Figure 4.7. (continued)

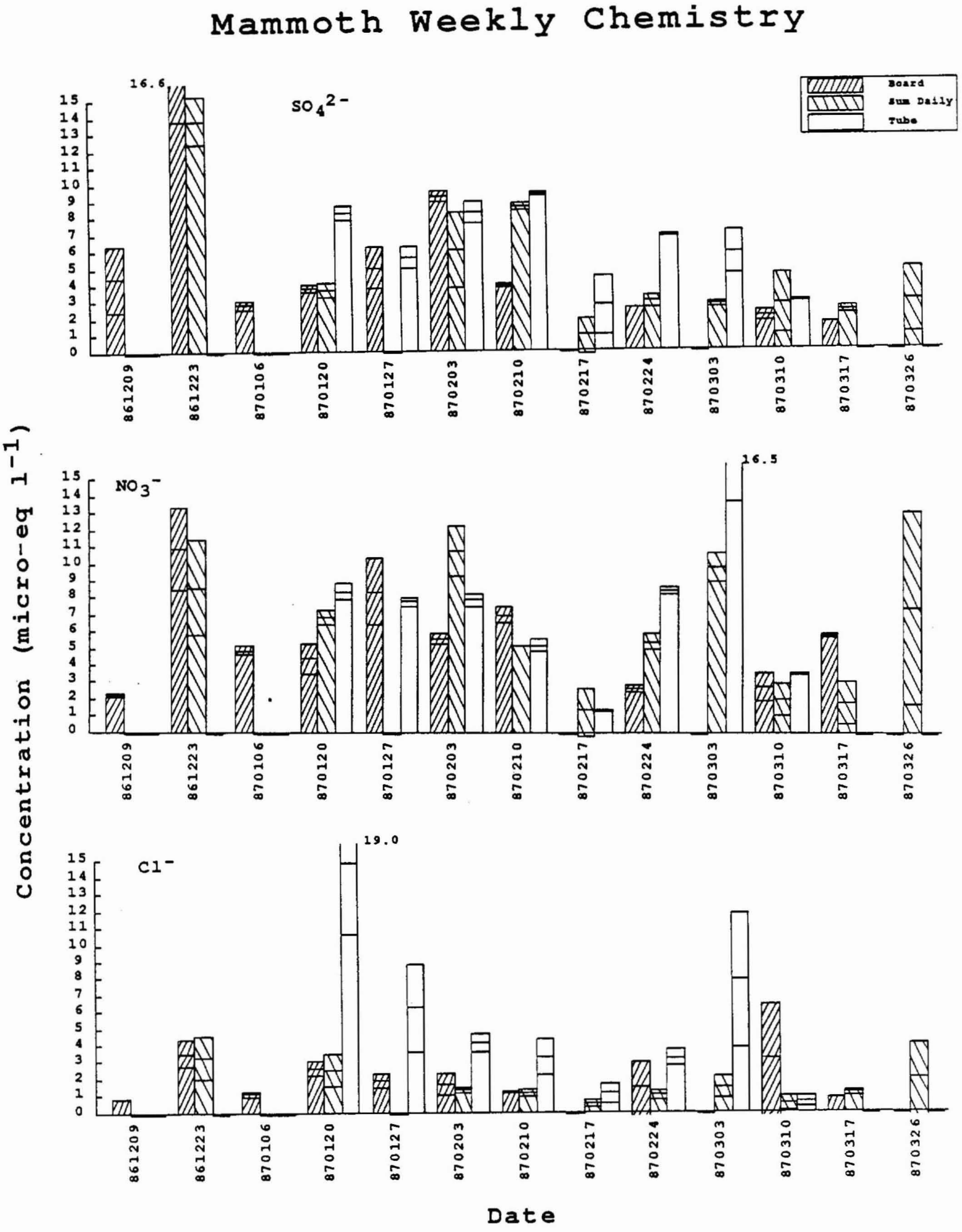


Figure 4.7. (continued)

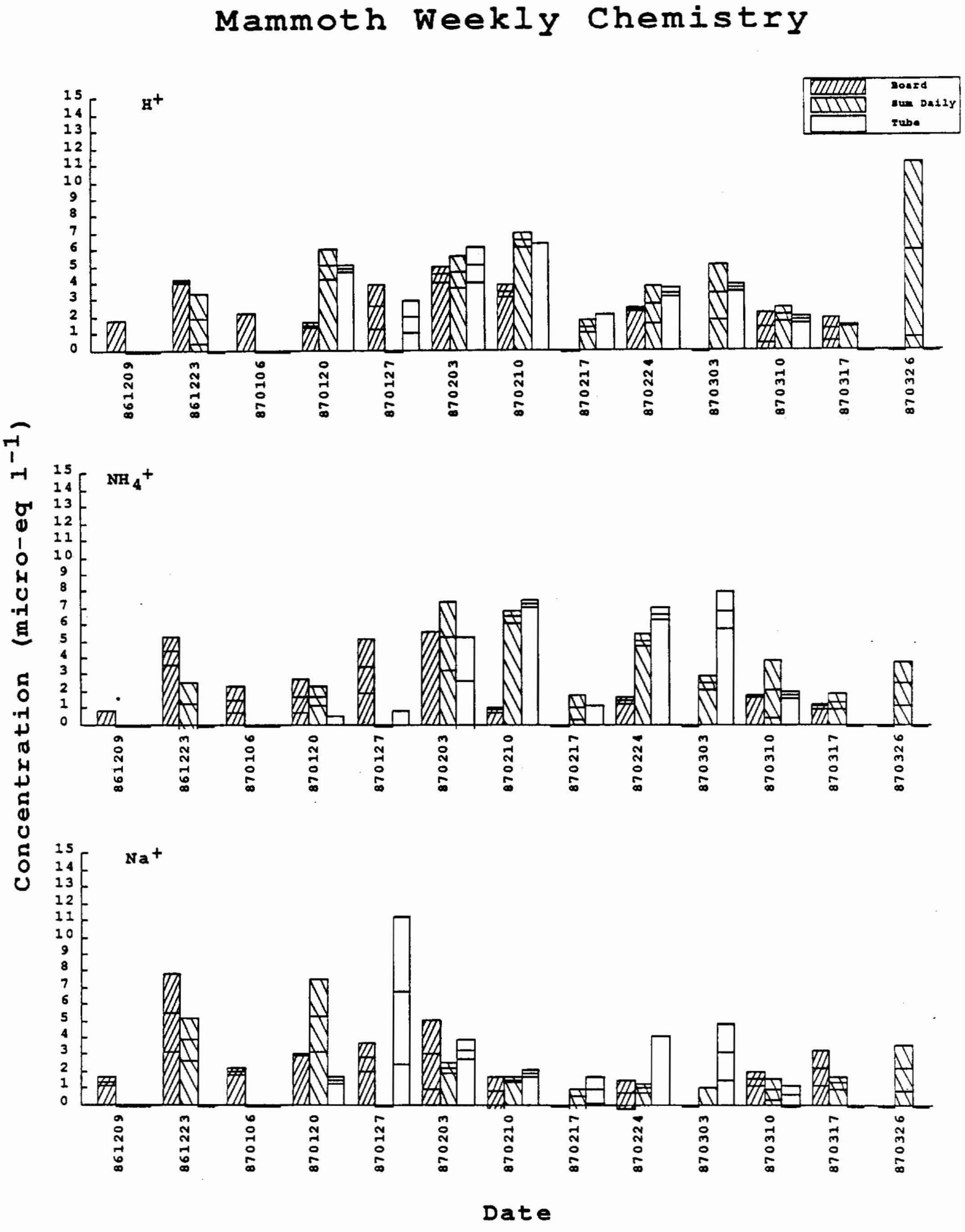
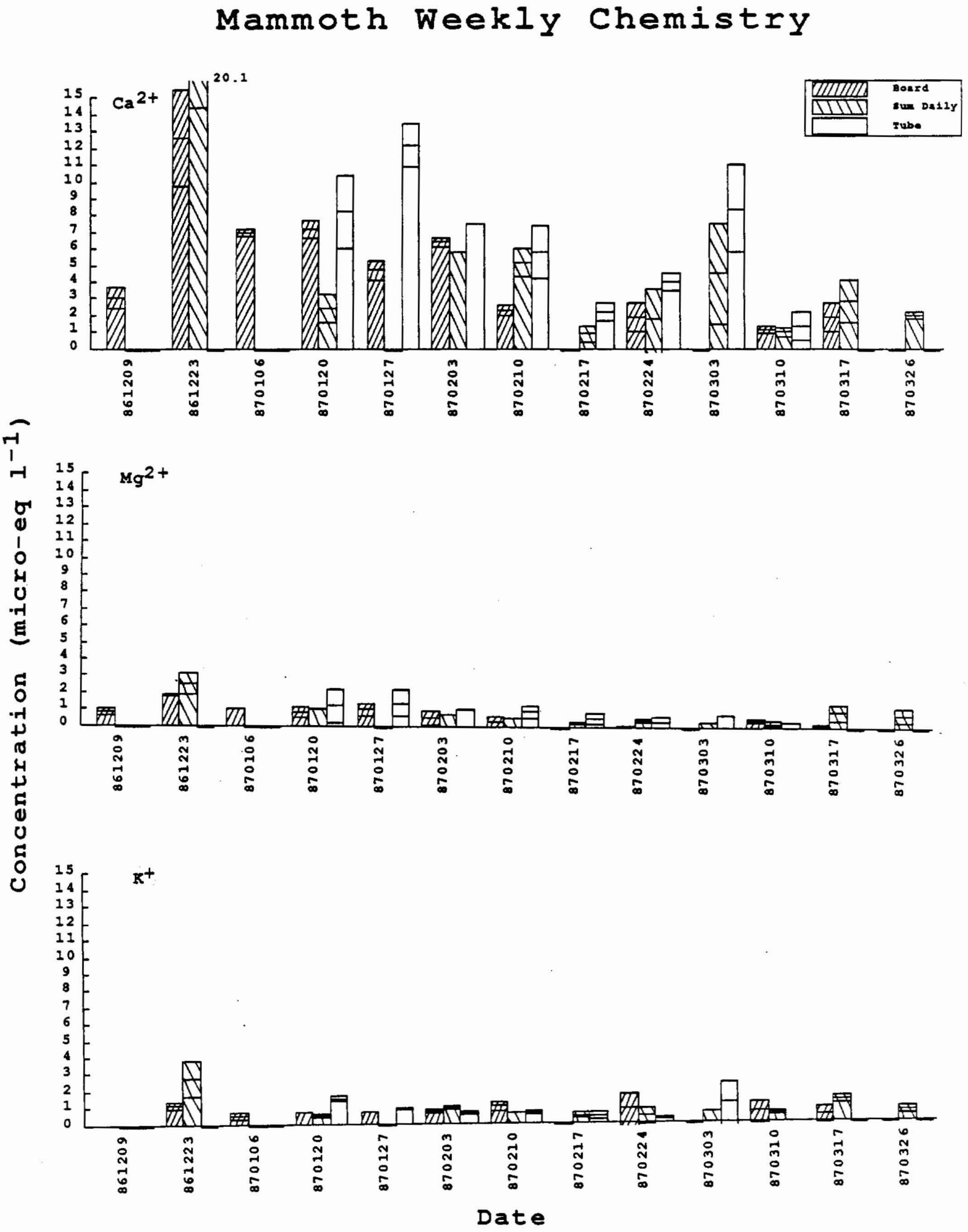


Figure 4.7. (continued)



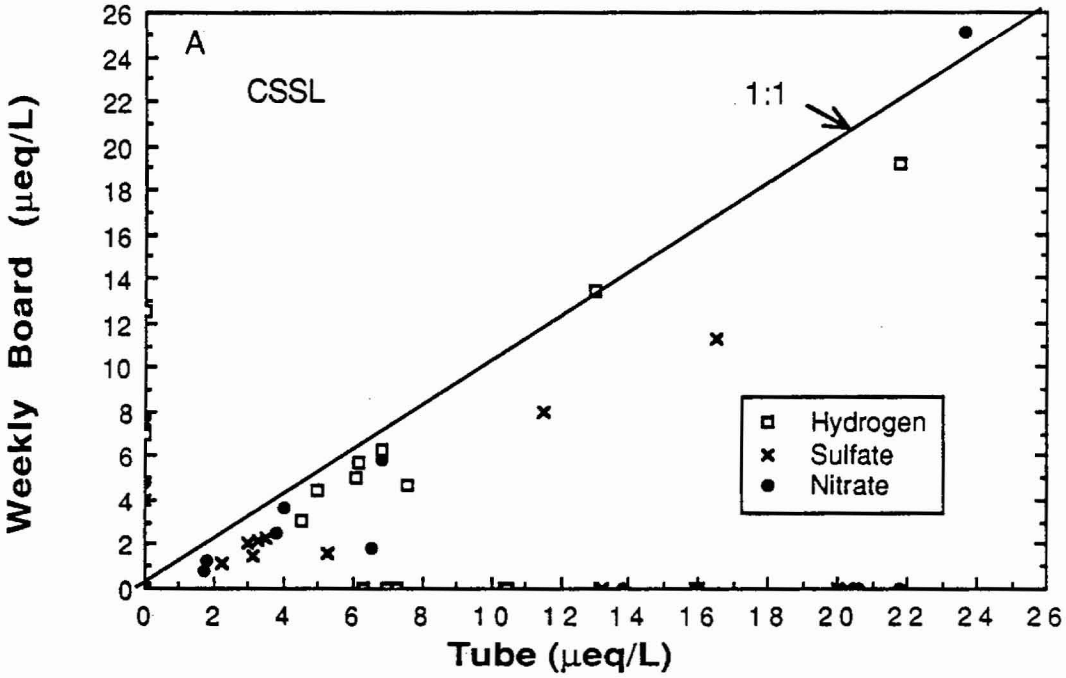
Both the concentrations of H^+, SO_4^{2-}, and NO_3^- and the snow volumes were generally greater from the tube samples at CSSL than from the weekly board samples (Figure 4.8A). The boards caught snow and the tube did not during two weeks, and the reverse occurred during six weeks. This situation is responsible for the points along the axes in Figure 4.8. The cumulative loading in the tubes during these six weeks was appreciable due to relatively high chemical concentrations. Therefore, the seasonal NO_3^- loading of 3.74 meq m^{-2} at CSSL estimated from the tube concentrations and SWEs greatly exceeded the NO_3^- loading of 2.04 meq m^{-2} estimated from the weekly board concentrations and SWEs (Table 4.8). Loadings from the tube samples for other ions were similarly elevated above samples from the weekly boards at CSSL (Table 4.8).

Samples from the tubes had generally higher concentrations than samples from the weekly boards at Mammoth (Figure 4.8B). However, because 25% less snow was caught in the tubes at Mammoth Mountain than on the boards (Table 4.4, Figure 4.8B), the tube's seasonal NO_3^- loading of 2.68 meq m^{-2} was less than the 2.98 meq m^{-2} NO_3^- estimated from the boards (Table 4.8). Although the tubes captured snow during 5 weeks when the boards did not, the volume was small and, unlike CSSL, the concentrations were similar to those found on the boards.

At CSSL, the NO_3^- loading estimate from the Aerochem Metrics sampler was 2.50 meq m^{-2}--23% more than the board's loading and 33% less than the tube's loading. Because the Aerochem also caught 28% less SWE than the tube, the volume-corrected loading would be close to the tube value. Because the sampler excludes dry deposition from the precipitation bucket, the larger loadings that result from the use of plastic collectors vs. boards are probably not related to dry deposition.

4.3.2. Field Quality Integrity--Concentrations of NH_4^+, Mg^{2+}, K^+, NO_3^-, and SO_4^{2-} in the deionized rinse water from the sampling devices (field blanks) were generally below detection limits (Table 4.11). In several cases at CSSL contamination is evident for most ions; in a few other cases, Cl^- contamination was detected. These data indicate that fastidious rinsing must be continuously maintained. Concentrations of the other constituents (Ca^{2+}, Na^+, Cl^-) were usually $\leq$ 2 ueq L^{-1} (Table 4.11). Field audit measurements for pH and specific conductance from each field site closely matched the results from the central laboratory (Table 4.12).

4.3.3. Laboratory Quality Assurance--Quality assurance data are presented in Tables 4.13 through 4.17. Plasticware cleaning at UCSB resulted in undetectable contamination in cylinders and bottles and negligible Cl^- in ziplock bags sent to the field sites (Table 4.13). No losses of cations or anions were evident from a mixture of synthetic standards in deionized water to PVC cylinders or plastic buckets employed in collecting or melting snow samples, respectively (Tables 4.14 and 4.15). Data in Table 4.16 indicate a significant difference in dissolved Cl^- and SO_4^{2-} in natural snow samples melted at 4°C versus 20°C. A test of ion leaching from different filter materials (glass fiber, polycarbonate membrane, HA membrane) indicated the polycarbonate filter to be the most appropriate for filtration of snowmelt water (Table 4.17). A more comprehensive evaluation of various filter materials and recommendations for future efforts are presented in Appendix C.



