0	250·0
1988 Synoptic												
1	Merced R. at Happy Isles gauge	14·20	6·90	43·4	4·9	35·7	5·6	15·8	2·8	8·3	56·7	68·3
3	Merced R. above Vernal Fall		6·88	36·4	3·3	29·1	4·6	13·0	3·8	7·9	43·0	56·7
4	Sunrise Creek		7·15	99·8	19·8	87·0	9·2	5·9	<1·0	2·5	185·6	216·7
5	Merced R. at Bunnel Cascade		6·97	35·9	6·6	26·5	3·6	11·6	3·3	8·1	38·2	55·0
6	Echo Creek above Merced R.		6·88	24·5	0·8	27·4	3·3	5·6	<1·0	4·6	39·4	71·7
7	Merced R. below Merced HSC		6·80	36·9	<0·8	26·5	3·6	14·4	4·7	9·4	35·6	48·3
9	Fletcher/Lewis Creek		6·78	33·9	<0·8	22·6	3·6	4·2	4·2	9·4	38·1	55·0
10	Merced R. below Washburn Lake		6·72	29·9	0·8	22·2	3·3	5·9	5·2	9·6	30·1	43·3
11	Merced Peak Fork		6·64	22·0	4·1	19·1	3·1	4·8	4·3	8·8	22·1	40·0
12	Lyell Fork		6·65	38·4	5·8	19·6	3·6	4·5	9·7	12·3	33·5	40·0
1981 Synoptic												
2	Illiluoette Creek above Merced R.	0·048	6·0	164·7	32·1	121·7	17·9	96·0	2·0	<20	200	199·7
17	Fletcher Creek above Vogelsang HSC	0·037	5·9	39·9	11·5	17·4	5·1	5·6	1·0	<20	40	36·6
7	Merced R. below Merced HSC	0·125	6·3	104·8	10·7	65·2	5·1	90·4	1·0	<20	60	31·6
21	Fletcher Creek above Fletcher Lake	1·9	5·9	54·9	18·9	17·4	5·1	2·8	2·0	<20		38·3
22	Nelson Lake		5·9	29·9	23·0	30·4	5·1	8·5	1·0	<20		33·3
23	Long Meadow Creek Tributary near HSC	0·2	6·7	30·9	4·9	21·7	2·6	2·8	2·0	<20	60	76·5

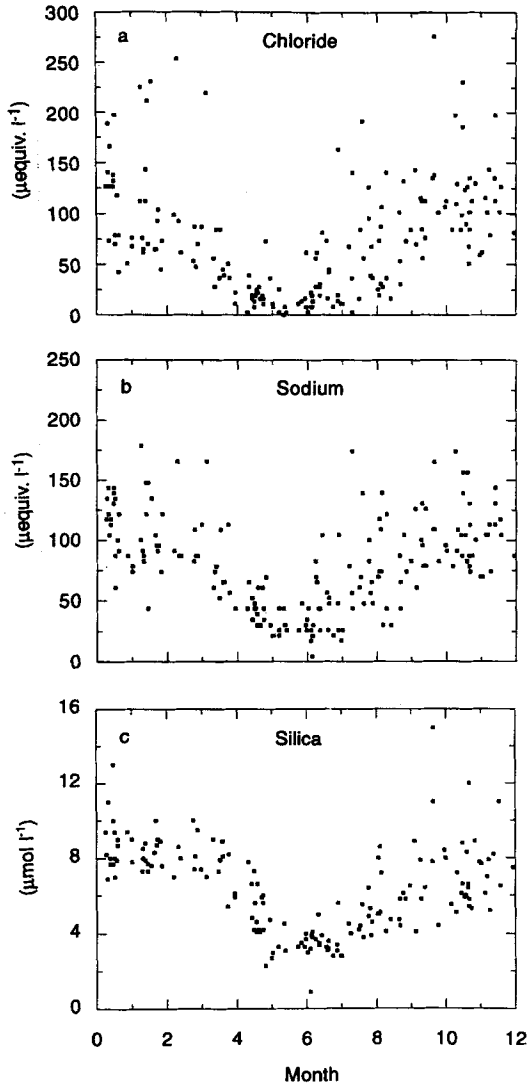

Figure 3. Seasonal variations in concentrations of (a) chloride, (b) sodium, and (c) silica at the Happy Isles gauging station (period of record 1968–1994)

The regional representativeness of the upper Merced River watershed synoptic chloride data was evaluated by comparing it with data from a lake survey conducted in the southern Sierra Nevada during the summer of 1981 (Melack *et al.*, 1982; 1985) and lake chemistry data for the entire Sierra Nevada collected in the Western Lake Survey, which took place during the summer of 1985 (Eilers *et al.*, 1987) (Table II). In the three USGS synoptic studies, the median chloride concentration was 6 μequiv. l^{-1}. In the 1981 southern Sierra lake study, the median chloride concentration was 8 μequiv. l^{-1} (Melack *et al.*, 1985) and the range of concentrations was similar to that measured in this study. In the Melack *et al.* (1985) study, chloride concentrations were significantly higher in lakes in the Yosemite region than farther south ($p < 0{\cdot}05$); the mean chloride in lakes near Yosemite was 21 μequiv. l^{-1}, compared with 12 μequiv. l^{-1} in the south. In the Western Lake Survey, the median chloride concentration for the target population of 2119 Sierran lakes was only 2 μequiv. l^{-1} (Eilers *et al.*, 1987; Landers *et al.*, 1987).