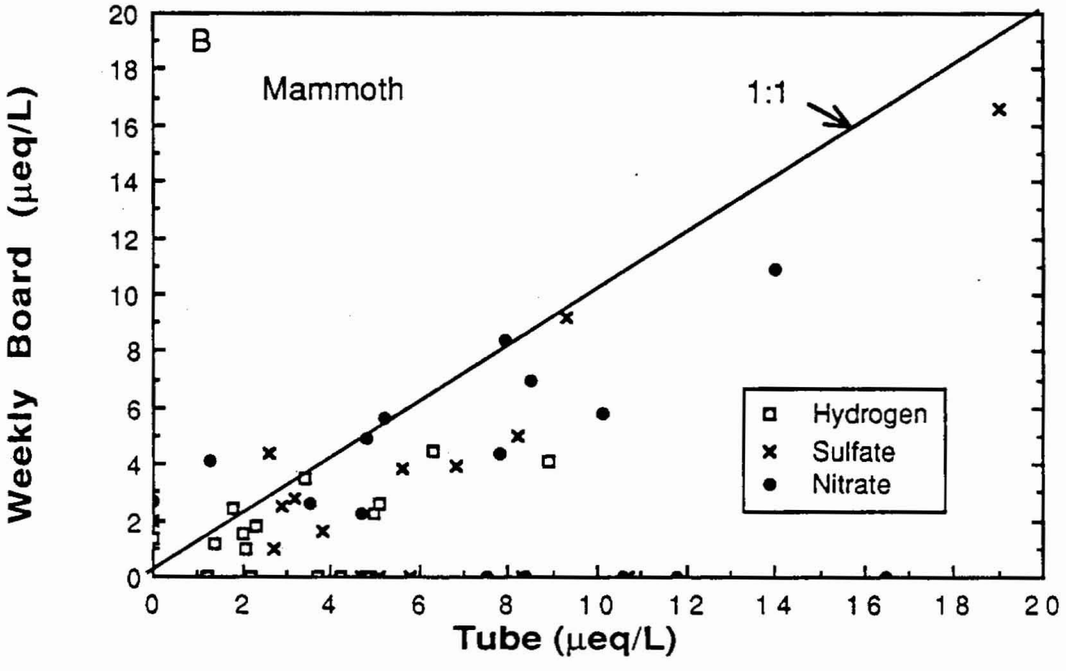


Figure 4.8. Hydrogen, nitrate, and sulfate volume-weighted concentrations at the Central Sierra Snow Laboratory (A) and Mammoth Mountain (B) as measured by PVC tubes and weekly snowboards during the winter of 1986-87.

Table 4.11. Chemistry data on the deionized rinse water from the acrylic sampler used in snowboard and snowpit sample collection (AS) and the cylinder collector (PVC) (see section 3.5.2.2). Field blank data are from the two field sites, CSSL (CFB) and Mammoth Mountain (MFB). Number suffixes designate different PVC cylinders and letter suffixes indicate replicate samples. The deionized water used to obtain the field blanks (CDIW) on some dates was also analyzed. Data are in ueq L^{-1} and u designates undetectable levels.

Collector	Date	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
CFBAS	870207	u	1.3	u	1.2	u	u	u	u
CFBAS	870217	u	2.5	u	1.2	u	u	u	u
CFBPVC	870219	u	1.3	u	u	u	u	u	u
CFBPVC	870219	u	3.9	0.5	1.6	4.7	u	u	u
CFBASa	870223	1.0	0.6	u	u	u	0.8	u	u
CFBASb	870223	u	1.3	u	3.7	0.6	0.8	u	u
CFBAS	870224	u	1.4	u	7.6	3.0	7.4	u	u
CFBPVC	870225	0.6	1.3	u	u	u	u	u	u
CFBPVC4	870303	u	u	u	0.8	u	u	u	u
CFBPVC1	870303	u	u	u	0.8	u	0.4	u	u
CFBASa	870310	u	3.9	0.4	2.0	0.9	0.8	u	u
CFBASb	870310	u	19.0	13.1	12.0	1.0	5.3	0	24.2
CDIW	870311	u	u	u	u	u	12.3	u	u
CFBPVC4	870311	u	0.7	u	u	u	10.3	u	u
CFBASa	870317	u	0.7	u	u	u	u	u	u
CFBASb	870317	u	2.5	0.5	2.8	1.2	27.0	u	0.3
CDIW	870319	u	1.3	u	0.8	u	u	u	u
CFBASa	870319	0.6	1.9	u	1.4	u	u	u	u
CFBASb	870319	u	3.7	1.7	4.2	2.5	u	u	u
CFBPVC1	870319	u	u	u	u	u	33.1	u	u
CFBAS	870324	0.8	0.9	0.8	13.0	11.9	10.2	0	0
CDIW	870326	u	0.7	u	u	u	u	u	u
CFBPVC3	870326	u	2.5	u	2.1	0.6	2.1	0.7	u
CFBPVC	870326	u	0.7	u	u	u	u	0.5	u
CDIW	870403	u	1.3	u	0.8	u	u	u	u
CFBAS	870403	u	1.3	u	2.0	0.6	2.1	u	u
CDIW	870409	u	1.3	u	1.2	u	u	u	u
CFBPVC3a	870409	u	3.9	0.7	1.8	1.5	1.2	u	u
CFBPVC3b	870409	u	u	u	0.8	u	u	u	u
CFBPVC4	870409	u	1.3	u	2.4	u	8.4	u	u
CFBAS	870411	u	2.5	0.6	1.8	0.8	u	u	u
CFBPVC2	870414	2.5	5.6	1.2	5.2	3.0	2.2	3.1	3.8
CFBPVC1	870414	u	8.7	1.4	5.1	2.5	7.6	4.4	9.2
CDIW	870505	u	0.7	u	u	u	u	u	u
CFBDVC3	870505	u	5.4	u	4.4	1.5	u	u	u
MFBPVC2	870215	u	2.5	1.0	1.2	u	u	u	u
MFBPVC4	870215	u	u	u	0.9	u	u	u	u
MFBPVC2	870224	u	u	u	1.0	u	u	u	u
MFBPVC1	870224	u	u	u	0.8	u	u	u	u
MFBAS	870224	u	2.5	u	1.0	u	u	u	u
MFBPVC3	870303	u	u	u	u	u	u	u	u
MFBPVC4	870303	u	u	u	u	u	u	u	u
MFBPVC2	870310	u	1.9	u	0.9	u	0.4	u	u
MFBPVC1	870310	u	u	u	2.0	u	4.0	u	u

Table 4.11. (continued)

Collector	Date	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
MFBAS	870310	u	u	u	u	u	u	u	u
MFBAS	870326	u	1.3	u	0.7	u	u	0.4	u
MFBAS	870330	u	1.3	u	1.0	0.8	0.6	0.8	2.1
MFBDVC1	870331	u	0.7	u	u	0.6	u	u	u
MFBPVC4	870408	u	1.3	u	1.2	u	u	u	u
MFBPVC	870414	0.6	1.3	u	1.2	u	1.3	u	u

Table 4.12. Chemistry data on field audits for pH (FA-pH) and specific conductance (FAC) at CSSL and Mammoth Mountain. The pH audit was prepared by diluting an Orion low ionic strength buffer with deionized water to a specific conductance of 67 uS cm^{-1}, 25°C; the diluted buffer measured 4.74 pH units at UCSB in April and May 1987. A 10^{-4} N KCl solution (theoretical specific conductance = 14.9 uS cm^{-1}, 25°C), a high conductance audit (FAC-high), and a low conductance audit (FAC-low) prepared and measured at UCSB on 2 February 1987 gave 17.6, 34.6, and 10.2 uS cm^{-1}, 25°C, respectively. UCSB corrected values for FAC-high and FAC-low are 29.3 and 8.6 uS cm^{-1}, 25°C, respectively.

	pH		Specific Conductance	
	FA-pH	10^{-4}N KCl	FAC-high	FAC-low
(Audit or theoretical values	4.74	14.9	29.3	8.6)
Site/Date				
CSSL				
18 Feb 87	4.70	15.2	28.7	8.0
25 Feb 87	4.66	14.8	28.7	8.1
03 Mar 87	4.71	16.4	30.7	9.3
09 Mar 87	4.69	14.6	28.0	7.9
19 Mar 87	4.66	14.7	28.2	8.0
25 Mar 87	4.67	14.9	28.4	8.0
04 Apr 87	4.69	14.6	28.4	7.6
08 Apr 87	4.73	-	28.2	8.2
21 Apr 87	4.74	-	28.4	8.2
05 May 87	4.72	-	28.7	8.3
Mammoth				
18 Feb 87	4.74	15.3	29.9	8.4
19 Feb 87	4.74	15.3	29.9	8.4
25 Feb 87	4.78	15.3	29.5	8.4
04 Mar 87	4.82	15.2	29.6	8.4
12 Mar 87	5.27	15.1	29.4	8.3
27 Mar 87	4.77	14.9	29.4	8.2
01 Apr 87	4.76	14.9	29.3	8.4
10 Apr 87	4.69	15.4	29.6	8.5
16 Apr 87	4.77	15.2	29.4	8.4

Table 4.13. Chemical contamination in PVC cylinders, polyethylene ziplock bags and 250-ml polyethylene bottles. In 1987, new cylinders, bags or bottles were first soaked in 10% HCl overnight. This was followed by 5 rinses with deionized water (DIW) of conductance less than 1 uS cm^{-1}, 25°C. The containers were then soaked overnight in DIW and then rinsed again 5 times with DIW. In 1988, the 10% HCl step was eliminated from the sequence. After the cleaning procedure, a volume of DIW was added, swirled and collected for analysis of dissolved ions. Chemical contamination checks on bags and bottles were performed at 5% frequency. Data are in ueq L^{-1} and u designates undetectable levels.

Date	Container	Vol DIW added (ml)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
Jan 87	ziplock	100	u	u	u	u	u	u	u
	ziplock	100	u	u	u	u	u	u	u
	ziplock	100	u	u	u	u	1.7	u	u
Jan 87	bottle	250	u	u	u	u	u	u	u
	bottle	250	u	u	u	u	u	u	u
	bottle	250	u	u	u	u	u	u	u
Feb 87	ziplock	100	u	u	u	u	0.9	u	0.7
	ziplock	100	u	u	u	u	0.9	u	u
	ziplock	100	u	u	u	u	0.9	u	u
Feb 87	bottle	250	u	u	u	u	u	u	u
	bottle	250	u	u	u	u	u	u	u
	bottle	250	u	u	u	u	u	u	u
Jan 87	Cylinder-1	2000	1.4	u	u	u	0.8	u	u
	Cylinder-2	2000	1.4	u	u	u	1.7	u	u
Feb 88	ziplock	100	u	u	u	u	0.6	u	u
	ziplock	100	u	u	u	u	u	u	u
	ziplock	100	u	u	u	u	0.8	u	u
	ziplock	100	u	u	u	u	0.5	u	u
	ziplock	100	u	u	u	u	u	u	u
	ziplock	100	u	u	u	u	u	u	u

Table 4.14. Ion desorption from and ion adsorption onto PVC cylinders (volume = 92 liters) used to collect snow for chemical analysis. Cylinders were washed with Liquinox, then with 10% HCl, and then allowed to soak in deionized water for four days. Just prior to the experiment, each cylinder was rinsed three times with 5 liters of Milli-Q water. Then 50 liters of Milli-Q water was added to each of two cylinders; samples were removed initially and after 1, 3, 4 and 6 days. After 6 days a known volume of synthetic standard was added to each cylinder yielding a final concentration of ca. 7 ueq L^{-1} in each ion except for Na which was ca. 1 ueq L^{-1}. Samples were removed initially after the known addition and 1, 2, 4 and 6 days thereafter. The data (ueq L^{-1}) are tabulated for cylinder 1 and for cylinder 2; the letter u designates undetectable levels. The methods detection limits for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, and SO_4^{2-} are 1.0, 0.3, 0.5, 0.5, 0.4, 0.2 and 0.4 ueq L^{-1} respectively. Desorption was assessed for cylinder 1 only.

Experiment	Sample	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
CYLINDER 1								
Desorption	initial	u	u	u	u	u	u	u
	1d	u	u	u	u	u	u	u
	2d	u	u	u	u	u	u	u
	4d	u	u	u	u	u	u	u
	6d	u	u	u	u	u	u	u
Adsorption	initial	5.7	6.8	0.7	5.1	5.2	6.5	6.9
	1d	6.2	6.8	0.7	5.3	5.6	6.6	7.0
	2d	6.2	6.8	0.4	5.3	5.4	7.2	7.1
	4d	6.2	6.8	1.8	5.1	5.6	6.7	6.8
	6d	6.2	6.6	0.7	5.1	5.4	7.0	7.0
CYLINDER 2								
Adsorption	initial	6.5	7.6	1.1	5.5	6.8	7.8	7.8
	1d	6.7	7.6	1.1	5.7	6.8	7.6	7.8
	2d	7.8	7.6	1.0	5.8	7.8	7.6	7.9
	4d	7.3	7.6	1.0	6.1	7.8	7.6	7.9
	6d	7.0	7.9	1.0	6.1	6.8	7.7	8.0

Table 4.15. Ion adsorption onto bucket walls used to contain snow during melt phase in the laboratory prior to analysis of cations and anions. One liter volumes of synthetic standards in deionized water at three levels (2, 5, and 10 ueq L^{-1}, final concentrations) were added to each of two 6-liter polypropylene buckets. Samples were removed initially and after 24-hour contact at room temperature. Each datum (ueq L^{-1}) is a mean of two replicates. Dash indicates contaminated sample.

Standard	Removal Time	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
2	initial	2.5	1.7	3.4	1.5	2.1	2.2	-
2	24 h	3.5	1.8	2.8	1.6	2.0	2.2	-
5	initial	5.3	4.8	4.7	3.5	4.7	5.1	6.0
5	24 h	5.7	5.0	4.8	3.5	4.4	5.1	5.1
10	initial	9.3	9.6	10	8.0	10	9.5	9.6
10	24 h	9.3	9.7	9.8	8.1	9.5	9.5	9.7

Table 4.16. Effect of ambient conditions during phase change on concentration of dissolved ions in snow melt. A single pool of snow from Wolverton, Sequoia National Park was distributed into 6-liter polypropylene buckets. Seven buckets were maintained at 4°C and seven were kept at room temperature until the snow samples melted. After thorough mixing, subsamples of meltwater from each bucket were filtered through prerinsed Nuclepore polycarbonate filters (47 mm, 0.4 micron) and analyzed for pH, specific conductance (uS cm^{-1}, 25°C), and dissolved ion concentrations (ueq L^{-1}). Standard deviations (SD) of the means (Mn) and the t-tests of significance between the means of the 20°C and the 4°C treatments are tabulated. Nonsignificance (ns) and significance (*) are indicated at the 95% confidence level; u designates undetectable levels.

Melt Condition	Bucket	pH	Specific Cond.	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
20°C	-1	5.32	2.6	2.6	2.5	1.3	0.7	0.7	0.4	1.3	0.4
	-2	5.39	2.7	3.1	2.5	1.3	0.9	0.8	0.6	1.7	0.5
	-3	5.37	2.6	2.1	2.5	1.2	0.7	0.6	0.5	1.1	0.5
	-4	5.37	2.7	2.0	2.5	1.2	0.7	0.7	0.9	0.5	0.3
	-5	5.47	2.9	2.0	3.9	1.4	0.6	0.7	0.8	1.6	0.4
	-6	5.32	2.8	2.3	2.5	1.5	0.8	1.0	1.2	1.6	0.9
	-7	5.41	2.8	2.2	2.5	1.2	0.8	0.7	1.6	1.3	u
	Mn	5.38	2.7	2.3	2.7	1.3	0.7	0.7	0.9	1.2	0.5
	SD	.05	0.1	0.4	0.5.	0.1	0.1	0.1	0.4	0.5	0.2
4°C	-8	5.38	2.7	2.4	2.5	1.2	0.7	0.6	2.2	1.5	1.0
	-9	5.55	2.6	2.7	2.5	1.0	0.7	0.5	1.3	1.4	0.8
	-10	5.52	2.8	2.2	1.8	1.2	0.9	0.7	1.8	1.5	0.8
	-11	5.48	2.7	2.6	3.2	1.3	1.2	0.7	1.5	1.7	1.5
	-12	5.50	3.0	2.8	2.5	1.3	1.1	0.9	2.2	1.4	1.5
	-13	5.57	3.0	2.3	2.5	1.3	0.9	0.9	1.8	1.6	0.9
	-14	5.52	2.8	3.1	2.5	1.3	1.1	0.8	1.7	2.0	1.0
	Mn	5.50	2.8	2.6	2.5	1.2	0.9	0.7	1.8	1.6	1.1
	SD	.06	0.2	0.3	0.4	0.1	0.2	0.1	0.3	0.2	0.3
t-test		ns	ns	ns	ns	ns	ns	ns	*	ns	*

Table 4.17. Ion leaching from three types of filters employed in analysis of water for dissolved chemical constituents. The filters tested were: Gelman A/E glass fiber, Nuclepore polycarbonate membrane (0.40 micron), and Millipore HA membrane. 100 ml of Milli-Q water was passed through both washed (50 ml of deionized water passed and discarded) and unwashed filters. Data (ueq L^{-1}) for each replicate are tabulated. Undetactable levels are designated by u.

Sample	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
Gelman unwashed	4.7	u	16	u	1.0	u	u
	4.5	u	17	u	1.1	u	u
	12.0	u	46	u	1.2	u	u
	0.4	u	20	u	1.0	u	u
Gelman washed	1.4	u	2.0	u	u	u	u
	2.0	u	1.2	u	u	u	u
	2.5	u	1.2	u	u	u	u
	2.0	u	1.3	u	u	u	u
Nuclepore unwashed	u	u	u	u	u	u	u
	2.8	u	u	u	u	u	u
	u	u	u	u	u	u	u
	u	u	u	u	u	u	u
Nuclepore washed	u	u	u	u	u	u	u
	1.4	u	u	u	u	u	u
	u	u	u	u	u	u	u
	u	u	u	u	u	u	u
Millipore unwashed	0.5	u	u	u	1.1	u	u
	0.4	u	u	u	1.1	u	u
	0.4	u	u	u	u	u	u
	0.4	u	u	u	1.2	u	u
Millipore washed	u	u	u	u	u	u	u
	u	u	u	u	u	u	u
	u	u	u	u	u	u	u
	u	u	u	u	u	u	u

Analytical performance at UCSB is documented in Tables 4.18 through 4.27. Detection limits for the analytical methods are given in Table 4.18. Table 4.19 shows upper and lower control limits (±3 standard deviations of the mean recovery) based on known additions of anions and the precision achieved with the Dionex 2010i ion chromatograph used to analyze chloride, nitrate, and sulfate. Accuracy of anion analysis evaluated with a USGS interlaboratory control is documented in Table 4.20. Results of the charge balance control check and of the three-month chemical stability test for cations and inorganic and organic anions are presented in Tables 4.21 and 4.22, respectively. Within-run precisions and analytical accuracy for analysis of cations are documented in Tables 4.23 and 4.24, respectively. For anions, inter-run precisions are documented at two levels (Tables 4.25 and 4.26) and accuracy evaluation is given in Table 4.27.

4.3.4. <u>Charge Balances</u>--Sums and differences of cations and anions are their ratios are given in Table 4.7A,B. Median charge balance differences $(\Sigma+)-(\Sigma-)$ in ueq L^{-1} and ratios (in parenthesis $\Sigma+/\Sigma-$) for the main sample types are as follows:

CSSL	Daily Board	3.3, (1.3); with organic acids 1.8, (1.2)
	Weekly Boards	4.5, (1.5)
	PVC Tube	4.6, (1.3)
Mammoth Mtn	Daily Boards	1.2, (1.5)
	Weekly Boards	1.0, (1.1)
	PVC Tube	0.4, (1.0)

Overall, these data show an excess of cations. Inclusion of the organic anions improves the charge balance, but the imbalance is still larger at CSSL than at Mammoth where only about 1 ueq L^{-1} on average is in excess (Table 4.7A,B).

Table 4.18. Standard deviation (SD) and method detection limit[1] (MDL = 2 SD) of chemical methods. Replicate determinations (n) of deionized water (DIW) or analyst-prepared standards[1] (the levels tabulated are the theoretical concentrations) were measured on separate days except where indicated (*) when a single trial on one day was used.

Constituent	n	Standard	SD	MDL
Ammonium, uM	10	DIW	0.15	0.30
Phosphate, uM	10	DIW	0.03	0.06
Silica, uM	7	DIW	0.20	0.40
Nitrate, ueq L^{-1}	7*	0.50	0.10	0.20
Chloride, ueq L^{-1}	7*	0.50	0.19	0.38
Sulfate, ueq L^{-1}	7*	0.75	0.22	0.44
Calcium, ueq L^{-1}	4	2.50	0.50	1.00
Magnesium, ueq L^{-1}	4	2.06	0.16	0.32
Sodium, ueq L^{-1}	6	1.09	0.25	0.50
Potassium, ueq L^{-1}	6	0.64	0.22	0.45

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[1] Limits of detection for major ions were established in accord with the Scientific Apparatus Makers Association definition for detection limit: that concentration which yields an absorbance equal to twice the standard deviation of a series of measurements of a solution whose concentration is detectable above, but close to the blank absorbance. Determination of method detection limits for ions by ion chromatography (Dionex 2010i ion chromatograph, 200-uL sample loop, 3-uS attenuation) or atomic absorption spectrophotometry (direct, air-acetylene) necessitated the use of a low-level standard as DIW gave no signal under our routine operating conditions.

Table 4.19. Single operator accuracy (mean percent recovery, R), precision (standard deviation, SD), upper control limit (UCL = R+3SD) and lower control limit (LCL = R-3SD) for the determination of anions on 23 December 1986 with a Dionex 2010i ion chromatograph employing a hollow-fiber suppressor, a 200-uL sample loop, water dip elimination by matrix matching sample to eluent, and an attenuation of 1-uS full scale. Known additions of 2.0 ueq L^{-1} each in Cl^-, NO_3^-, and SO_4^{2-} were made to eight separate aliquots of USGS-P10 reference material and assayed along with eight unspiked replicates of USGS-P10 reference material.

Constitutent	Measured Concentrations (mean ± SD, ueq L^{-1}) initial	final	R	SD of R	UCL	LCL
Chloride	2.4±0.2	4.8±0.3	109	8.6	135	83
Nitrate	3.5±0.1	5.5±0.1	100	2.5	108	92
Sulfate	9.2±0.2	10.8±0.2	96	2.2	103	89

Table 4.20. Accuracy evaluation of anions determination by analysis of an interlaboratory control and also by recovery of known additions to this control on 23 December 1986. Aliquots (5.0 ml) of USGS-P10 precipitation (snow melt) reference sample were dispensed into deionized water-rinsed vials and distributed throughout a single 66-position run for automated analysis on a Dionex 2010i ion chromatograph. The water dip was eliminated by matrix matching samples of HCO_3-CO_3 eluent and the injection volume was 200 uL. A recovery spike volume of 20 uL yielded a final concentration of 2.0 ueq L^{-1} greater than the original concentration. Peak areas (at attenuation = 1 uS) were integrated and converted to ueq L^{-1} on line by best fit, non-linear regression to calibration standards of 1.0, 2.0, 4.0, and 8.0 ueq L^{-1}. The USGS values for Cl^-, NO_3^- and SO_4^{2-} are 3.4 ± 2.5, 2.7 ± 2.4, and 9.4 ± 2.7 ueq L^{-1}, respectively. Those values were calculated from data submitted to USGS for anions determined by the ion chromatograph technique; this represents only 4-6 individual laboratories and is reflected in the large SD of the USGS reported value. Means and standard deviations of measured values are in ueq L^{-1}. Each sample was replicated eight times.

Sample	Cl^-	NO_3^-	SO_4^{2-}
USGS-P10	2.4±0.2	3.5±0.1	9.2±0.2
USGS-P10 (known addition)	4.8±0.3	5.5±0.1	10.8±0.2
Recovery, %	109	100	96

Table 4.21. Ion-balance evaluation for synthetic change-balance controls (CBC) diluted from stock standard solutions to obtain 3 ueq L^{-1} each in calcium chloride, sodium nitrate, and magnesium sulfate in Milli-Q water of specific conductance <1 uS cm^{-1}, 25^{o}C. Unfiltered CBC's were analyzed throughout the study period at UCSB in 1987, and values (ueq L^{-1}) were calculated from calibration standards diluted from stock standard solutions of different origin than those used for CBC's. The pH and specific conductance of the CBC solution were typically 5.6 pH units, and 3 uS cm^{-1}, 25^{o}C, respectively.

CBC Prec. Date	Assay date	Ca^{2+}	Mg^{2+}	Na^{+}	pos	Cl^{-}	NO_3^{-}	SO_4^{2-}	neg	pos/ neg
22 May 87	4 Jun	2.5	2.7	2.4	7.6	3.1	3.0	3.2	9.3	0.8
22 May 87	23-25 Jun	1.9	3.1	2.5	7.5	3.6	3.1	3.0	9.7	0.8
2 Jun 87	23-25 Jun	2.2	3.0	2.6	7.8	2.2	2.8	2.8	7.8	1.0
20 Jul 87	1-5 Oct	2.3	3.5	2.1	7.9	2.1	3.1	3.1	8.3	1.0
29 Jul 87	1-5 Oct	2.5	3.6	2.2	8.3	2.1	3.0	2.8	7.9	1.1
22 Sep 87	1-5 Oct	2.3	3.4	2.1	7.8	2.1	2.9	2.9	7.9	1.0

Table 4.22. Evaluation of filtration and storage at 4^{o}C for three months as a means of preservation of solutes in snowmelt and in Milli-Q water (specific conductance ≤ 1 uS cm^{-1}, 25^{o}C). Four replicates each of two filtered snowmelt samples and of one Milli-Q water sample had known additions of 5 ueq L^{-1} of each ion, except for SO_4^{2-} which was a 10 ueq L^{-1} addition. The replicates were maintained at 4^{o}C for three months before analysis of final concentrations (ueq L^{-1}). Unspiked concentrations (ueq L^{-1}) for NH_4^{+}, and cations and anions were measured within 24 hours and three weeks, respectively. Acetate ($CH_3CH_2O^{-}$) and formate (HCO_2^{-}) were measured in chloroform preserved samples after three months at 4^{o}C. Initial and final (end) hydrogen ion concentrations in ueq L^{-1} are calculated from measured pH. Mean recovery (R) and percent relative standard deviation (RSD) are tabulated for each ion. Dash indicates no data.

Sample		H^{+}	NH_4^{+}	Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	$CH_3CH_2O^{-}$	HCO_2^{-}
Milli-Q water	End Conc.	4.0	4.9	4.9	4.6	5.0	4.1	5.0	10.5	5.8	5.0
Roch Ramp	Unspiked Conc.	3.2	1.0	0.6	0.4	0.5	1.2	1.8	0.7	1.2	1.1
	End Conc.	6.3	6.0	5.1	5.0	5.6	4.7	6.8	11.3	6.2	6.2
	R	-	100	91	93	102	76	97	106	100	101
	RSD	-	7.2	17.2	0.5	1.4	3.5	1.0	1.4	3.5	5.4
Log Meadow	Unspiked Conc.	4.0	3.1	2.2	3.2	0.7	1.5	0	1.7	2.9	0.9
	End Conc.	4.0	1.9	-	8.3	6.1	5.0	6.6	12.2	3.6	2.0
	R	-	23	-	101	108	79	132	105	46	34
	RSD	-	31	-	2.5	0.5	8.7	1.0	0.6	10	5

Table 4.23. Within-run precision for analyses of cations by atomic absorption spectrophotometry. Precision was assessed as percent relative standard deviation (RSD) of the means of duplicated samples to which known additions of cations were made. Each replicate was separated by 10-15 samples in each run. Measured mean concentrations (conc.) are in ueq L^{-1}. Dash indicates no data.

Run/Sample[1]	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}	
	Conc.	RSD	Conc.	RSD	Conc.	RSD	Conc.	RSD
13 February 1987								
MTW003	6.3	10.0	5.1	0	5.0	1.4	1.9	7.4
CBW008	4.4	8.1	5.1	1.5	5.0	0	1.6	4.6
MBW003	16.9	0	6.0	7.0	-	-	2.6	19.0
4 December 1987								
Deionized Water	2.5	0	4.1	0	2.0	3.6	1.0	0
CT011	7.1	6.0	4.8	3.0	6.7	1.1	1.4	5.2
MBW019	4.4	0	4.3	3.3	3.3	4.3	1.1	0
MPW034	3.7	0	4.4	0	3.3	6.5	1.4	5.2
MTW023	6.8	0	4.9	3.0	4.4	0	1.4	0
CBD041	6.2	0	6.0	3.6	14.9	0.5	3.1	0
CP031	3.4	12.5	4.7	0	6.0	2.4	-	-

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[1] Sample codes refer to location of collection (M=Mammoth Mountain; C=CSSL), collection methods (T=PVC tube; B=snowboard; P=snowpit), and frequency of collection (W=weekly; D=daily).

Table 4.24. Accuracy of analyses of cations by atomic absorption spectrophotometry. Accuracy was assessed by (1) comparing measured values with certified values for NBS 2964-I, USGS-P10, and EPA simulated rainwater certified controls (reported in ueq L^{-1}), and (2) by recovery after known additions to a) laboratory duplicates (KALD) of randomly selected samples and to b) deionized water (KALD-DIW). Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration (ueq L^{-1}).

Run/Sample		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
13 February 1987					
USGS-P10	Meas:	5.1	0.8	1.1	0.3
	Cert:	6.0±2.0	1.7±0.6	2.1±1.1	1.3±1.3
KALD-MTW003	R	95	102	115	119
	(final conc)	(6.3)	(5.1)	(5.0)	(1.9)
KALD-CBW008	R	97	105	135	104
	(final conc)	(4.4)	(5.1)	(5.0)	(1.6)
KALD-MBW003	R	101	102	104	99
	(final conc)	(16.9)	(6.1)	(5.9)	(2.4)
4 December 1987					
NBS 2694-I	Meas:	3.0	2.0	8.8	1.3
	Cert:	0.7±0.2	2.0±0.2	8.9±0.4	1.3±0.2
EPA-2	Meas:	9.3	7.1	14.2	1.6
	Cert:	13.2±1.0	7.4±0.8	17.8±1.1	2.7±0.3
KALD-DIW	R	100	100	91	77
	(final conc)	(2.5)	(4.1)	(2.0)	(1.0)
KALD-CT011	R	108	103	75	77
	(final conc)	(7.1)	(4.8)	(6.7)	(1.4)
KALD-MBW019	R	124	98	64	85
	(final conc)	(4.4)	(4.3)	(3.3)	(1.1)
KALD-MPW034	R	96	105	80	77
	(final conc)	(3.7)	(4.4)	(3.3)	(1.4)
KALD-MTW023	R	72	98	77	77
	(final conc)	(6.8)	(4.9)	(4.4)	(1.4)
KALD-CBD041	R	72	97	127	92
	(final conc)	(6.2)	(5.9)	(14.9)	(3.1)
KALD-CP031	R	84	95	109	92
	(final conc)	(3.4)	(4.7)	(6.0)	(1.2)

Table 4.25. Within-run precision at actual sample concentrations for analyses of anions by ion chromatography (Dionex 2010i, 200-uL sample loop, attenuation = 3). Precision was assessed as percent relative standard deviation (RSD) of the means of laboratory duplicates of randomly selected samples and of a duplicated 2 ueq L^{-1} synthetic standard. Each replicate was separated by ca. 10 samples in each run. Mean, measured concentrations (conc.) are in ueq L^{-1}.

Run/Sample	Cl^-		NO_3^-		SO_4^{2-}	
	Conc.	RSD	Conc.	RSD	Conc.	RSD
29 October 87						
CBD 026	2.3	17.6	6.2	0.2	3.3	0.3
2 ueq L^{-1}	1.8	12.0	2.0	0.5	2.2	0.2
4 November 87						
MTW 010	4.5	0.8	8.1	0.5	7.8	0.5
2 ueq L^{-1}	2.0	7.8	2.0	0.5	2.0	1.5
20 November 87						
MPW 034	1.0	1.9	3.9	0.9	2.1	0.5
CBD 029	2.8	3.7	1.3	0.8	1.4	1.0
CT 016	36.2	1.4	32.0	0.2	47.0	0.3
2 ueq L^{-1}	2.1	11.1	2.0	1.0	2.2	0.9
23 November 87						
CBD 041	13.6	1.8	33.7	0.9	17.1	0.3
2 ueq L^{-1}	1.8	1.4	1.9	2.3	1.9	1.0
15 December 87						
MPW 019	0.6	9.1	1.9	0.3	1.8	3.8
MPW 021	0.2	10.5	5.0	0.3	3.1	0.8
MBW 013	0.4	14.4	1.7	1.5	1.1	3.5
2 ueq L^{-1}	1.7	5.4	2.1	0.5	2.1	1.9
16 December 87						
MBD 014	0.7	12.8	5.9	0.1	3.4	2.2
MBD 018	0.0	0.0	0.3	1.6	0.2	4.6
MBD 033	6.6	6.3	21.4	0.2	7.2	1.3
2 ueq L^{-1}	2.1	15.4	2.0	1.0	2.0	1.3
17 December 87						
MBW 018	1.8	19.0	2.5	1.8	2.3	8.2
MPW 035	2.3	2.4	4.8	0.2	2.7	0.4
2 ueq L^{-1}	1.9	6.8	2.0	0.5	1.9	3.1
22 December 87						
CBW 027	3.9	0.1	3.5	1.7	2.8	0.2
2 ueq L^{-1}	1.6	0.3	2.0	3.0	2.0	1.3

Table 4.26. Within-run precision at an augmented level for anions analyzed by ion chromatography (Dionex 2010; 200-uL simple loop, attenuation = 3). Precision was assessed as percent relative standard deviation (RSD) of the means of actual samples and of a synthetic 2 ueq L^{-1} standard to which a known addition of 3 ueq L^{-1} in Cl^{-}, NO$_3^{-}$, and SO$_4^{2-}$ was made. Each known addition was made in duplicate and the individual replicates were separated by ca. 10 samples in each run. Mean, measured concentrations (conc.) are in ueq L^{-1}.

Run/Sample	Cl^{-}		NO$_3^{-}$		SO$_4^{2-}$	
	Conc.	RSD	Conc.	RSD	Conc.	RSD
29 October 87						
KALD-CBO 026	5.3	2.4	8.9	0.2	7.1	0.9
KALD-2 ueq L^{-1}	4.9	1.7	5.1	0.1	5.1	1.5
4 November 87						
KALD-MTW 010	7.5	0.3	10.9	0.3	10.6	0.4
KALD-2 ueq L^{-1}	5.0	2.0	5.1	0.9	5.0	1.1
20 November 87						
KALD-MPW 034	3.7	0.8	6.9	0.3	5.3	0.7
KALD-CBD 029	5.6	1.7	4.5	1.1	4.6	1.3
KALD-CT 016	37.7	0.6	32.7	0.2	47.1	0.1
KALD-2 ueq L^{-1}	4.9	0.7	5.0	0.8	5.0	0.8
23 November 87						
KALD-CBD 041	16.6	1.2	37.1	0.1	19.2	0.3
KALD-2 ueq L^{-1}	4.8	3.2	4.9	3.1	5.0	2.5
15 December 87						
KALD-MPW 019	2.9	3.5	4.7	0.9	4.9	1.3
KALD-MPW 021	3.4	2.3	7.7	0.3	6.1	0.7
KALD-MBW 013	3.7	0.3	4.7	1.0	4.3	0.5
KALD-2 ueq L^{-1}	4.6	0.2	4.9	0.7	5.1	1.2
16 December 87						
KALD-MBD 014	3.9	1.3	9.0	0.0	6.8	0.2
KALD-MBD 018	3.1	1.1	3.6	0.1	3.6	0.6
KALD-MBD 033	9.8	2.5	23.7	0.3	10.2	1.2
KALD-2 ueq L^{-1}	5.0	12.6	5.4	4.2	5.3	2.1
17 December 87						
KALD-MBW 018	4.8	4.5	5.2	0.5	5.3	0.2
KALD-MPW 035	5.6	0.1	7.9	0.3	6.1	1.5
KALD-2 ueq L^{-1}	4.8	5.4	5.4	2.9	5.4	1.4
22 December 87						
KALD-CBW 027	6.9	1.4	6.7	0.9	6.0	0.1
KALD-2 ueq L^{-1}	4.9	3.6	5.1	0.2	5.2	0.3

Table 4.27. Accuracy of analyses of anions by ion chromatography (Dionex 2010i, 200-uL sample loop, attenuation = 3). Accuracy was assessed by (1) comparing measured values with certified values for 15-fold diluted NBS 2694-II simulated rain water control (the 1.9 ueq L^{-1} was not NBS certified), and (2) by recovery after known additions to a) laboratory duplicates (KALD) of randomly selected samples and to b) a 2 ueq L^{-1} synthetic standard. Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration (ueq L^{-1}).