The high chloride concentrations in the upper Merced River and some other localities in the Yosemite region (Melack *et al.*, 1985) were unexpected given the concentrations in precipitation and relatively low

Table II. Comparison of major ion chemistry and elevation data from four surface water synoptics in the Sierra Nevada. Median values (first and third quantiles in parentheses) given in μequiv. l^{-1}, except SiO_2 in μmol l^{-1}

	Elevation (m)	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}	SiO_2
This study ($n = 27$)	2164	6·8 (6·7–7·0)	39 (34–83)	7 (5–12)	28 (22–59)	4·2 (4–6)	6 (5–18)	2·1 (0·0–3·9)	10 (7–12)	42 (36–64)	56 (39–84)
Melack *et al.* (1985), granitic ($n = 44$)	3389	6·9 (6·4–7·2)	37 (22–54)	5 (3–7)	16 (10–24)	6 (4–15)	8 (5–16)	0·4 (0·1–2·4)	13 (9–20)	44 (25–65)	
Melack *et al.* (1985), non-granitic ($n = 29$)	3121	7·2 (7·0–7·8)	70 (34–308)	10 (5–25)	26 (18–48)	12 (7–20)	12 (8–21)	0·2 (0·1–0·9)	31 (18–91)	71 (41–258)	
WLS (population) ($n = 2119$)	3008	6·9 (6·6–7·3)	43 (29–104)	6 (3–9)	19 (11–21)	4	2 (1–3)	0·4 (0·1–1·7)	7 (4–7)	60 (37–130)	33 (22–60)

chlorine content of common granitic minerals (Deer *et al.*, 1966; Feth, 1981). Although hornblende can contain significant amounts of chlorine (Peters, 1991), the distribution of high chloride-type waters in the Merced basin does not follow the distribution of hornblende-containing bedrock (granodiorites and diorites). The following three possibilities were explored to explain the high chloride concentrations in the upper Merced basin: (1) leakage of chloride from wastewater facilities at campgrounds; (2) evaporative concentration of dissolved solids; and (3) mixing of saline spring water with stream water.

The possibility that chloride from wastewater facilities at the campgrounds was contaminating stream water was tested by comparing concentrations in water samples collected below the camps with concentrations in samples collected above the camps, or to background values. There was little difference in chloride concentrations in samples taken above and below the campground near Lake Merced during the 1991 synoptic; chloride concentrations in samples taken above and below the camp were 68 and 62 μequiv. l^{-1}, respectively. Chloride concentrations in water samples collected in 1981 above and below Vogelsang High Sierra Camp, in the eastern part of the watershed, were both 6 μequiv. l^{-1}. These results indicate that even during high use periods, the campgrounds are not a significant source of chloride and cannot explain the high chloride concentrations in the upper Merced River.

Water yield in the upper Merced basin averages about 50%, based on runoff at the Happy Isles gauge and precipitation records collected at Crane Flat and Tuloumne Meadows (NADP; Mark Butler, NPS, pers. comm.). Thus evapotranspiration could account for an approximate doubling of the annual volume- weighted mean (AVWM) chloride concentration measured in precipitation. The AVWM chloride concentration in precipitation averaged 4 μequiv. l^{-1} from 1982 through 1992. The AVWM chloride concentration in the Merced River at the Happy Isles gauge during the same period averaged 26 μequiv. l^{-1}, more than five times the concentrations found in precipitation. This concentration is much higher than can be accounted for by evapotranspiration and indicates that the upper Merced River drainage basin contains a major internal source of chloride.

The third explanation explored is that surface water is a mixture of concentrated spring waters with dilute snowmelt. Several studies have reported the occurrence of high-chloride groundwater and spring water from Sierran granites (Feth *et al.*, 1964; Barnes, *et al.*, 1981; Mack and Schmidt, 1981; Nimz *et al.*, 1993). Feth *et al.* (1964) noted that in the Sierra Nevada, springs are often structurally controlled and discharge at the surface through joints or faults. Meteoric water may enter joints or faults high on a hillside, circulate through deep fractures and emerge lower on the hillside. The effect of springs on surface water chemistry would tend to be greatest low in the basin, such as near the main river channel. In this study, geological data and spatial variations in chloride concentrations were consistent with this model. Two prominent vertical to subvertical joint sets dissect bedrock in the main drainage of the upper Merced River, and the high chloride values were found only at lower elevations in the main Merced drainage and Illilouette Creek.

Although the data are consistent with the concept of joint-controlled springs, the question remains as to what the source of chloride is in the granitic bedrock. Feth (1981) noted that degassing of buried magmas, a common source of chloride in some groundwaters, was not supported in the case of Sierran groundwaters by the low concentrations of sulphate.

Several workers have suggested that saline and soda springs in the Sierra Nevada result from the mixing of meteoric water with connate water derived from the compaction of marine sediments at the margins of plutons (Barnes *et al.*, 1981; Mack and Schmidt, 1981). Geochemical and isotopic evidence from spring water supports deep circulation of meteoric water through fractures in the granite into underlying metasedimentary rocks, with subsequent emergence of spring water from fractures or faults in low-lying areas (Barnes *et al.*, 1981; Nimz *et al.*, 1993).

Another hypothesis is that the salt components (Na–Ca–Cl) are derived from fluid inclusions in the granitic bedrock. This mechanism has been proposed to explain the high saline component in groundwaters from the Stripa granite in Sweden (Nordstrom *et al.*, 1989; Waber and Nordstrom, 1992). Although we cannot verify this mechanism for the Merced basin, fluid inclusions are common in Sierran granitic rocks (Bateman, 1992).