Run/Sample		Cl^-	NO_3^-	SO_4^{2-}
29 October 87				
NBS 2694-II/15	Meas:	1.4	7.7	16.0
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-CBD 026	R	131	90	127
	(final conc)	(5.3)	(8.9)	(7.1)
KALD-2 ueq L^{-1}	R	103	103	97
	(final conc)	(4.9)	(5.1)	(5.1)
4 November 87				
NBS 2694-II/15	Meas:	1.7	7.8	15.9
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-MTW 010	R	102	92	90
	(final conc)	(7.5)	(10.9)	(10.6)
KALD-2 ueq L^{-1}	R	97	104	101
	(final conc)	(5.0)	(5.1)	(5.0)
20 November 87				
NBS 2694-II/15	Meas:	2.0	7.7	15.9
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-MPW 037	R	90	100	109
	(final conc)	(3.7)	(6.9)	(5.3)
KALD-CBD 029	R	92	107	107
	(final conc)	(5.6)	(4.5)	(4.6)
KALD-2 ueq L^{-1}	R	96	98	94
	(final conc)	(4.9)	(5.0)	(5.0)
23 November 87				
NBS 2694-II/15	Meas:	1.6	7.8	16.0
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-2 ueq L^{-1}	R	100	98	102
	(final conc)	(4.8)	(4.9)	(5.0)
15 December 87				
NBS 2694-II/15	Meas:	1.7	7.9	16.2
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-MPW 019	R	80	96	102
	(final conc)	(2.9)	(4.7)	(4.9)

Table 4.27. (continued)

Run/Sample		Cl^-	NO_3^-	SO_4^{2-}
KALD-MPW 021	R	106	93	101
	(final conc)	(3.4)	(7.7)	(6.1)
KALD-MBW 013	R	109	100	106
	(final conc)	(3.7)	(4.7)	(4.3)
KALD-2 ueq L^{-1}	R	98	96	101
	(final conc)	(4.6)	(4.9)	(5.1)
<u>16 December 87</u>				
NBS 2694-II/15	Meas:	1.7	7.9	16.1
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-MBD 014	R	108	102	113
	(final conc)	(3.9)	(9.0)	(6.8)
KALD-MBD 018	R	102	107	114
	(final conc)	(3.1)	(3.6)	(3.6)
KALD-2 ueq L^{-1}	R	98	114	111
	(final conc)	(5.0)	(5.4)	(5.3)
<u>17 December 87</u>				
NBS 2694-II/15	Meas:	1.7	8.0	16.0
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-MBW 018	R	102	90	101
	(final conc)	(4.8)	(5.2)	(5.3)
KALD-MPW 035	R	110	104	114
	(final conc)	(5.6)	(7.9)	(6.1)
KALD-CFB - acrylic	R	89	110	114
no. 3A	(final conc)	(4.9)	(3.3)	(3.5)
KALD-2 ueq L^{-1}	R	96	113	115
	(final conc)	(4.8)	(5.4)	(5.4)
<u>22 December 87</u>				
NBS 2694-II/15	Meas:	1.8	7.8	16.0
	Cert:	1.9	7.6±0.2	15.1±0.3
KALD-CFB - acrylic	R	114	109	112
19 Mar 87	(final conc)	(3.4)	(3.3)	(3.4)
KALD-CFB-PVC-4	R	95	112	112
21 Mar 87	(final conc)	(2.9)	(3.4)	(3.4)
KALD-CBW 027	R	100	107	106
	(final conc)	(6.9)	(6.7)	(6.0)
KALD-2 ueq L^{-1}	R	109	103	107
	(final conc)	(4.9)	(5.1)	(5.2)

4.4. Snowpack (pit) Water Equivalent and Chemistry

SWE determinations and depth-integrated snowpack samples were collected at two-week intervals at CSSL and Mammoth Mountain from January to April, 1987, during the snowpack accumulation period and into the first weeks of ablation (Table 4.7C). SWE measurements were also made at two-week intervals at CSSL during 1988.

At CSSL, SWE from the pit technique matched closely SWE from the weekly board and Belfort gauge measurements through much of the snowpack accumulation period (Figure 4.9). In 1988 the pit values were always slightly lower than the Belfort and board values, whereas in 1987, until the mid-March sampling, the pit values were equal or slightly higher than the board and Belfort values. Major rain-on-snow events on February 10 and 11 and March 4 and 5 1987 primed the snowpack and caused appreciable runoff prior to the mid-March measurements. No rain-on-snow events occurred during the winter of 1987-1988 at CSSL.

At a windy location like Mammoth Mountain, careful selection of a measurement site is extremely important. The large differences between board and Belfort precipitation values noted in section 4.2 are probably due to a combination of reduced precipitation input to the Belforts due to wind effects and possible positioning of the weekly boards in a local wind deposition zone. In that the pit SWE values are intermediate between the board and Belfort measurements at Mammoth (Figure 4.10), the pit technique may provide a more accurate and less site-sensitive approach for determining SWE. Pit location, however, has the same problems as board positioning. The criticality of knowledge of local wind speed and patterns of wind redistribution of snow is shown by the variation in SWE among the three techniques. At a high-elevation, cold locality like Mammoth Mountain, losses from the snowpack to melt should be minimal. Losses to evaporation and sublimation, however, may be large (Beaty 1975, Stewart 1982) and an alternate cause for a lack of correspondence between the pit and weekly board values.

Comparison of snowpack chemical loadings through time at CSSL and Mammoth Mountain during the 1986-1987 winter (Figures 4.11 and 4.12) demonstrate an unexpected finding: maximum loadings are not necessarily concurrent with maximum SWE. A once-a-year pit sampling at the presumed time of maximum SWE could underestimate total loadings by an appreciable percentage. At CSSL, for instance, the 28 March sample (peak SWE) had peak loadings for only five of the nine solutes monitored (Figure 4.11 and Table 4.7A). In addition, Ca^{2+}, H^+, and NO_3^- loadings were higher at two or three other sampling times, and the 28 March Ca^{2+} loading was 64% of the maximum loading of 13 January. At Mammoth Mountain a similar phenomenon was observed (Figure 4.12 and Table 4.7A); only five of the nine solutes monitored had peak loadings at the 15 March sampling when SWE peaked and the Ca^{2+} loading on 15 March was 53% of the maximum Ca^{2+} loading observed on 26 March.

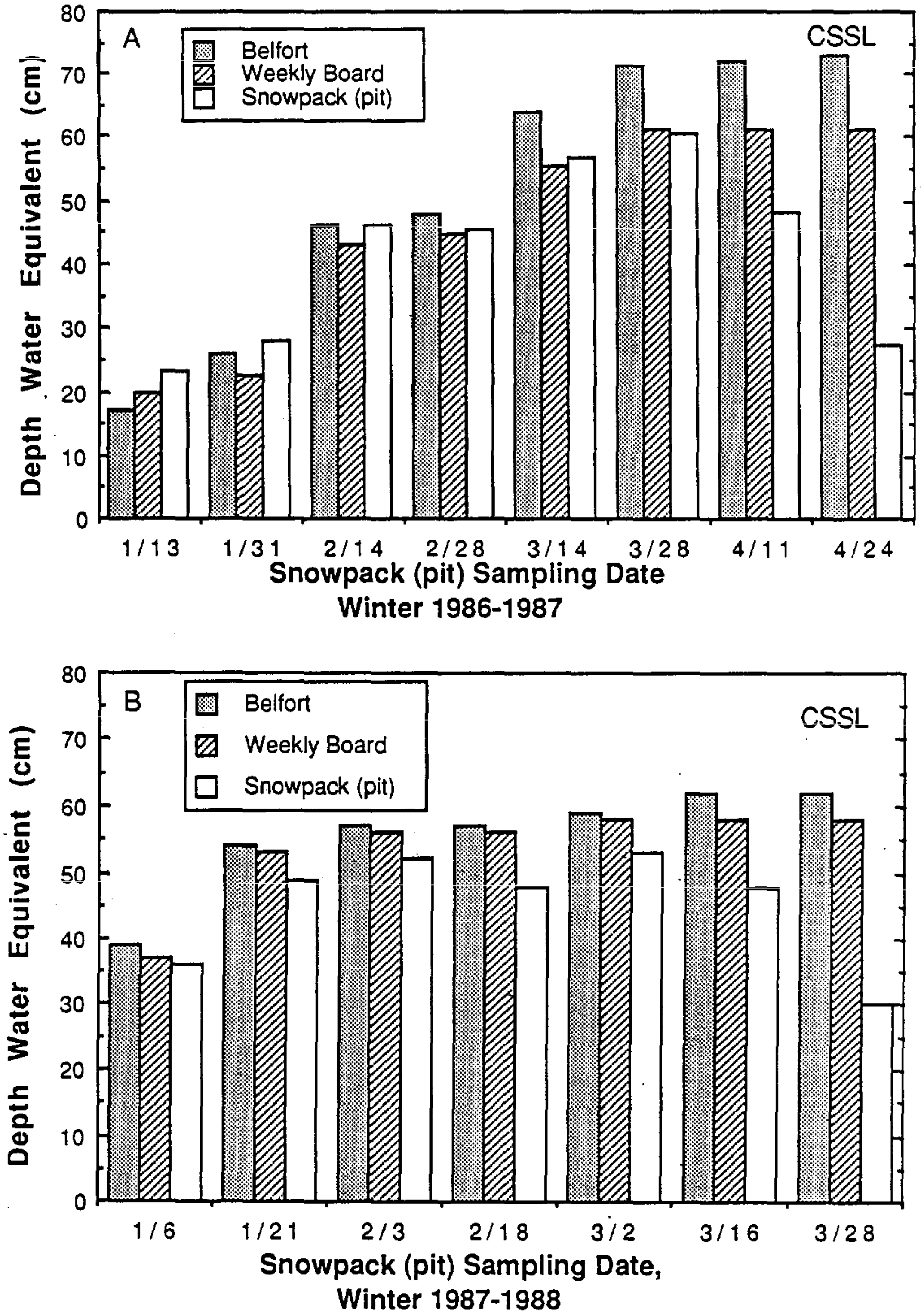

Figure 4.9. Comparison of cumulative water equivalents derived from Belfort precipitation gauge, weekly snowboard, and snowpack (pit) measurements, Central Sierra Snow Laboratory, 1987 (A) and 1988 (B).

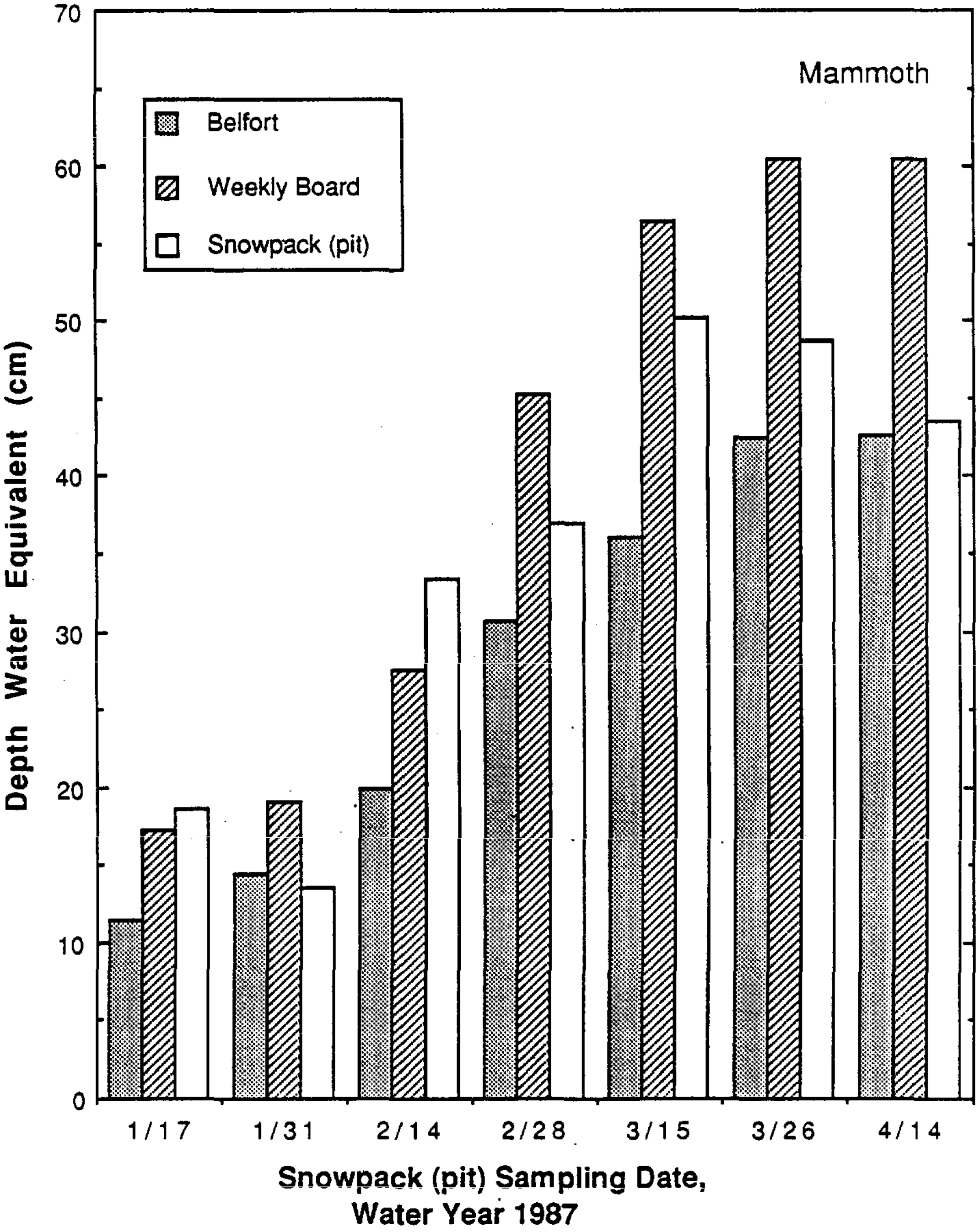

Figure 4.10. Comparison of cumulative water equivalents derived from Belfort precipitation gauge, weekly snowboard, and snowpack (pit) measurements, Mammoth Mountain study site, 1987.

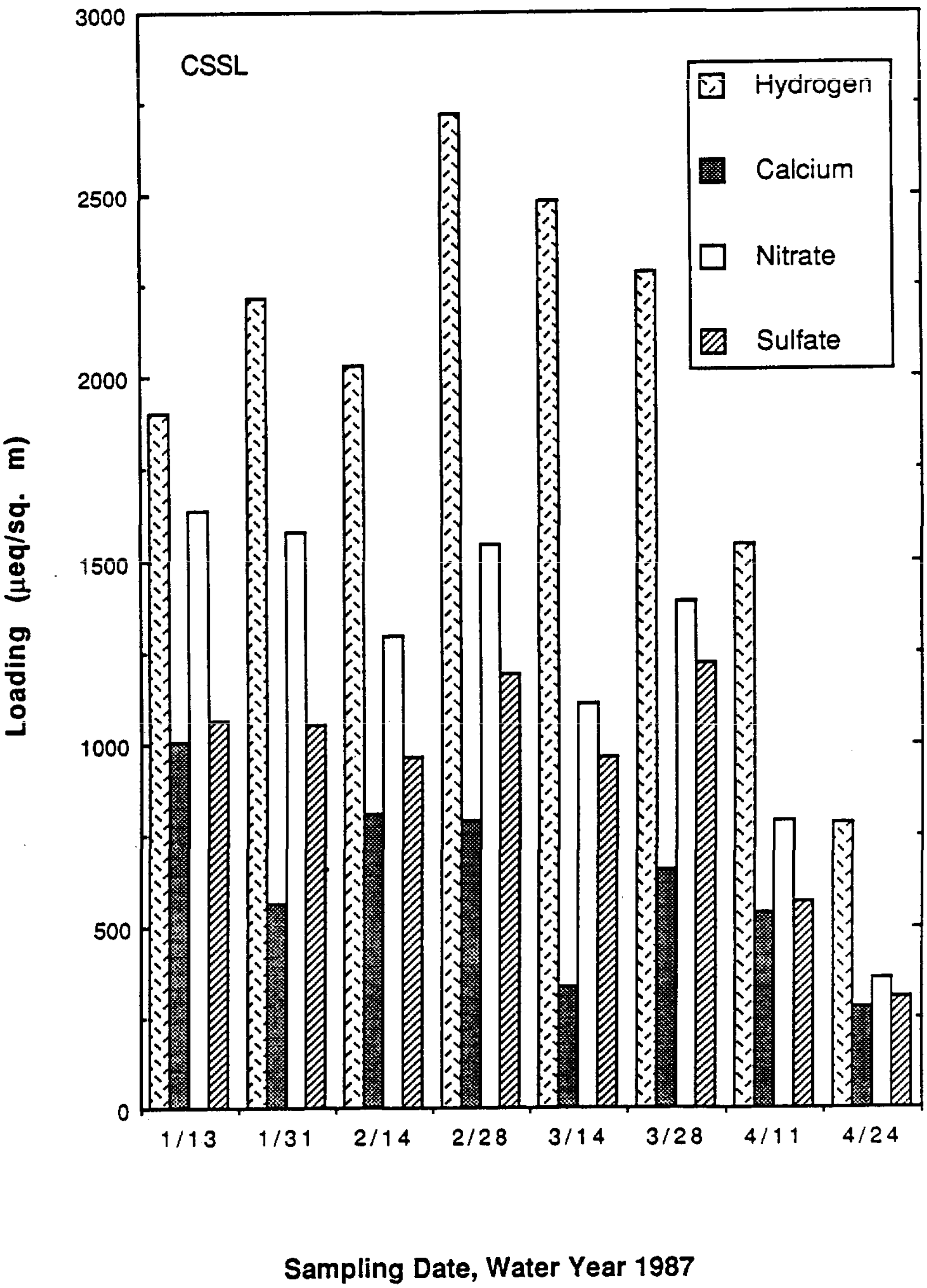

Figure 4.11. Hydrogen, calcium, nitrate, and sulfate loadings of snowpack samples collected at two-week intervals at the Central Sierra Snow Laboratory, winter 1986-1987.

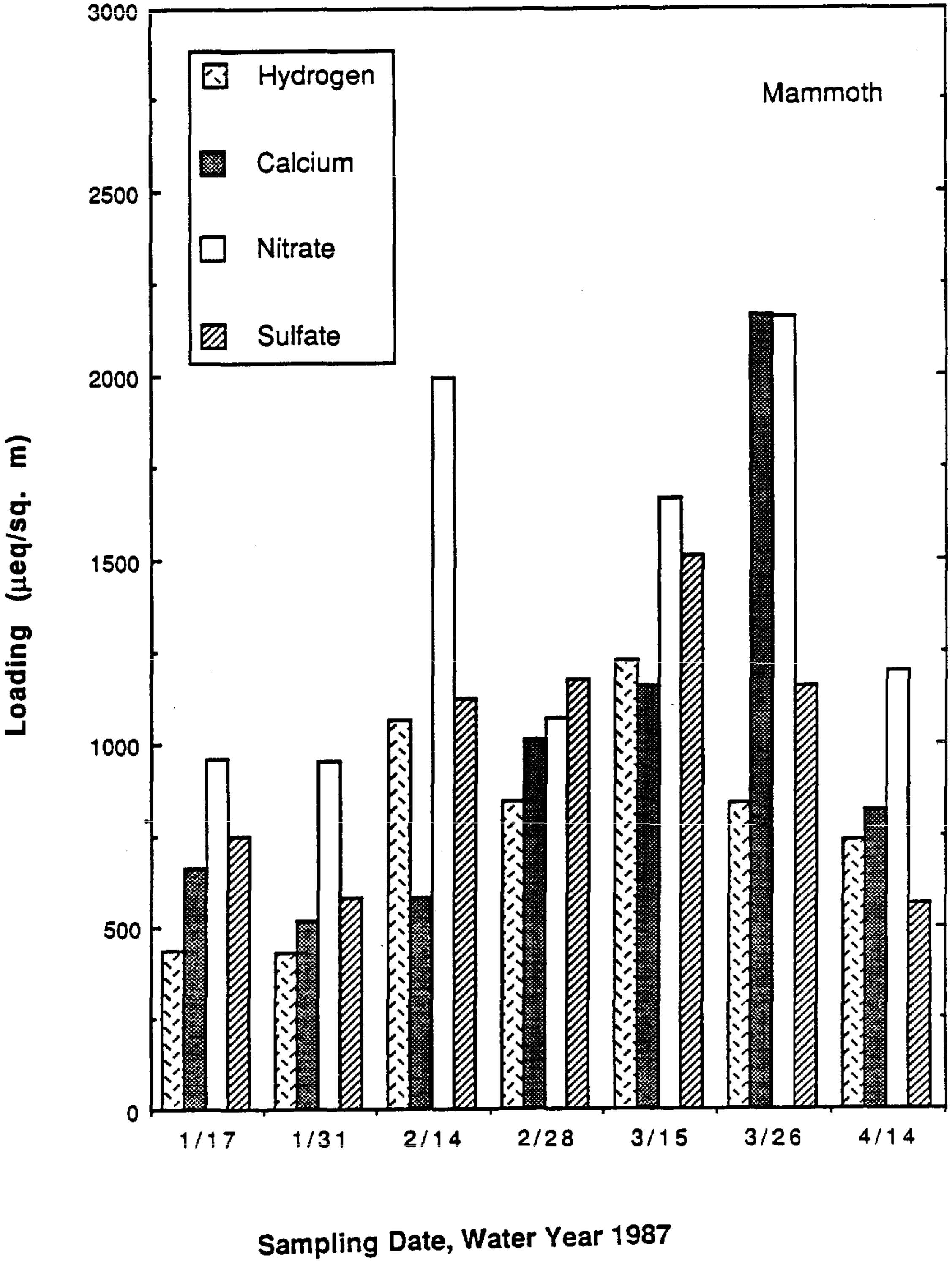

Figure 4.12. Hydrogen, calcium, nitrate, and sulfate loadings of snowpack samples collected at two-week intervals at Mammoth Mountain, winter 1986-1987.

4.5. Statewide Survey of Snowpack Water Equivalent and Chemistry

A summary of volume-weighted mean concentrations and areal loadings for all sites derived from snow pit samples collected near the time of maximum snow accumulation (Table 4.7D) shows:

1) variation in concentrations among the 8 sites sampled in the Sierra Nevada was fairly small. For example, pHs ranged from 5.13 to 5.76; SO_4^{2-} ranged from 2.3 to 5.8 ueq L^{-1}; NO_3^- ranged from 2.1 to 4.6 ueq L^{-1}.

2) The highest recorded concentrations for the majority of solutes were from the samples from Snow Summit in the San Bernardino Mountains (NH_4^+ = 19.5 ueq L^{-1}, Cl^- = 14.4 ueq L^{-1}, NO_3^- = 17.8 ueq L^{-1}, SO_4^{-2} = 10.7 ueq L^{-1}, and Na^+ = 6.3 ueq L^{-1}; Table 4.7A and Figure 4.13).

3) Low SWE at the San Bernardino sites (Figure 4.14), in combination with moderate concentrations of several solutes in the Sierra samples, resulted in maximum loadings for most solutes from the Sierra samples (Figure 4.15). Heavenly Valley in particular had high loadings. Local sources might explain the high loadings at Heavenly, but other Sierra samples had loadings equal to or greater than samples from the San Bernardino Mountains.

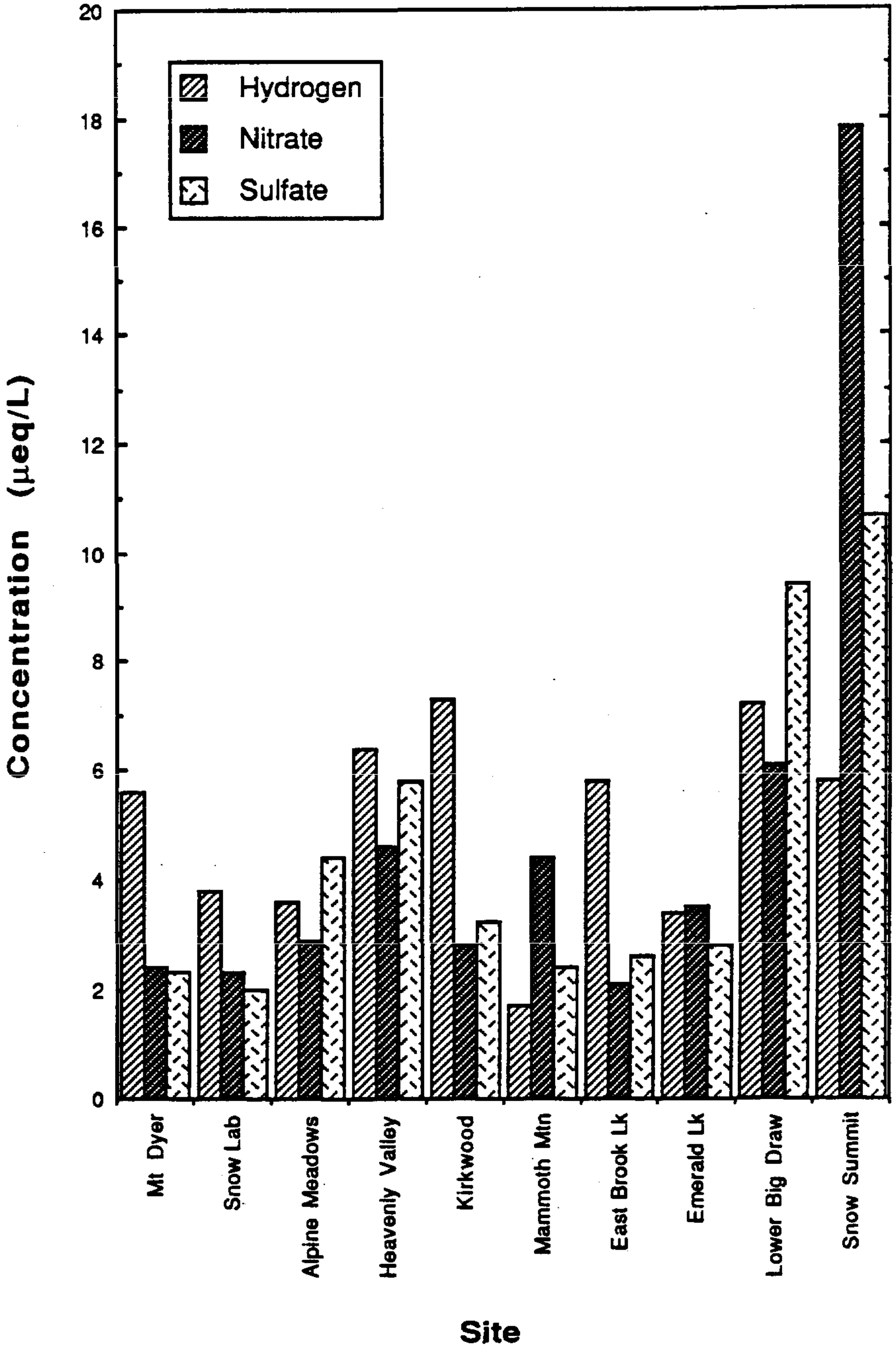

Figure 4.13. Hydrogen, nitrate, and sulfate concentrations of snowpack samples collected at 10 sites in the Sierra Nevada and San Bernardino Mountains between 18 and 30 March, 1987.

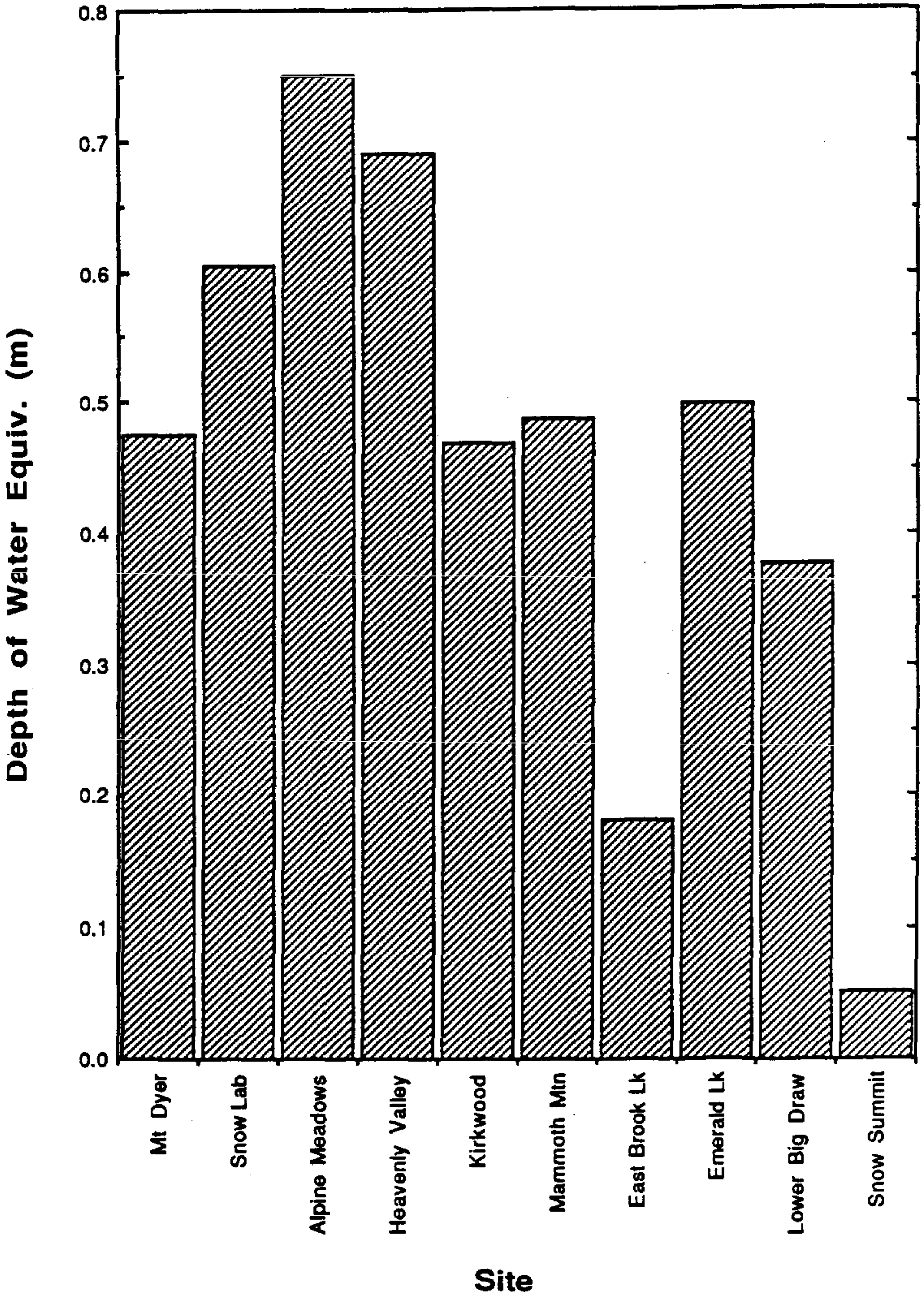

Figure 4.14. Snowpack water equivalent at 10 sites sampled in the Sierra Nevada and San Bernardino Mountains between 18 and 30 March, 1987.

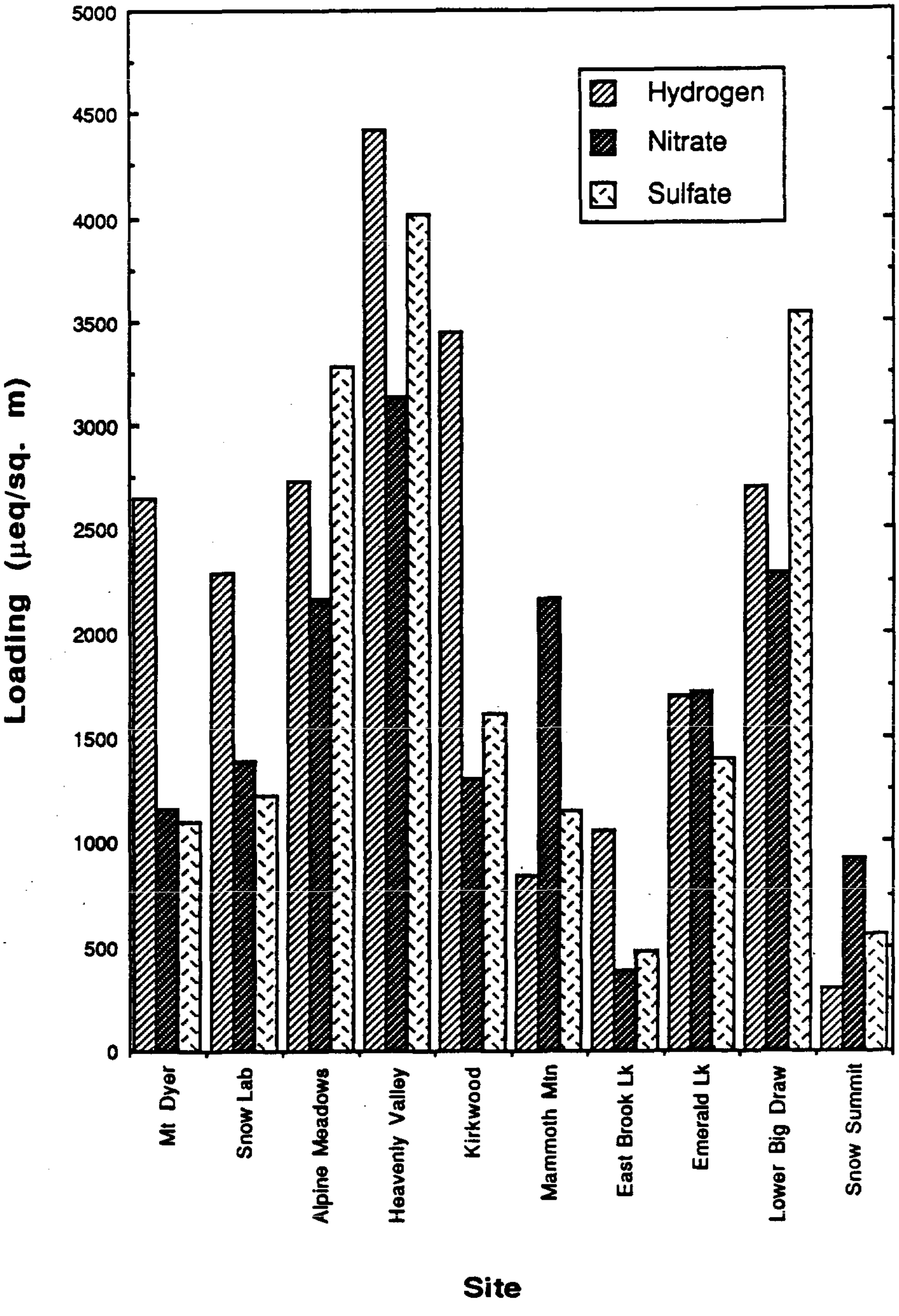

Figure 4.15. Hydrogen, nitrate, and sulfate loadings from snowpack samples collected at the time of maximum snowpack accumulation at 10 sites in the Sierra Nevada and San Bernardino Mountains, 1987.