The ratios of sulfate : calcium : sodium, normalized to chloride, in the Merced River and its tributaries

Table III. Molar ratios of sulphate, calcium and sodium normalized to chloride in springs and groundwater (GW) from the Sierra Nevada. Ion ratios in surface waters from the Upper Merced basin and fluid inclusions in granitic rock included for comparison

Water type	*n*	Sulphate	Calcium	Sodium	Reference
Ephemeral springs	15	1·50	5·5	9·3	Feth *et al.* (1964)
Perennial springs	56	0·36	3·8	3·6	
Thermal springs	8	0·32	0·2	2·8	
Low chloride GW	3	0·15	2·9	9·1	Mack *et al.* (1981)
High chloride GW	12	0·02	0·2	0·7	
Soda springs	22	0·04	1·7	2·8	Barnes *et al.* (1981)
Fluid inclusions		0·05	0·2	0·6	Waber *et al.* (1992)
Merced River (low flow)	4	0·08	0·5	0·9	This study
Merced tributaries	12	0·88	5·8	9·0	

were compared with ratios in spring and groundwater samples reported by Feth *et al.* (1964), Mack and Schmidt (1981) and Barnes *et al.* (1981), and in fluid inclusions characterized by Waber and Nordstrom (1992) (Table III). The tributary streams have ratios most similar to the ephemeral springs in Feth *et al.* (1964), which he described as a mixture of meteoric water and weathering products from granitic minerals. In contrast, the main stem of the Merced River has ion ratios closer to those measured in fluid inclusions (Waber and Nordstrom, 1992) and high chloride groundwaters from the Sierran foothills (Mack and Schmidt, 1981). This suggests that the most likely source of chloride is connate water or fluid inclusions rather than thermal or soda springs. The lack of water chemistry data for springs within the study basin precludes assigning a definite source of the chloride. Further research is needed to better define the source of chloride in surface and groundwaters and should include comparison of major and minor element chemistry in surface waters and springs. The ratio of ^{36}Cl to total chlorine and ratios of chloride : bromide and chloride : iodide have been used in previous studies to identify likely sources of chloride in groundwater (Barnes *et al.*, 1981; Nimz *et al.*, 1993).

Nitrate

Nitrate concentrations in samples collected during the 1981, 1988 and 1991 synoptics were low, ranging from <1 to 10 μequiv. l^{-1}. Median and quartile nitrate concentrations were similar to those measured in the 1981 survey of lakes in the southern Sierra Nevada (Melack *et al.*, 1985) and in the Western Lake Survey (Eilers *et al.*, 1987; Landers *et al.*, 1987) (see Table II). Median nitrate concentrations in all of these studies were much lower than the median AVWM nitrate concentrations of 7 μequiv. l^{-1} measured in precipitation at Crane Flat between 1982 and 1992 (NADP). This can be explained by the seasonal trends in nitrate concentrations observed in surface waters in Yosemite and at other alpine watersheds in the western USA (Williams and Melack, 1991; Campbell *et al.*, in press).

At Emerald Lake, in the southern Sierra Nevada, and at Loch Vale, in the central Rocky Mountains, nitrate concentrations in surface waters tend to be relatively high during the early stages of snowmelt, after which they decrease rapidly (Williams and Melack, 1991; Campbell *et al.*, in press). Williams and Melack (1991) proposed that the high initial nitrate concentrations in surface waters could be explained by the preferential elution of strong acid anions from the snowpack, or flushing of nitrate from soil solutions. By the middle to late summer, when each of the surface water synoptics used in this study occurred, nitrate concentrations in streams are generally at or below concentrations commonly measured in precipitation. The low concentrations could be due to nitrate consumption by biota, or dilution of nitrate in soil water by snowmelt.

In this study, the highest nitrate concentrations in the basin were measured in the Lyell Fork and its tributaries (sites 12 and 14, Table I). In a synoptic conducted in the Merced River basin in the summer of 1977, Sorenson and Hoffman (1981) found similar spatial trends. In that study, samples collected from Washburn Lake and the Merced River just below the confluence with the Lyell Fork had much higher total nitrogen (0·6 mg l^{-1}) than sites elsewhere in the watershed ($<0{\cdot}1$ mg l^{-1}) (Sorenson and

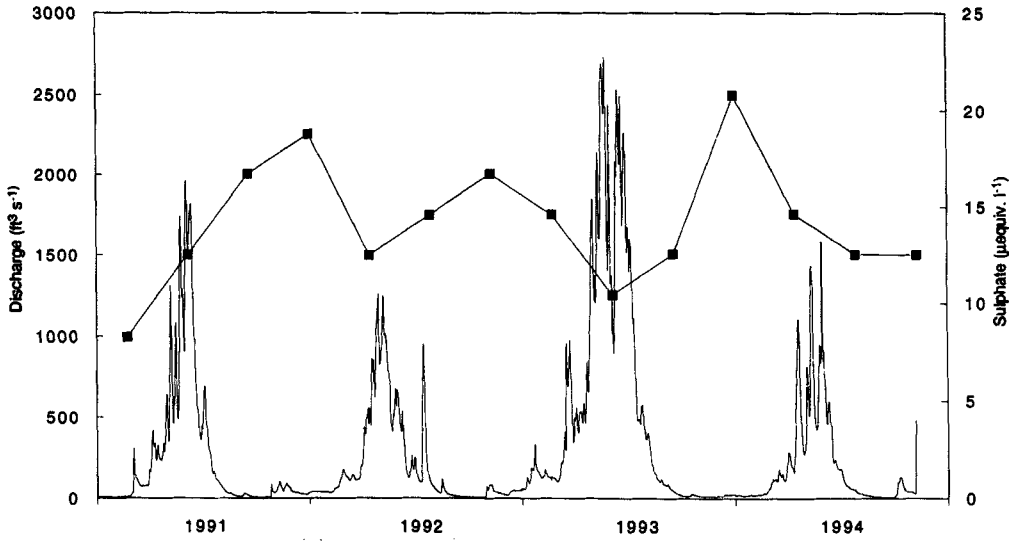

Figure 4. Time series plot of sulphate concentrations and discharge at the Happy Isles gauge from 1991–1994

Hoffman, 1981). Most of the nitrogen in samples in the upper part of the watershed was in the organic form, suggesting that the main control on nitrate in that area could be biological activity (Sorenson and Hoffman, 1981).