5. DISCUSSION

5.1. Methods Comparisons

5.1.1. Experimental Collectors and Snowboards--Comparison of deposition among collection methods is confounded by differences in SWE obtained for each method. This effect is most pronounced for comparisons at Mammoth Mountain. Volume-weighted means are less influenced by differences in total SWE and are indicative of real differences in the chemical composition among collection methods. At CSSL volume-weighted mean concentrations of PVC tube samples were higher than board samples, which were usually higher than snow pit samples for each solute measured. The same pattern was generally followed for Mammoth Mountain.

Storms that deposited less than 1.5 cm of SWE had higher concentrations of solutes than storms that deposited at least 1.5 cm of SWE (Tables 4.9 and 4.10). This disparity was greater at CSSL than at Mammoth Mountain. Moreover, the samples from PVC tube collections had higher concentrations than the samples from boards for both storm size categories for most solutes.

Solute composition data are available concurrently from the PVC tubes, as weekly sums of the daily board samples, and as weekly board samples for eight out of 16 weeks for CSSL and to five out of 13 weeks for Mammoth Mountain. Among these subsets, a tabulation of the frequency of occurrences of differences exceeding one standard deviation further illustrates that solute concentrations were generally greater in tube samples than board samples at both CSSL and Mammoth Mountain:

CSSL	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	NH_4^+
Weekly Board > Sum Daily Boards	1	1	0	1	0	0	0	1	1
Tubes > Both Boards	2	1	1	4	1	2	1	0	0
Mammoth Mountain									
Weekly Board > Sum Event Boards	1	1	1	2	0	1	0	0	0
Tubes > Both Boards	4	3	4	0	0	3	3	0	0

Some of these differences could result from the inclusion of rain in tube samples while concurrently sampled precipitation on the boards was affected chemically to some unknown degree by rain passing through, and out of, the mixed rain-and-snow board sample.

At both sites, mean concentrations of the differences between replicates for most constituents were greater in tube samples than in weekly board samples

(Tables 4.7A and 5.1). Except for H^+, 95% confidence intervals (CI) around the difference between the replicates for each constituent at CSSL were greater (up to 30-fold) for the tube samples than for the weekly board samples. At CSSL, CI for the weekly boards varied from ±0.3 ueq L^{-1} for SO_4^{2-} to ±2.3 ueq L^{-1} for Cl^- and from ±1.0 ueq L^{-1} for H^+ to ±12.9 ueq L^{-1} for Cl^- in the tube. At Mammoth, the 95% CI for the boards and tubes were more similar. For the weekly boards, CI ranged from ±0.4 ueq L^{-1} for K^+ to ±5.4 ueq L^{-1} for Ca^{2+} and from ±0.5 ueq L^{-1} for H^+ and K^+ to ±2.9 ueq L^{-1} for Cl^- in the tube. Variability was greatest for Cl^-, Ca^{2+}, and Na^+.

During both years at CSSL, the tubes recorded larger seasonal SWE values than the "ground truth" boards. Most of this difference could be attributed to rainfall losses from the boards. At Mammoth Mountain, the reverse occurred and could be attributed to wind--as undercatch from the tubes and/or positioning of the boards in a snow deposition zone. Therefore, depending upon the site's windiness and propensity for rain, different monitoring techniques might be advisable. Sites receiving rain could be equipped with shielded tubes, and all others could use weekly snowboards.

This result is confounded, however, by the analysis of variance results that indicate that at both Mammoth and CSSL, the board and tube chemical concentrations differed. Snow collected from a weekly board is assumed to be closest to reality. In that the chemistry from the tubes differs from the board's chemistry, the PVC tubes are suspect. This study did not evaluate the chemistry samples collected from the LPE tubes used in 1987-1988, so additional research is needed. The reasons for the PVC tube's high concentrations in the low-volume samples at CSSL are unknown, but the difference was observed at Mammoth Mountain even without this complicating factor.

Other undesirable features of the tubes are the expense and hazard associated with their use. They require towers and windscreens, and they expose service staff to potential falls during servicing. They also require a pair of tubes for weekly exchanging and a storage location. Further, they require a high-quality deionized water source for weekly cleaning. And time must be allowed for the snow sample to melt before volumetric determination of SWE. The tubes are bulky to transport and moderately expensive (ca. $300 each) to fabricate.

Weekly snowboards have some disadvantages, but they have many advantages for inclusion in a monitoring network. The largest problem is their loss of mass and chemical load during rain. Care in the field must also be taken to assure that uncontaminated samples are collected. Beyond these problems the boards are inexpensive to produce, straightforward to service, and require no expensive towers or windscreens. Snow depth and density are obtained onsite with a minimum of equipment and delay. Snow samples for chemical analysis can be extracted with simple, disposable cutters and placed in LPE bottles for shipment to a central laboratory.

Several other options exist for overcoming the rain and melt problems associated with snowboards. More frequent monitoring yielded higher SWE values (Figures 4.5 and 4.6). A modified board with low walls that was lined with plastic and channeled melt or rain water into an LPE reservoir might overcome most of these problems. Alternately, rain-and-snow areas may require the operation of simultaneous LPE tubes and snowboards.

Table 5.2. Potential contamination and protocols to avoid contamination during collection and manipulation of precipitation chemistry samples. Deionized water should have a specific conductance <1 uS cm^{-1}, 25^{o}C. Field blanks consist of special-cleaned bottles filled with deionized water used to rinse the collector at the field site. Field audits for pH and conductance were prepared at UCSB and shipped to field sites.

Step	Contamination sources	Protocol to avoid contamination
1. Collector vessel (initial set-up)	Collector and corer plastic	Wash with Liquinox, rinse with with deionized water Wash with 10% HCl, rinse with with deionized water Soak 4 days in deionized water, rinse with deionized water
2. Collector vessel and corers (subsequent collections	Previous sample	Rinse thoroughly with deionized water before replacement for next collection Field blanks
3. Removal of sample from collector	Fingerprints, dirt, perspiration, etc.	Operator conscientiousness Wear powder-free, hole-free vinyl gloves Do not touch inside of collector
4. Sample bottles	Plasticware	Specially-cleaned HDPE bottles: bottles washed with 10% HCl; rinsed with deionized water (3x); soaked overnight in deionnized water bottles rinsed (5x) with deionized water Field blanks
5. Ziplock bags	Plasticware	Soak overnight in deionized water Rinse 5x with deionized water
6. Sample transfers	Fingerprints, dirt, perspiration	Operator conscientiousness; use powder-free vinyl gloves; do not touch inside lip of bottles/cap
7. Field measurements	Cross contamination with subsample	Discard subsamples after each measurement Use field audit samples
8. Sample transport (field to lab)	Sample leakage	Ensure caps are tight

5.2. Quality Assurance and Control

5.2.1. Sample Collection and Processing--Collection and manipulation of precipitation chemistry samples involves many steps (Table 5.2 modified from Vet and Onlock 1986). The checks for sample integrity incorporated in Table 5.2 were selected to avoid and detect any contamination from background sources or handling procedures during field operations.

An evaluation of chemical contamination in PVC cylinders, polyethylene ziplock bags, and polyethylene bottles after special cleaning indicated negligible chemical contamination in plasticware (Table 4.13). The 10% HCl step was later eliminated from the wash sequence because this source of Cl^- can be difficult to rinse from the zip portion of ziplock bags. Plasticware blanks were thereafter increased from 5% to 10% frequency. PVC cylinders were tested for desorption or adsorption of dissolved ions (Table 4.14). Neither process occurred in 50-liter volumes of the solutions tested.

For the state-wide pit survey, snow samples were maintained at -30°C until analysis. They were then melted at 4°C in acid-cleaned 6-liter polypropylene buckets with closable lids. As a test of this technique, these buckets were evaluated for ion adsorption at three levels (2, 5 and 10 ueq L^{-1}) at room temperature. Within the analytical precisions, no differences in dissolved cations and anions were detected over a 24-hour period (Table 4.15). However, a test of the effect of ambient temperature versus cold temperature (4°C) during phase change on the concentration of dissolved ions in snow melt showed a significant difference by Student's t test for Cl^- and for SO_4^{2-} (Table 4.16). Although the results in Tables 4.14 and 4.15 are in agreement with Chan et al.'s (1983) report that no contamination was detected in deionized water leachates from polyethylene bags, Chan et al. (1983) also reported that no short-term (48 hour) desorption or adsorption of major ions occurred from or onto polyethylene surfaces. The results in Table 4.16 indicate that melting in polypropylene containers should be at 4°C.

Meltwater should be filtered through Nuclepore 0.4-micron polycarbonate filters (Table 4.17) and maintained at 4°C until analysis. The necessity of filtration as the appropriate means for preservation of dissolved constituents has been documented (Peden and Skowron 1978). The use of membrane-type filters is based on an extensive evaluation of various filter materials; recommendations are discussed in Appendix C. We further assessed the efficacy of filtration with storage (three months) at 4°C as a means of preserving dissolved ammonium, major cations and anions and organic acids (Table 4.22). Two snow samples of different chemical composition were selected for this test. The more dilute Rochs Ramp sample (Emerald Lake watershed) gave acceptable recoveries (±10% of 100%) for all ions except Cl^- which experienced a 24% loss from solution. The Log Meadow sample with a more concentrated and complex chemistry showed a decrease in NH_4^+ and an increase in NO_3^-. Chloride loss was similar to the decrease detected in the Rochs Ramp sample. In addition, a severe loss of acetate and formate occurred in the Log Meadow sample. These results suggest that ion stability can be a function of their particular matrix and that changes may occur even after filtration and storage at 4°C over a three-month time period. In particular, low levels of Cl^- are apt to decrease over time and, while K^+ was not investigated here, Chan et al. (1983) document

Table 5.1. Replicate variation, by constituent, for weekly snowboard and tube measurements, Central Sierra Snow Laboratory and Mammoth Mountain, winter 1986-1987.

Location/ Method	Constituent	Sample[1] Size	Mean[2] (ueq L^{-1})	Stan. Err.[3] (ueq L^{-1})	Con. Interval[4] (ueq L^{-1})
CSSL/ Weekly Board	H^+	10	-0.18	0.45	(-1.19, 0.83)
	NH_4^+	10	-0.15	0.44	(-1.15, 0.85)
	Ca^{2+}	10	-0.01	0.35	(-0.81, 0.79)
	Mg^{2+}	10	0.02	0.07	(-0.13, 0.17)
	Na^+	10	-0.04	0.69	(-1.60, 1.52)
	K^+	10	-0.18	0.15	(-0.53, 0.17)
	Cl^-	10	1.75	1.02	(-0.55, 4.05)
	NO_3^-	10	-0.30	0.22	(-0.80, 0.20)
	SO_4^{2-}	10	-0.17	0.13	(-0.46, 0.12)
CSSL/ Tube	H^+	14	-0.53	0.47	(-1.54, 0.48)
	NH_4^+	14	-0.27	0.78	(-1.95, 1.40)
	Ca^{2+}	14	-4.41	4.75	(-14.7, 5.85)
	Mg^{2+}	14	0.27	0.30	(-0.38, 0.92)
	Na^+	14	3.24	2.47	(-2.10, 8.57)
	K^+	14	1.39	1.69	(-2.25, 5.04)
	Cl^-	14	-5.79	5.96	(-18.7, 7.10)
	NO_3^-	14	-4.14	3.25	(-11.2, 2.90)
	SO_4^{2-}	14	-1.04	4.43	(-10.6, 8.52)
Mammoth Weekly Board	H^+	10	0.16	0.28	(-0.47, 0.79)
	NH_4^+	10	-1.17	0.79	(-2.95, 0.61)
	Ca^{2+}	10	2.40	2.38	(-2.98, 7.78)
	Mg^{2+}	10	-0.03	0.11	(-0.27, 0.21)
	Na^+	10	-0.05	0.54	(-1.27, 1.17)
	K^+	10	-0.22	0.16	(-0.59, 0.15)
	Cl^-	10	0.33	0.54	(-0.90, 1.56)
	NO_3^-	10	-2.60	0.51	(-1.42, 0.90)
	SO_4^{2-}	10	-0.60	0.52	(-1.77, 0.57)
Mammoth Tube	H^+	8	-0.53	0.21	(-1.02, -0.03)
	NH_4^+	8	-0.20	0.54	(-1.48, 1.08)
	Ca^{2+}	8	0.14	0.81	(-1.77, 2.05)
	Mg^{2+}	8	0.15	0.26	(-0.47, 0.77)
	Na^+	8	0.94	0.84	(-1.06, 2.93)
	K^+	8	0.16	0.22	(-0.35, 0.67)
	Cl^-	8	0.25	1.23	(-2.66, 3.16)
	NO_3^-	8	0.53	0.49	(-0.64, 1.69)
	SO_4^{2-}	8	0.05	0.45	(-1.02, 1.12)

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[1] Sample size (number of weekly measurements).
[2] Mean of the differences between replicates (2).
[3] Standard error around the mean of the differences between replicates.
[4] 95% confidence interval around the mean of the replicate differences.

5.1.2. Snowpack (pit) Sampling--As a "snapshot" method to estimate chemical loading, the merits of snowpack (pit) sampling are the potential for a one-time measurement each year that incorporates both wet and dry fall over potentially a 4-to-6 month period of seasonal snowpack accumulation. The pit monitoring shows wide variability in SWE, with peak SWE at CSSL occurring on 28 March in 1987 and 2 March 1988 (Figure 4.9). In terms of routine monitoring from the standpoint of a state-wide network, selection of a consistent date each year for sampling at CSSL would be difficult, as illustrated by the 26-day difference in peak SWE between 1987 and 1988. Analysis of a 20-year record of daily SWE measurements at CSSL suggests that the difference in date of maximum SWE between 1987 and 1988 is not atypical. Between 1969 and 1988 the mean date of maximum SWE was 20 March (at 92.1 cm SWE), with a standard deviation of 23.4 days. Over this period the date of maximum SWE ranged from 19 January to 13 May. A similar condition is shown in the water year 1987 data from Mammoth (Figure 4.10); SWE on 26 March, close to the 1 April date conventionnally assumed to be the date of maximum snowpack accumulation, was slightly less than the SWE measured two weeks previously.

Near-daily measurements of SWE at CSSL (not described here) placed the dates of maximum SWE in 1988 at 19 January and in 1987 at 25 March. The 28 March and 25 March 1987 dates are similar, and reliance on the 28 March 1987 pit data would be appropriate. The 2 March and 19 January 1988 dates are dissimilar, and reliance on the 2 March 1988 pit data would lead to an inaccurate estimate of peak SWE (as noted above, however, the 19 January date for maximum SWE is the extreme of a 20-year record). Difficulties in projecting the specific time of maximum snow accumulation during the mid-March to mid-April period add considerable variability to the precision of this technique.

From a logistics standpoint, snowpack (pit) monitoring presents several difficulties. If comparison between sites is a goal, then the sampling should be done concurrently. On a state-wide scale this implies the need for numerous trained crews available for concurrent field work. Use of dry ice as a coolant is necessary, and the availability of dry ice in remote areas is problematic. The care needed to assure low risk of sample contamination is high for this type of sampling, and extensive training of field crews would be required.

If an objective is comparison of seasonal loadings between sites, a limitation of this technique at low elevation sites and locations in the southern part of California is the potential for ablation to mask the true total accumulation through loss of both mass and chemicals. The 5.2 cm SWE at Snow Summit was probably not the seasonal total SWE, but rather the SWE from the most recent storm; prior snow having ablated.

5.1.3. Aerochem Metrics Collector--The Aerochem Metrics sampler is not well suited for a snow monitoring network in the Sierra Nevada. It seriously undermeasures precipitation volume, a fact recognized by CARB as seen in their inclusion of a precipitation gauge at each Aerochem Metrics site. The further problems associated with the need for line power, the freezeups of the moveable arm, and the mechanical damage and miss-sampling in high winds make it unsuitable.

Table 5.2. (continued)

Step	Contamination sources	Protocol to avoid contamination
9. Sample storage	Microbial growth, sample leakage	Option 1: filter homogeneous liquid sample into special-cleaned bottle and store at 4°C; preserve an organic acid subsample with chloroform. Option 2: transfer unfiltered subsample of homogeneous liquid to special-cleaned bottle (see 4); store at -20°C Ensure caps are tight
10. Sample shipping	Microbial growth, sample leakage	Ensure caps are tight Keep samples frozen or cool with gel packs triple-sealed in ziplock bags Use insulated shipping container Use 1-day shipment

loss of this ion to polyethylene surfaces over a 29-day period. Galloway et al. (1982) documented rapid decrease of organic anions in unpreserved precipitation samples due to biologic activity. The data here indicate that even in chloroform, for preserved samples stored at 4°C, organic anions may deteriorate; the Log Meadow sample clearly had biological interaction with respect to NH_4^+ and NO_3^- alterations.