Sulphate

Median sulphate concentrations in surface water samples collected in the 1988 and 1991 synoptics were approximately 10 μequiv. l^{-1} and ranged from 3 to 14 μequiv. l^{-1}; there was no apparent trend in spatial variability during the synoptics. Median sulphate concentrations in surface water were in the range that could be expected from evapotranspiration, approximately 1·5 times the average sulphate concentration measured in wet deposition. Sulphate concentrations measured in the Merced River basin were similar to those measured in granitic lakes by Melack *et al.* (1985) and in the Western Lake synoptic (Eilers *et al.*, 1987; Landers *et al.*, 1987) (see Table II). Sulphate concentrations in the non-granitic lakes sampled by Melack *et al.* (1985) were much higher than in the granitic lakes, indicating that the metavolcanic or marine rocks in the non-granitic basins may contain sulphide-bearing minerals.

Sulphate concentrations in the Merced River at the Happy Isles gauge tend to be lowest during snowmelt, and increase gradually throughout the summer and autumn (Figure 4). The amount of seasonal variance in sulphate concentrations is lower than might be expected from the effects of snowmelt dilution during the spring and evapotranspiration during the late summer. At watersheds where sulphate and chloride are derived mainly from precipitation, a comparison of the seasonal variation in those elements in stream water can provide a gauge of the effect of soil processes on stream water concentrations. This assumes that the effect of evapotranspiration and preferential elution from the snowpack are similar for both elements. Although this approach is not possible at the upper Merced River watershed because of the apparent internal source of chloride, it can be used at Emerald Lake, a catchment with similar bedrock, soil and climate characteristics located 150 km to the south. At the main inflow to Emerald Lake in 1986, chloride decreased from 9 μequiv. l^{-1} before to the initiation of snowmelt to 1 μequiv. l^{-1} at peak discharge, but sulphate went from 8 μequiv. l^{-1} down to only 5 μequiv. l^{-1} (Williams *et al.*, 1993). By late autumn, chloride had increased to 10 μequiv. l^{-1} and sulphate had risen back to 8 μequiv. l^{-1}. The amount of variance in sulphate in the Merced River at the Happy Isles gauge is similar to that measured in streams at the Emerald Lake watershed. For example, at the Happy Isles gauge in 1992, sulphate ranged from 12 μequiv. l^{-1} during snowmelt to 16 μequiv. l^{-1} in the autumn (Figure 4).

The lack of variance in sulphate concentrations suggests that there is a process or combination of

processes which regulate sulphate in these surface waters, at least to a minor extent. Retention of sulphur can occur by a variety of processes, including adsorption onto the surfaces of Al and Fe sesquioxides in the soil (Nodvin *et al.*, 1986; 1988; Reuss and Johnson, 1986; Schindler *et al.*, 1986; Fuller *et al.*, 1987; Dhamala *et al.*, 1990; Shanley, 1992; Shanley and Peters, 1993), incorporation into soil organic matter (Reuss and Johnson, 1986; Schindler *et al.*, 1986; Mitchell and Fuller, 1988), uptake by plants (Turner *et al.*, 1990; Huntington *et al.*, 1994) and sulphate reduction/oxidation in seasonally anoxic areas such as lakes or boggy meadows that undergo cyclical wetting and drying (Connell and Patrick, 1968; 1969; Berner, 1984; Kirchner *et al.*, 1992). Of these four mechanisms, sulphur cycling in organic matter and sulphate adsorption are likely to be the most important in the upper Merced River basin. Sulphur cycling in soil organic matter (leaf and root litter and microbes) can be important in subalpine/alpine soils because cold temperatures slow organic matter decomposition, allowing it to accumulate. In the Loch Vale watershed, in the central Rocky mountains, 90–95% of the soil sulphur is organically bound (Baron *et al.*, 1992). Organically bound sulphur is most important in the shallow soil horizons and adsorbed sulphate tends to be more important at depth, where Al and Fe sesquioxides tend to accumulate (Schindler *et al.*, 1986).

Turner *et al.* (1990) noted that the uptake of sulphur by plants generally does not exceed 10% of the total amount of sulphur retained by ecosystems, and the sparsity of lakes and boggy areas, which account for less than 5% of the total watershed area, make it unlikely that redox reactions could have a major impact on sulphur budgets for the basin as a whole.

Several studies have identified sulphate adsorption/retention in soils as an important process regulating sulphate in streams in the western USA (Williams and Melack, 1991; Finley and Drever, 1992). At the Emerald Lake watershed and the West Glacier Lake watershed, in the central Rocky Mountains, soil solutions collected during snowmelt using suction lysimeters showed minimal variation in sulphate concentrations (Brown *et al.*, 1990; Williams and Melack, 1991; Finley and Drever, 1992). At West Glacier Lake in 1988, sulphate ranged from 9 to 13 μequiv. l^{-1} in soil solutions, compared with 15–40 μequiv. l^{-1} in stream water and 10–110 μequiv. l^{-1} in snowmelt (Finley and Drever, 1992). At Emerald Lake in 1987, sulphate in a nest of soil lysimeters ranged from approximately 8 to 12 μequiv. l^{-1}, versus 5 to 8 μequiv. l^{-1} in stream water and 2 to 45 μequiv. l^{-1} in snowmelt (Brown *et al.*, 1990; Williams and Melack, 1991).

Few studies have measured the sulphate adsorption capacities of soils in mountainous regions of the western USA. It is likely that adsorption capacities are low in western mountain soils compared with those in the east. This is because the immature soils in the west usually lack well-developed B horizons containing crystalline Al and Fe oxides that provide much of the sulphate adsorption capacity in northern temperate forests (Drever, 1988). Baron *et al.* (1992) noted that the sulphate adsorption capacities of soils in Loch Vale, in the central Rocky Mountains, were much lower than the adsorption capacities of several other forest soils in the eastern USA. No information is available on the sulphate adsorption capacities of soils in the upper Merced River drainage; however, evidence for a limited amount of adsorption capacity in cold granitic soils is provided by adsorption isotherm experiments conducted on Cryorthent and Cryumbrept subsoils from the Emerald Lake watershed (Wyels, 1986). In these experiments, Wyels (1986) noted that when incrementally adding up to 1 mequiv. of dilute sulphuric acid to 100 g of soil, between 50 and 100% of added sulphate was adsorbed.

In summary, soils in the upper Merced River drainage may have a small, but sufficient, capacity to regulate sulphate concentrations in surface waters under existing deposition conditions. Sulphate adsorption in mineral horizons and sulphur cycling in organic matter are the most likely processes for this apparent regulation.

Base cations, alkalinity, and silica

Concentrations of mineral weathering products in surface water at most of the synoptic sites were as low as those measured in Sierran lakes during the Western Lake Survey (Landers *et al.*, 1987) (Table II). For example, 75% of the streams sampled in this study had alkalinities less than 60 μequiv. l^{-1}. Synoptic samples were collected during the falling limb of the snowmelt hydrograph, when the composition of

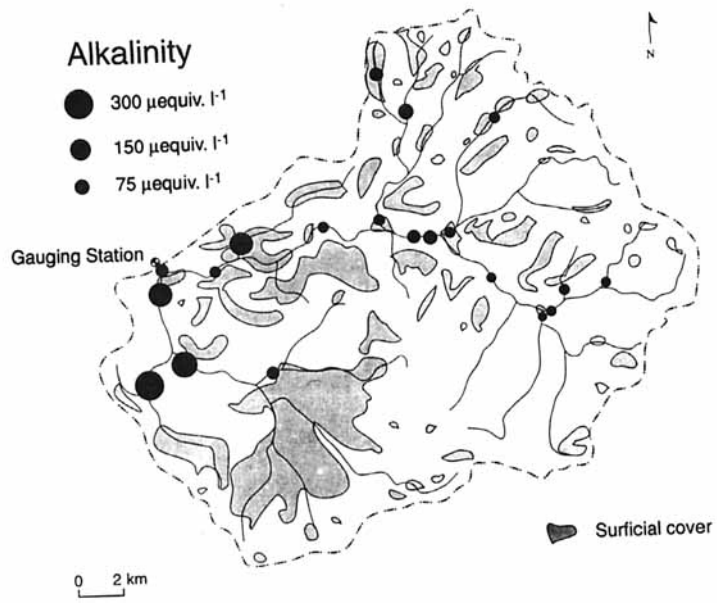

Figure 5. Bubble plot showing alkalinity concentrations in samples collected during 1981, 1988 and 1991 synoptics overlayed on a map of surfical cover in the basin

stream water is dominated by weathering. The characterization of surface water chemistry at this time allows reconstruction of the types of mineral weathering reactions taking place without the chemical interferences of snowmelt inputs.

Figure 5 is a bubble plot showing the concentrations of alkalinity in stream samples collected during the three synoptics. Although the average concentrations were low, there was considerable variability in the concentrations of weathering products in this study, with the highest concentrations localized in the Illilouette and Sunrise drainage basins (sites 2, 4, 18–20 in Table I). Figure 6 is a box plot that compares alkalinity and silica concentrations in samples from the Illilouette and Sunrise drainage basins with samples from the main stem and upper tributaries. In contrast with the very low concentrations of alkalinity and silica in samples from the main stem and upper tributaries, the median concentrations of these constituents in the Illilouette and Sunrise drainage basins were 200 and 199 μmol l^{-1}. Base cation concentrations showed similar spatial patterns (Table I).

Several previous studies have had some success in predicting the alkalinity of lakes based on information available on topographic, geological or vegetation maps (Turk and Adams, 1983; Melack *et al.*, 1985; Turk and Campbell, 1987). Melack *et al.* (1985) found that in lakes in the southern Sierra Nevada, alkalinity was correlated with the percentage areal coverage of granitic, volcanic or calcareous rocks in the basin. Altitude, basin area and lake area were not good predictors of lake alkalinity.

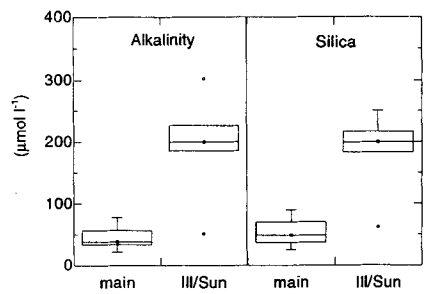

Figure 6. Box plots comparing alkalinity and silica concentrations in the main stem of the Merced to streams in the Illiluoette and Sunrise Creek sub-basins

Table IV. Subcatchment characteristics used in regression analysis and Ca : Na ratios in surface waters draining each basin. Site numbers correspond to sampling locations on Figure 1 and chemical analyses in Table I

Site No.	Subcatchment name	Surfical cover (%)	Basin area (ha)	Weathering index	Ca : Na molar ratio
13	North Fork Lyell Creek	3	3·0	1·25	0·44
11	Merced Peak Fork	4	55·3	1·70	1·17
10	Merced R. below Washburn Lake	5	115·1	1·59	0·68
14	Hutching Creek	8	7·9	2·00	1·05
12	Lyell Fork	8	30·3	1·77	0·98
8	Merced R. above HSC	10	189·2	1·52	0·71
22	Nelson Lake	10	2·4	1·00	0·49
15	Echo Creek above Cathedral Fork	11	16·4	1·00	0·43
5	Merced R. at Bunnell Cascade	12	250·8	1·40	0·68
9	Fletcher/Lewis Creek	14	51·9	1·63	0·75
21	Fletcher Creek above Fletcher Lake	14	1·9	2·10	1·58
3	Merced R. above Vernal Falls	16	316·9	1·30	0·63
6	Echo Creek	18	48·7	1·00	0·45
1	Merced R. at Happy Isles Gauge	19	468·0	1·45	0·69
18	Clark Fork	24	69·8	1·20	1·00
16	Cathedral Fork	25	17·0	1·00	0·53
20	Mono Meadow Tributary	28	47·4	2·00	0·73
2	Illiluoette Creek above Merced R.	29	163·0	1·61	0·68
4	Sunrise Creek	31	30·9	1·00	0·57
19	Illiluoette above Mono Meadow	33	253·0	1·60	0·77
23	Long Meadow Creek Tributary	40	4·5	1·00	0·66