5.2.2. Field Sampling Quality Integrity--Although detectable chemical contamination was measured in many of the field blanks from CSSL and Mammoth Mountain (Table 4.11), most measured values were near the detection limits of the methods (Table 4.18). However, some field blanks from CSSL had severe contamination. Contamination in Mountain Mountain field blanks ranged from 1 - 4 ueq L^{-1} whereas CSSL field blanks ranged from 1 - 33 ueq L^{-1} in dissolved ions (Table 4.11). The data indicate a more rigid adherence to plasticware cleaning procedures is required. A comparison of measurements for pH at UCSB, CSSL and Mammoth Mountain agreed within ± 0.1 pH units (Table 4.12). The good agreement among pH measurements is within the accepted overall precision (±0.1 units) for pH determination in the field. Likewise, the two field sites agreed well in their conductance measurements of the 10^{-4}N KCl standard and the high and low conductance audits. Both sites agreed with corrected UCSB values (Table 4.12).

5.2.3. Laboratory Quality Assurance at UCSB--The quality control program at UCSB yielded data (Tables 4.18 through 4.27) which assures the credibility and integrity of the analytical results.

Single-operator accuracies as recovery-after-known-addition for the determination of anions by ion chromatography within ±10% of 100% were typical

(Tables 4.19 and 4.20). Upper and lower control limits (±3 standard deviations of the mean recovery) of 135 to 83, 108 to 92, and 103 to 89 were allowed for chloride, nitrate and sulfate, respectively (Table 4.19). To estimate within-run precision, laboratory duplicates were run at a 3% frequency. Mean analytical precisions for Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} over the entire study period were 4%, 2%, 2%, and 5% relative standard deviation (RSD), respectively (Table 4.23). Analysis of low levels (<2 ueq L^{-1}) of chloride in natural samples showed greater inherent variability (Tables 4.19 and 4.25) than nitrate or sulfate at similar levels; hence the wider tolerance in the control limits for this ion. For higher chloride levels (≥ 5 ueq L^{-1}), precision calculated from KALD's (Table 4.26) improved. Overall precisions for NO_3^- and SO_4^{2-}, for low level Cl^-, and for high level Cl^- were < 1, 6, 2 and 8 RSD, respectively.

Inaccuracy propagated through the analytical methodology can result in biased results for the data set. An innovation at UCSB was the incorporation of a synthetic charge balance control (CBC) in analytical runs of cations and anions. The CBC consisted of an unfiltered solution of six ions (only) in Milli-Q water. This solution was not filtered and thereby allowed a calculation of ion balance due to measurement alone. Within the precision of the methods, the analyses had an insignificant effect on the theoretical ion balance (Table 4.21).

The rationale for analytical accuracy at the UCSB laboratory was based upon assessment of the degree of conformity of values obtained to an accepted true value. That is, the degree of difference between measured and known values on certified samples was determined. Certified controls were included in each analytical run. Additional, known additions of synthetic standards to actual samples were made at a 3% frequency per run. Accuracy statements as percent spike recovery after known addition as well as measured values on certified controls are given in Tables 4.24 and 4.27 for cations and anions, respectively. Table 4.24 shows an overall acceptable recovery of added cations in the February run and a tendency to underestimate Na^+ and K^+ in the December run. No corrections were applied to sample data; the mean recoveries for Na^+ and K^+ were 89% and 82%, respectively, for the run. Likewise recoveries averaged over the seven anion runs (Table 4.27) were within ±10% of 100% for Cl^-, NO_3^- and SO_4^{2-}. Overall agreement of measured values of cations and anions with NBS and EPA certified controls warranted no corrections of sample values.

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Appendix A.

MAMMOTH MOUNTAIN/CSSL SNOW STUDY SAMPLING PROTOCOL

I. DAILY
   A. Perform between 0900 and 1100 hours if possible.
   B. Prepare and label sample bottles and forms before going into field.
   C. If depth on 2 or 3 boards is less than 3 cm, note "Trace" and do not turn snowboards, no density or chemistry samples.
   D. Dig down to edge of snowboard with shovel, use spatula or density cutter lid to shear back a clean wall, take care to leave enough snow on the board for chemistry and density samples.
   E. Put on new disposible latex gloves.
   F. Take one chemistry sample from each of two boards (before doing densities).
      1. Cleanliness is all important: a single fingerprint on the inside of the sample bottle, a single drop of perspiration will ruin the sample.
      2. for 3-35 cm of snow
         a. note snowboard number and snow sampler number on daily form
         b. push acrylic chem sampler down through snow to plastic board surface just behind shearwall
         c. push spatual under tube opening and tip the tube out of the snow column
         d. using a clean plastic-gloved hand, wipe excess snow off outside of tube
         e. tip tube into mouth of clean, 2 liter sample bottle, tap tube with it's cap to dislodge snow
         f. place as many replicate cores in same sample bottle as required for adequate meltwater volume, depending on snow depth and density. A minimum of 350-500 mls of meltwater is required
         g. one way to ensure (f) is to tare empty bottle and weigh with cores
         h. record sample ID # on form
      3. greater than 35 cm of snow
         a. note snowboard number and sampler number on daily form
         b. place ruler or tape against shearwall with zero at board
         c. push sampler down through snow column to approximately 2/3 its lenght (35 cm)
         d. carefully shear back snow to expose sampler
         e. record snow sample height increment from ruler or tape
         f. tip sampler out of snow column
         g. clean outside of sampler and dump sample into bottle
         h. record sample ID # on form
         i. place sampler back into hole from which you removed it, push down through next 35 cm of snow, and record height increment
         j. tip out of column and put in a different sample bottle
         h. record this sample ID # on form
         k. procede this way all the way down to the snowboard putting each sample in a different bottle

G. Take density (mass and depth) measurements from each of the three boards.
   1. 3-10 cm of snow depth
      a. record snowboard number and density corer number on form
      b. place bucket on scale and tare
      c. push density tube down through snow to board, place spatula underneath and tip out
      d. scrape excess snow off outside of tube
      e. dump snow from tube into bucket, scrape inside as necessary
      f. measure and record depth adjacent to that core
      g. repeat 4 more times on same board
      h. record total mass of the 5 combined cores on form
   2. 10-35 cm of snow depth
      a. record snowboard number and density corer number on form
      b. place bucket with empty corer in it on scale and tare
      c. push density tube down through snow to board, place spatula underneath and tip out
      d. scrape excess snow off outside of tube
      e. place tube with sample inside in bucket, on scale and record mass on form
      f. scrape out inside of tube and repeat b-e above on same board
   3. greater than 35 cm of snow
      a. record snowboard number and density cutter number and volumne
      b. place ruler or tape against shearwall with zero at board
      c. place empty cutter without lid on scale and tare
      d. push cutter into shearwall vertically at top of wall keeping cutter as square as possible
      e. record snow height increment (top and bottom of cutter) of density sample
      f. push cutter lid in parallel to cutter edges, pull cutter and lid out together, turn upright and remove lid
      g. wipe excess snow off outside of cutter, place on scale with sample inside and record mass
      h. dump out sample, retare empty cutter
      i. procede down shearwall, inserting cutter just below previous cut (leave 3-10 mm between cuts)
      j. cutter must be full each time to get accurate measurements, if you mess up a sample, discard it and just redo it with a sample from the same height, from either side of the bad one
      k. the snowpack will not be an integral number of cuts high; make sure the snow adjacent to the board is sampled, leaving an unsampled area somewhere just above in the column

H. Place all samples in freezer.

II. <u>WEEKLY</u> (Tuesdays at 0900 ± 1 hour).
   A. Perform all daily procedures (as needed) .
   B. Take 1 chemistry sample from each of two weekly boards using daily procedures (as above).
   C. Take a density determination from each of two weekly boards. This will consist of 1 multiple core, two single cores or a single profile depending on depth (as above).
   D. Turn 2 weekly boards.

E. Exchange two bulk (tube) collectors (even if empty).
    1. Cap exposed collector.
    2. Verify that collector number and exposure interval (dates and times) are recorded.
    3. Replace with two capped collectors.
    4. Record new collector numbers and interval start (date and time).
    5. Uncap new collectors.

F. Change weekly weighing rain gauge charts (see manual). Provide all information on end tab of chart.

G. Place bulk (tube) collectors and previous week's daily samples in a heated lab to melt. Keep them capped.

III. <u>BIWEEKLY</u>

A. Perform all daily procedures (as needed)

B. Perform all weekly procedures (as needed)

C. Dig a snowpit to the ground. Take 2 chemistry profiles and 2 density profiles as described above in procedures for depths greater than 35 cm.

D. Exchange EZ logger DSP. Make sure it is labeled with site name and interval start and stop dates and times.

IV. <u>WEEKLY LAB PROCEDURES</u>

A. Allow samples to melt, capped, and get to near room temperature. This is usually accomplished by Weds. morning.

B. In general, the governing document for procedures is the CADMP "Acid Precipitation Field Operation and Analysis Procedures".

C. For the purposes of this protocol "clean", when used in reference to labware or equipment, means that the article was washed with 10% HCL when first acquired then rinsed copiously with high quality distilled water, Milli-Q water or equivalent (hereafter referred to as distilled water). Following contact with a snow sample article has been rinsed 3 times with such water.

D. Great care must be taken with cleanliness at all times. A single fingerprint on the inside of a sample bottle or a drop of perspiration will ruin a sample. When in doubt, give things extra rinses and never skimp on distilled water.

E. Determine the volume and water equivalence for the bulk (tube) sampler
    1. Using extreme care not to spill or contaminate, pour sample from tube into a smaller, clean, more manageable bucket. An Aerochemetrics wet/dry collector bucket works well.
    2. From Aerochem bucket pour sample into a large, clean graduated cylinder. It may require multiple refills to measure entire volume. For large samples save at least the last 500 mls for rinsing and analysis. Record total volume on form.
    3. Divide volume in mls (cm^3) by cross-sectional area of collector 740.2 cm^3 to calculate water equivalence. Record on form.

F. Determine conductivity of daily and tube samples
    1. Following CADMP procedure and manufacturer's instructions calibrate instrument. Record temperature of standard if used.
    2. Rinse the cell and thermistor 3 times with distilled water
    3. If adequate sample is available, rinse cell with small amount of sample and discard
    4. Record the temperature and conductivity of first sample on form. Note whether conductivity recorded is corrected to 25 °C or not.
    5. Rinse cell and thermistor 2 times
    6 Repeat 3-5 for each sample

G. Determine ph of daily and tube samples
   1. Following CADMP procedure and manufacturer's instructions calibrate instrument
   2. Following calibration and before sample measurement clean electrode and temp. probe by submerging in stirred distilled water for 5 minutes.
   3. Rinse a very small, clean beaker with a small amount of sample and discard. Fill with sample and immerse electrode and temp. probe, swirl sample momentarily.
   4. Allow 5 minutes for equilibration then record ph and sample temperature on form. Note whether value recorded is corrected to 25 °C or not.
   5. Rinse electrode and temp. probe with distilled water from a spray bottle. Rinse sample beaker 2 times with distilled water.
   6. Repeat 3-6 for remaining samples.

H. Package sample
   1. Prepare a clean 250 ml sample bottle with label identical to that on sample.
   2. Rinse bottle with a small amount of sample and discard.
   3. Fill bottle with sample to within 3 cm of top (within 6 mm of neck).
   4. Place in freezer for eventual transport (frozen) to UCSB.

I. Clean equipment
   1. Rinse 2 liter snow sample bottles, graduated cylinders and other labware 2 times with distilled water.
   2. Pour a large aliquot (ca. 2 liters) of distilled water into tube collector and replace cap.
   3. Rock tube back and forth while holding horizontally and rotating and standing on one foot and chewing gum.
   4. Discard rinse water and repeat twice more.

MAMMOTH MOUNTAIN/CSSL
SNOW STUDY SITE MAINTENANCE SCHEDULE

<u>DAILY</u>

- -check EZ logger
- -record total snow depth from reference stake (measured from 0 at ground level)
- -if it has snowed less than 3 cm, take no measurement, record "trace" and <u>do not</u> turn snowboards
- -if it has snowed more than 3 cm do all of the following:
- -take 1 chemistry sample from each of two boards
- -take density measurements from each of 3 boards
  - <3 cm. snow...no measurement
  - 3-10 cm snow...one mass det'n that is the sum of several cores
  - 10-35 cm snow...two density cores
  - >35 cm snow...one density profile with cutter
- -turn daily boards
- -place samples in freezer

<u>WEEKLY</u>

- -do all of daily sampling procedure
- -take 1 chemistry sample from each of 2 weekly boards
- -take 2 density cores or profiles from each of two boards (same as above)
- -turn 2 weekly snowboards
- -exchange two bulk (tube) collectors (even if empty)
- -change rain gauge charts
- -place bulk collectors and previous week's daily samples in lab to melt
- -when sample have melted and come to room temp.: perform analysis, repackage and refreeze

<u>BIWEEKLY</u>

- -do all daily sampling procedure
- -do all weekly sampling procedure
- -do a snow pit to the ground: 2 density profiles, 2 chemistry profiles
- -exchange EZ logger DSP

Appendix B. Field Worksheets.

ARB – SNOW COLLECTION EXPERIMENT
CHEMISTRY DATA FORM

Site:______ Date:______ Time:________ Who:________

ph meter:____________________ calibrated? y/n buffer temps:___________°C

conductivity meter:_____________________ cell cnst. k=______

conductance std: conductivity__________µmhos temperature_______°C

field audits: high, conductivity______µmhos temperature_______°C
low, ______µmhos _______°C
ph ________ temperature ______°C corrected to 25°C? y/n

SNOW TUBES

	date	time
start:	____________	______________
stop:	____________	______________

sample ID #: ____________ volume:________mls ÷ ____cm^2 = ______cm SWE

ph:____________ temperature:__________°C corrected to 25°C? y/n

conductivity:__________ µmhos temperature:_____°C
(report real conductivity and temp., do not correct to 25°C)

sample ID #: ____________ volume:________mls ÷ ____cm^2 = ______cm SWE

ph:____________ temperature:__________°C corrected to 25°C y/n

conductivity:__________ µmhos temperature:_______°C

PIT/BOARD SAMPLES

sample ID#: ____________ conductivity:__________µmhos temp.________°C

ph:____________ temperature:__________°C corrected to 25°C y/n

....

sample ID#: ____________ conductivity:__________µmhos temp.________°C

ph:____________ temperature:__________°C corrected to 25°C y/n

....

sample ID#: ____________ conductivity:__________µmhos temp.________°C

ph:____________ temperature:__________°C corrected to 25°C y/n

....

sample ID#: ____________ conductivity:__________µmhos temp.________°C

ph:____________ temperature:__________°C corrected to 25°C y/n

....

NOTES:

ARB - SNOW COLLECTION EXPERIMENT

SNOWBOARD WORKSHEETS (≤ 35cm) Winter 1986 - 1987

Site: **Date:** **Time:**_____ **(PST/PDT)** **Who:**

Corer # Core diameter (cm) Corer Area $(cm)^2$

ID. #	Sample HT. (cm) above board	Corer (cm^2) Area	wt. (g)	Density (gm/m^3)	SWE (cm)	Chemistry		
						# cores	net wt.	S #
	Ave. HT. (cm)			Ave. SWE (cm)				
	Ave. HT. (cm)			Ave. SWE (cm)				
	Ave. HT. (cm)			Ave. SWE (cm)				
	Ave. HT. (cm)			Ave. SWE (cm)				
	Ave. HT. (cm)			Ave. SWE (cm)				

ARB - SNOW COLLECTION EXPERIMENT

SNOWBOARD TOTALS Winter 1986 - 1987

Site: **Board ID. #:**

DATE	Snowfall (m) event	 total	Ave. Density (kg/m^3)	SWE (m) event	 total	PVC BULK sample #	 volume	NOTES

ARB - SNOW COLLECTION EXPERIMENT
SNOWPIT/BOARD (> 35 cm) DATA WORKSHEETS Winter 1986 - 1987

Site: Date: Time:______ (PST/PDT) Who: PIT ID. #

Cutter # Cutter Vol. (cm^3)

Ht above ground (cm)		Temp	wt.	Density	SWE	Ht above ground (cm)		Chemistry	Sample
TOP	BOTTOM	(C)	(g)	(g/m^3)	(cm)	TOP	BOTTOM	net wt. (g)	#

Snowpit Depth (cm)	Average Snowpit Density (gm/cm^3): Total SWE/Snowpit Depth)	Total SWE (cm):

CSSL DATA FROM ARB SNOW PIT

LOCATION	DATE	TIME	OBSERVER	HEIGHT ABOVE SOIL (CM)	SNOW		"DENOTH"		SNOW WETNESS (% VOL)
					DENSITY (GM/CC)	TEMP °C	AIR	SNOW	

ARB SNOW COLLECTION STUDY

Sample Description Worksheet

Sample Designation	Depth cm	Density gm/cc	SWE cm	Bulk Tube Vol.--ml	Where Appropriate		
					pH	Conductivity	Al

Appendix C. Evaluation of Chemical Contamination Derived from Filters.

The quality assurance program at UCSB included an evaluation of chemical contamination in different kinds of filters. Tests of ion leaching from Nucleopore polycarbonate, Micro Separations Inc. (MSI) polypropylene, Corning disposable nylon filter unit, Gelman-Acrodisc Versapor, and MSI-Cameo-IV Nylon 66, and Gelman A/E binder-free glass fiber filters were performed (Tables A1 through A7).