The prevalence of glacial till has been found to exert an important control on the alkalinity of surface waters elsewhere in the USA (Turk and Adams, 1983; Peters and Murdoch, 1985; Peters and Driscoll, 1987; Newton *et al.*, 1987; Turk and Campbell, 1987; Ross *et al.*, 1994). For example, Peters and Murdoch (1985) determined that the thickness of glacial till controlled the amount of groundwater contributed to surface waters, and thus surface water chemistry. In adjacent basins, surface water in one catchment with thin till (<3 m) was acidic, whereas surface water in another catchment with thick till (24 m) was neutral. They noted that till and other types of surficial materials tend to slow the movement of water through a watershed, increasing the residence time and providing additional time for weathering reactions to occur. Also, as till can contain considerable amounts of fine material, it provides abundant mineral surfaces with which water can react.

The feasibility of using map variables to predict the concentrations of weathering products in stream water was explored by performing a multiple stepwise regression using basin area, percentage areal coverage of surficial material and bedrock type as independent variables (Table IV). Basin area and percentage areal coverage of surficial material were calculated for the drainage above each sampling point from digitized topographic and geological map data. A surrogate variable or 'weathering index' was calculated to describe the weathering characteristics of the dominant bedrock types in each subdrainage area. Rock units described on the geological maps of Huber *et al.* (1989) and Bateman (1992) were divided into four categories and assigned a rank based on their assumed relative weathering rates (Goldich, 1938; Stumm and Morgan, 1981; Drever, 1988). The least weatherable rock types, granites and light-coloured granodiorites, were assigned a rank of 1, dark granodiorites and tonalites $=2$, diorite and gabbro $=3$ and metavolcanics and metasediments $=4$. This rank was multiplied by the fraction of the subdrainage area underlain by geological material in each category, producing weathering indices ranging from 1 to 2·1. Results of the regression analysis are summarized in Table V. Percentage areal coverage of surficial material was the best predictor of weathering product concentration, accounting for between 37 and 54% of the variance in calcium, sodium, alkalinity and silica concentrations. Adding 'weathering index' as a variable explained another 22% of the variance in calcium and 24% of the variance in alkalinity,

Table V. Percentage of variance in weathering products explained by a one-variable regression model using surficial cover and a two-variable regression model using surficial cover and weathering index

Dependent variable	One-variable model (surfical) (%)	Two-variable model (surficial and weathering) (%)	*p* Value*
Calcium	42	64	0·000
Sodium	44	49	0·009
Alkalinity	37	61	0·006
Silica	54	58	0·003

* Probability of the overall *F*-test for the two-variable model

but less than 5% of the variance in sodium and silica. Basin area was not a statistically significant descriptor for any the dependent variables tested and was not included in the final regression model. The greater importance of bedrock type in describing the variance in stream water calcium and alkalinity compared with sodium and silica is probably due to the increasing calcium content of the bedrock as the weathering index increases. Where the relations between dependent and independent variables were statistically significant, they were positive, indicating that as the percentage areal coverage of surficial material or 'weathering index' increased, concentrations of weathering products in surface waters did also.

Mineral weathering reactions

Pioneering work on the topic of mineral weathering reactions and their controls on surface water chemistry was conducted by Feth *et al.* (1964) and Garrels and Mackenzie (1967) in the Sierra Nevada. Garrels and Mackenzie (1967) compared the ratio of cations and silica released from common silicate minerals in granitic rocks during weathering with the cation and silica ratios found in spring waters emanating from granitic terranes to determine what the most important mineral weathering reactions were. Their work established that the conversion of plagioclase to kaolinite was the most important weathering reaction in determining the composition of the Sierran springs which they studied. For the major type of plagioclase present in the upper Merced River basin, this reaction can be written as

$$\underset{\text{(plagioclase)}}{Ca_{0\cdot3}Na_{0\cdot7}Al_{1\cdot3}Si_{2\cdot7}O_8} + 1\cdot3CO_2 + 4\cdot75H_2O \rightarrow$$

$$\underset{\text{(kaolinite)}}{0\cdot65Al_2Si_2O_5(OH)_4} + 0\cdot3Ca^{2+} + 0\cdot7Na^{+} + 1\cdot4H_4SiO_4 + 1\cdot3HCO_3^{-}$$

In this weathering reaction, 0·3 moles of calcium and 0·7 moles of sodium are released for each mole of plagioclase weathered. However, the ratio of calcium to sodium in plagioclase in granitic rocks is not constant — the calcium : sodium ratio in plagioclase increases from granites to granodiorites to diorites. Furthermore, mafic rocks such as dark granodiorites and diorites contain a greater abundance of calcium-containing minerals than felsic rocks such as granite. In general, the ratio of calcium to sodium released from weathering of mafic rocks tends to be higher than that from felsic rocks.

The spatial trends in calcium : sodium ratios in the surface waters match the trends in ratios expected in the silicate minerals in the basin based on geological information (Bateman, 1992). The granites and light granodiorites contain plagioclase with a calcium : sodium ratio of approximately 0·2 to 0·4, and the surrounding dark granodiorites and tonalites contain plagioclase with calcium : sodium ratios ranging from 0·4 to 1·0 (Bateman, 1992). Figure 7 shows that calcium : sodium ratios in surface waters are relatively low in streams draining granites and light coloured granodiorites and are higher in streams passing through dark granodiorites, tonalites and metavolcanics. The more weatherable rock types contain hornblende, which is a calcium-silicate mineral that could contribute calcium, but no sodium, to stream water.

These observed relations are further supported by the good correlation between rock type and the calcium

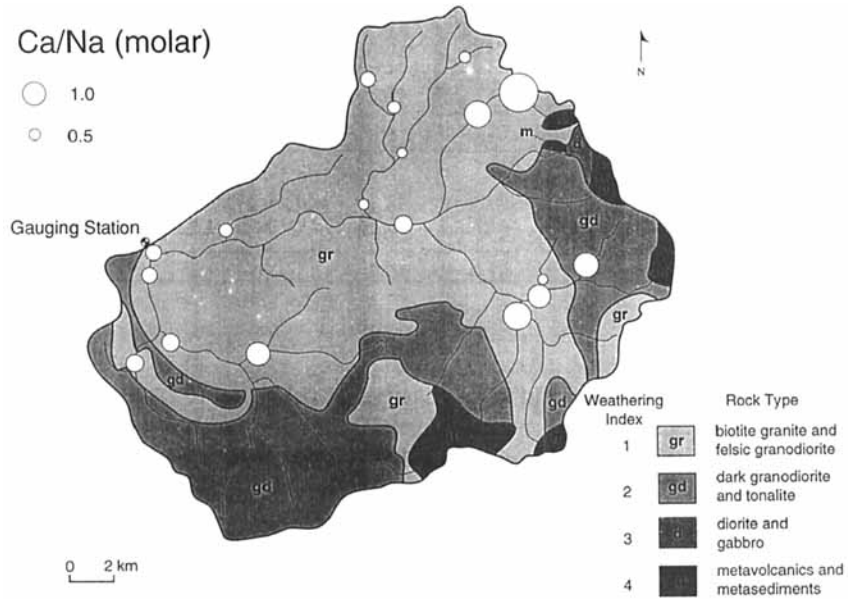

Figure 7. Bubble plot showing calcium to sodium ratios in samples collected during the 1981, 1988 and 1991 synoptics overlayed on a simplified geological map (after Bateman, 1992)

to sodium ratio in stream water draining a given terrane (Figure 7). In a linear regression of the calcium : sodium ratio in stream water to the 'weathering index' of bedrock in each subdrainage, 'weathering index' was found to explain 54% of the variance in the calcium : sodium ratios and the correlation was significant at $p < 0{\cdot}05$. Molar calcium to sodium ratios in surface water samples collected in the upper Merced River basin synoptics ranged from 0·43 to 1·17, except for one sample from Fletcher Creek, which has a ratio of 1·58. This sample is the only one that drains the diorite and metasediments, which crop out only along the eastern border of the watershed, and could contain carbonate minerals.

In summary, these data indicate that for almost all of the samples collected in the surface water synoptics, the calcium : sodium ratios in stream water can be described by the stoichiometric weathering of common silicate minerals, including plagioclase and hornblende. Other minerals likely to contribute base cations, alkalinity and silicate to surface waters include biotite and K-feldspar. Biotite weathering releases magnesium and potassium, and K-feldspar weathering releases potassium to surface waters.

The median calcium : sodium ratio in lakes sampled in granitic terrane in the southern Sierra Nevada by Melack *et al.* (1985) is much higher (1·17) than in stream water samples collected in this study (0·69) (see Table II). Silicate weathering alone cannot account for the calcium : sodium ratio in the granitic lakes. Trace amounts of easily weathered calcite have been shown to have a major impact on surface water chemistry in several watersheds in the Rocky Mountains (Turk and Spahr, 1991; Mast *et al.*, 1990) and the Cascades (Drever and Hurcomb, 1986). Physical weathering is thought to play an important part in exposing trace amount of calcite to chemical attack (Mast *et al.*, 1990; Drever and Zorbrist, 1992; Blum *et al.*, 1994). Physical weathering is more effective in high-elevation headwater cirques than lower in the basin. The mean elevation of granitic lakes sampled by Melack *et al.* (1985) was 3389 m, compared with 2164 m for surface waters in the upper Merced synoptics; this could explain the observed differences in calcium : sodium ratios in surface waters.

Principal component analysis

Statistical tests can sometimes be helpful in summarizing trends in large sets of data. Principal component analysis (PCA) is a statistical technique that tests for interrelations between variables in complex data sets. Statistically significant interrelations among variables are represented by components. The

Table VI. Component loadings and percentage of variance explained by the first four rotated principal components

	1	2	3	4
Ca^{2+}	0·97	0·22	0·12	0·00
Mg^{2+}	0·95	−0·06	0·12	0·14
Na^{+}	0·92	0·16	0·33	0·05
K^{+}	0·96	0·14	0·12	0·12
Cl^{-}	0·09	0·97	0·07	−0·22
SO_4^{2-}	−0·18	0·25	−0·20	−0·93
HCO_3^{-}	0·97	−0·04	0·17	0·13
NO_3^{-}	−0·29	−0·07	−0·93	−0·21
SiO_2	0·87	−0·23	0·31	0·28
% Variance	60	13	13	13

components may in turn be interpreted as indicating a common source for solutes or that a common process acted on them. For more detailed descriptions of the use of PCA in the analysis of temporal and spatial trends in surface water chemistry, see Joreskog *et al.* (1976), Lins (1986) and Puckett and Bricker (1992).

A PCA was performed using a linear correlation matrix of the surface water chemistry data from the 1988 and 1991 synoptics. At sites where chemical data were collected during both synoptics, only one case was used to prevent over-weighting the data from that site. Generally, the sample with the best charge balance was retained. Components that explained at least 4% of the variance in the data were rotated using the varimax method. The loadings that each chemical variable have for each of four components are shown in Table VI. Loadings may be interpreted as correlation coefficients between chemical variables and components (Puckett and Bricker, 1992).

Component 1 was strongly associated with base cations, alkalinity and silica. We interpret this component

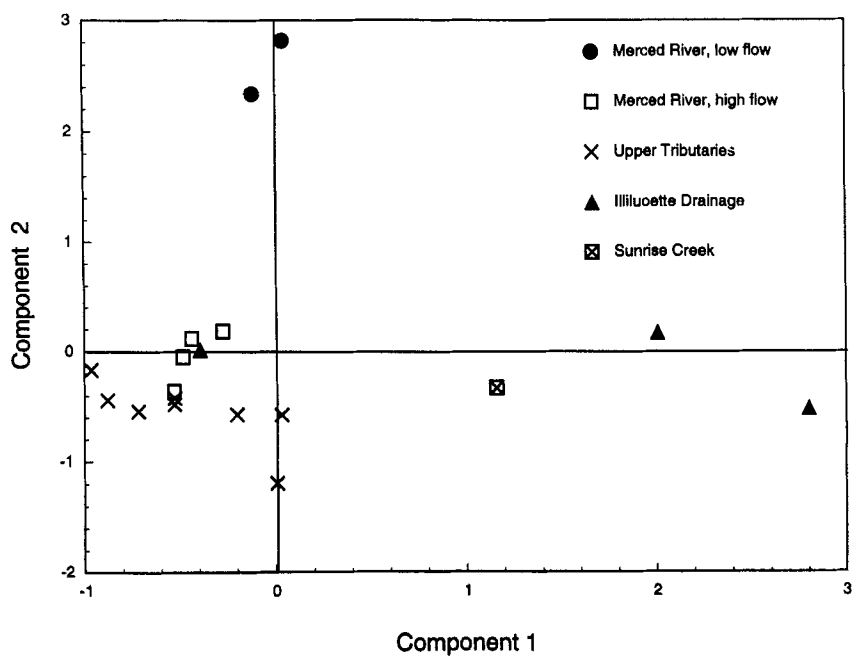

Figure 8. Plot of the rotated scores for component 1 (silicate weathering) and component 2 (Cl)

to represent chemical weathering of silicate minerals. It is the most important component, accounting for 60% of the variance in the data. The second component has a high loading for chloride, suggesting that it may represent the source of water with high chloride concentrations, i.e., groundwater springs. Nitrate is the only variable strongly associated with component 3, which indicates that nitrate varies independently of other solutes. As nitrogen is often a limiting nutrient in alpine ecosystems, biological activity probably plays an important part in controlling nitrogen concentrations in surface waters. Sulphate is the only solute strongly associated with the fourth component, indicating that it also varies independently of other solutes. The combined source/process that controls sulphate concentrations is interpreted to be atmospheric deposition coupled with sulphate adsorption. Components 2, 3 and 4 each account for 13% of the total variance. The total variance explained by the four components is 99%.

A plot of the scores for components 1 and 2 illustrates how the different factors controlling surface water vary spatially in the watershed (Figure 8). Stream water samples from the Illilouette and Sunrise drainage basins scored high for component 1, indicating the importance of chemical weathering in those basins. Samples from the main stem of the Merced River collected during base flow (August 1991) scored high for component 2, indicating that during low-flow conditions the main drainage can be strongly affected by high-chloride spring water. Samples from the Merced River during high flow scored low (near zero) for both components, indicating that the high-chloride water that is presumably derived from springs was diluted by snowmelt. Samples collected in the upper tributaries also scored low for both components, probably because influences from silicate weathering and saline springs were minimal.

CONCLUSIONS

Surface water in most of the upper Merced River basin is very dilute, making the ecosystem sensitive to anthropogenic disturbances. Water chemistry varies considerably despite the relative homogeneity of bedrock composition. The variation may be attributed to the relative importance of the variety of processes and water sources that control water chemistry in the basin. Geological factors exert strong controls on water chemistry; these factors include the distribution of glacial till, a structurally controlled system of groundwater springs and geographical patterns in bedrock type.

High chloride concentrations along the main stem of the Merced River are most likely caused by the inflow of Cl–Na–Ca type spring water. Well-developed vertical joints in the main drainage of the upper Merced River basin could provide conduits for meteoric water to move through the bedrock. Water probably enters joints high on hillsides, percolates through the fracture system obtaining solutes at depth, and discharges where joints intersect the surface water system low in the drainage. The source of the chloride in the spring water is likely to be either fluid inclusions in the bedrock or connate water trapped between ancient marine sediments and the granitic plutons. Further research using trace element ratios or naturally occurring isotopes in the spring water is needed to determine which of these two sources is dominant.

Concentrations of base cations, alkalinity and silica are much higher in subcatchments that have a high percentage of surficial cover than in other subcatchments, reflecting the importance of glacial till in controlling water chemistry in glaciated terranes. Variations in bedrock chemistry are reflected in the calcium : sodium ratios in surface waters. Streams in the northern part of the basin, which drain granite and light-coloured granodiorites terranes, have relatively low calcium : sodium ratios, but streams draining dark granodiorites and tonalites, in the south and east, tend to have higher ratios. Cation and silica ratios in surface waters indicate that silicate mineral weathering is the dominant control on alkalinity, silica and base cation concentrations in the basin.

Sulphate concentrations displayed little seasonal variation in samples collected at the Happy Isles gauge, despite widely fluctuating discharge, indicating that a within-basin process acts to regulate sulphate concentrations in surface water. Processes that could provide this regulation include sulphate adsorption associated with amorphous Al and Fe phases or anion exchange on soil organic matter.

The surprisingly large variations in water composition throughout the watershed suggest that collection of hydrological data at one site, such as the gauge at Happy Isles, is not adequate to characterize the surface water chemistry in the watershed. Identification of temporal trends is dependent on the spatial variation in

water chemistry. In the case of the upper Merced River basin, trends that are not detectable at the gauge might be evident in smaller, more homogeneous subcatchments. A few additional carefully selected sampling sites could provide a much more sensitive data set for the analysis of temporal trends.

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