While desorption of cations and anions from Nucleopore polycarbonate and Corning nylon membranes was negligible (Tables A1 and A2), other membrane materials had detectable levels (Tables A3, A4 and A5). Glass fiber filters leached significant quantities of ions into the filtrate (Tables A6 and A7). After rinsing in the filter holder with 250 ml of deionized water (specific conductance < 1 uS cm^{-1}, 25°C), Gelman A/E glass fiber filters continued to desorb Ca^{2+}, Na^{+}, and F^{-} ions (Tables A6 and A7). High leachable ion contents of Gelman A/E filters have previously been documented (Jay 1985).

Our results indicate that prerinsing any of the above membrane filters by flushing ca. 100 ml of deionized water through the filter in the holder is sufficient to reduce leachable ions to below detection limits. UCSB uses a Nuclepore, 47-mm, luer-tipped, filter holder to contain the filter. This type of housing results in a negligible unexposed portion of a filter during rinsing and filtration. Water samples are processed through a 140 cc-syringe attached to the filter holder. Typically, 60-125 ml of filtered water is collected for chemical analyses.

A disadvantage of membranes of 0.45-micron nominal pore retention is their low flow rates; the MSI polypropylene filter offered the least resistance. The Cameo-IV (MSI) is a self-contained, disposable unit with an effective filtration area of 15 cm^2 and reasonable flow rate. Since there is strong evidence that immediate filtration of precipitation samples is requisite to ensure ionic stability and prevention of adsorption - desorption reactions (Peden and Skowron, 1978), Cameo-IV individually packaged filters could be used for prompt filtration in the field with minimal chance of contamination from extraneous sources. With the Cameo-IV a volume of about 100 ml of low-particulate water could be filtered, after a prerinse with 100 ml of deionized water. For larger volumes containing more particulates, hand-vacuum filtration through a Corning 25935 disposable filter unit which contains a 47-mm, 0.45-micron nylon filter and reclosable reservoir would be more suitable.

Table A1. Desorption of cations and anions from Nuclepore polycarbonate filters (47-mm diameter, 0.4-micron pore size) determined in sequential leachates of deionized water. Three 30-ml aliquots of Milli-Q water (specific conductance ≤1 uS cm^{-1}, 25°C) were filtered sequentially through each of four Nuclepore (N) filters. Leachates were analyzed for ammonium by the indophenol colorimetric method, for cations by atomic absorption spectrophotometry (direct aspiration, air-acetylene), and for anions by ion chromatography. Data are tabulated in ueq L^{-1} and undetectable levels are designated by u. Method detection limits for NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} are 0.3, 1.0, 0.3, 0.5, 0.5, 0.4, 0.2 and 0.4 ueq L^{-1}, respectively.

Filter	Aliquot	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
N-1	1	u	u	u	u	u	u	u	1.4
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
N-2	1	u	u	u	u	u	u	u	u
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
N-3	1	0.3	u	u	u	u	u	u	u
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
N-4	1	0.4	u	u	u	u	u	u	u
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u

Figure 4.7. (continued)

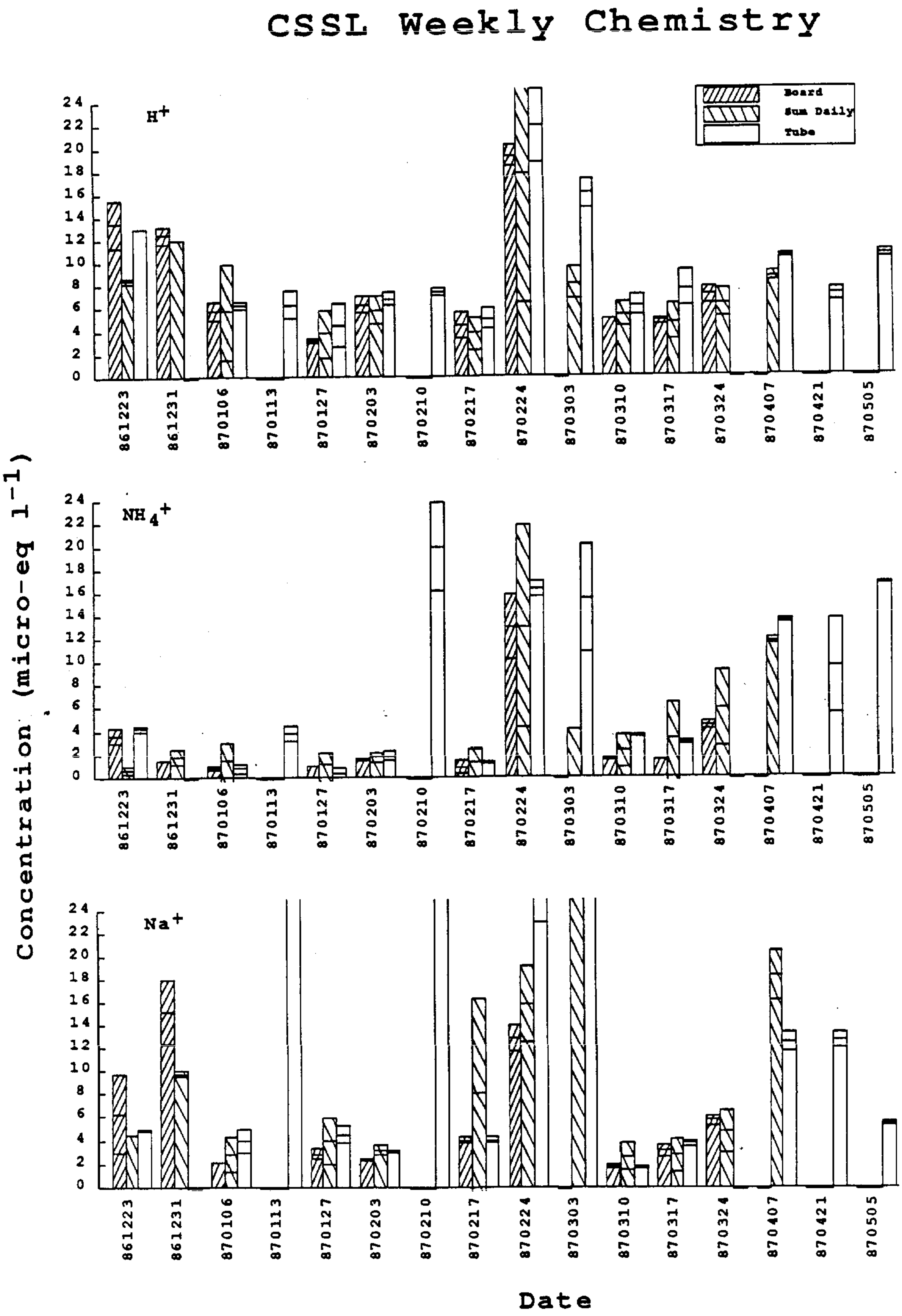

Figure 4.7. (continued)

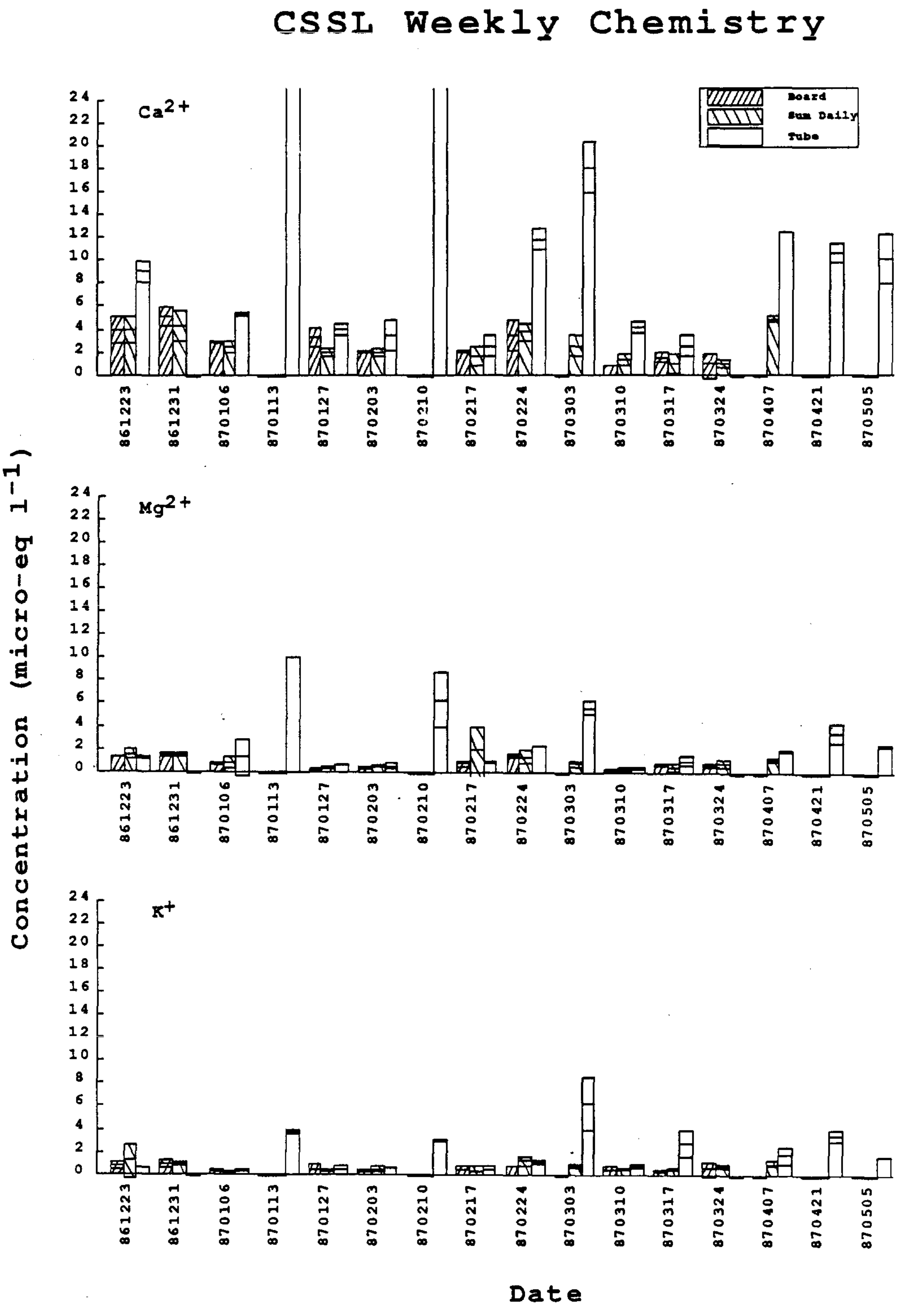

Table A2. Desorption of cations and anions from Corning 25935 disposable filter units (47-mm, 0.45-micron nylon filter). After a pre-rinse with 300 ml Milli-Q water (specific conductance $\leq$ 1 uS cm^{-1}, 25°C), 100 ml of Milli-Q water was filtered and analyzed for ammonium by the indophenol colorimetric method, for cations by atomic absorption spectrophotometry (direct aspiration, air-acetylene), and for anions by ion chromatography. Data are tabulated in ueq L^{-1} and undetectable levels are designed by u. Method detection limits for NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} are 0.3, 1.0, 0.3, 0.5, 0.5, 0.4, 0.2, and 0.4 ueq L^{-1}, respectively.

Filter	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
C-1	u	u	u	u	u	u	u	u
C-2	u	u	u	u	u	u	u	u
C-3	u	u	u	u	u	u	0.2	u
C-4	u	u	u	u	u	u	0.2	u
C-5	u	u	u	u	u	u	0.2	u
C-6	u	u	u	u	u	u	0.2	u
C-7	u	u	u	u	u	u	0.2	u
C-8	u	u	u	u	u	u	0.2	u

Table A3. Desorption of cations and anions from Micron Separations, Inc. polypropylene filters (47-mm diameter, 1-micron pore size) determined in sequential leachates of deionized water. Five 50-ml aliquots of Milli-Q water (specific conductance ≤ 1 uS cm^{-1}, 25°C) were filtered sequentially through each of four polypropylene (PP) filters. Leachates were analyzed for ammonium by the indophenol colorimetric method, for cations by atomic absorption spectrophotometry (direct aspiration, air-acetylene), and for anions by ion chromatogrphy. Data are tabulated in ueq L^{-1} and undetectable levels are designated by u. Method detection limits for NH_4^+, Ca^{2+}, Mg^+, Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} are 0.3, 1.0, 0.3, 0.5, 0.5, 0.4, 0.2, and 0.4 ueq.L^{-1}, respectively.

Filter	Aliquot	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
PP-1	1	u	u	u	u	0.6	0.9	u	u
	2	0.3	u	u	u	0.8	0.9	u	u
	3	u	u	u	u	u	-	u	u
	4	u	u	u	u	u	0.7	u	u
	5	u	u	u	u	u	1.1	u	u
PP-2	1	u	u	u	u	1.0	1.4	u	u
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	0.6	u	u
	5	u	u	u	u	u	u	u	u
PP-3	1	u	u	u	0.3	0.6	-	u	u
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	u	u	u
	5	u	u	u	u	u	u	u	u
PP-4	1	u	u	u	u	u	0.4	u	u
	2	u	u	u	u	u	0.5	u	u
	3	u	u	u	u	u	1.2	u	u
	4	u	u	u	u	u	1.0	u	u
	5	u	u	u	u	u	u	u	u

Table A4. Evaluation of chemical contamination in sealed Gelman Acrodisc filters (Versapor, membrane). Three sequential 30-ml aliquots of Milli-Q water (≤1 uS cm^{-1}, 25°C) were passed through each of four Acrodiscs. Each 30-ml aliquot was analyzed for cations and anions. Data are in ueq L^{-1} and undetectable levels are designated by u. Method detection limits for Ca^{2+}, Mg^{+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, and SO_4^{2-} are 1.0, 0.3, 0.5, 0.5, 0.4, 0.4, and 0.4, respectively.

Acrodisc	Aliquot	Ca^{2+}	Mg^{+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
1	first	1.5	u	u	u	1.0	u	0.6
1	second	1.3	u	u	u	0.5	u	u
1	third	1.6	u	u	u	0.5	u	u
2	first	1.0	u	u	u	0.9	u	u
2	second	1.0	u	u	u	0.5	u	u
2	third	1.0	u	u	u	0.6	u	u
3	first	u	u	u	u	0.5	u	u
3	second	1.0	u	u	u	0.4	u	u
3	third	1.3	u	u	u	u	u	u
4	first	1.3	u	u	u	u	u	u
4	second	1.0	u	u	u	u	u	u
4	third	1.0	u	u	u	u	u	u

Table A5. Desorption of cations and anions from Micron Separations, Inc. Cameo-IV Nylon 66 filters (15-cm^2 filtration area, 0.45-micron pore size) determined in sequential leachates of deionized water. Five 50-ml aliquots of Milli-Q water (specific conductance ≤1 uS cm^{-1}, 25°C) were filtered sequentially through each of four Cameo (CAM) filters. Leachates were analyzed for ammonium by the indophenol colorimetric method, for cations by atomic absorption spectrophotometry (direct aspiration, air-acetylene), and for anions by ion chromatography. Data are tabulated in ueq L^{-1} and undetectable levels are designated by u. Method detection limits for NH_4^+, Ca^{2+}, Mg^+, Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} are 0.3, 1.0, 0.3, 0.5, 0.5, 0.4, 0.2, and 0.4 ueq L^{-1}, respectively.

Filter	Aliquot	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
CAM-1	1	u	1.0	0.2	0.8	0.3	1.6	u	1.3
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	u	u	u
	5	u	u	u	u	u	u	u	u
CAM-2	1	u	1.6	0.2	0.9	0.4	2.3	u	1.2
	2	u	1.0	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	u	u	u
	5	u	u	u	u	u	u	u	u
CAM-3	1	u	u	0.2	2.3	0.3	6.4	u	2.5
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	u	u	u
	5	u	u	u	u	u	u	u	u
CAM-4	1	u	u	u	0.9	0.5	3.0	u	1.7
	2	u	u	u	u	u	u	u	u
	3	u	u	u	u	u	u	u	u
	4	u	u	u	u	u	u	u	u
	5	u	u	u	u	u	u	u	u

Table A6. Desorption of cations and anions from Gelman A/E 47-mm, glass-fiber filters determined in sequential leachates of deionized water. Five 50-ml aliquots of Milli-Q water (specific conductance <1 uS cm^{-1}, 25^{o}C) were filtered sequentially through each of two A/E filters from different lots of filters. Leachates were analyzed for cations by atomic absorption spectrophotometry (direct aspiration, air-acetylene) and for anions with a Dionex 2010i ion chromatograph. Data are tabulated in ueq L^{-1} and undetectable levels are designated by u. Method detection limits for Ca^{2+}, Mg^{+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, and SiO_2 are 1.0, 0.3, 0.5, 0.5, 0.5, 0.4. 0.4, and 0.4 ueq L^{-1}, respectively.

Lot No.	Specific Conductance uS cm^{-1}	Ca^{2+}	Mg^{+}	Na^{+}	K^{+}	Al^{3+}	Cl^{-}	F^{-}	NO_3^{-}	SO_4^{2-}	SiO_2
749	8.9	4.7	1.9	58.1	0.6	u	2.8	1.3	u	0.9	0.4
	2.2	1.6	1.0	8.6	u	u	1.7	0.5	u	u	u
	2.2	1.1	0.9	5.0	u	u	u	u	u	u	u
	2.0	1.0	0.9	2.7	u	u	0.5	u	u	u	u
	2.0	u	0.7	1.4	u	u	u	u	u	u	u
749	12.6	6.5	2.7	85.9	0.6	u	4.0	1.2	u	1.0	0.7
	2.7	1.0	1.1	8.7	u	u	u	0.5	u	u	u
	1.9	1.0	0.8	1.7	u	u	u	u	u	u	u
	1.9	1.0	0.8	2.8	u	u	u	u	u	u	u
	1.9	1.0	0.7	0.7	u	u	u	u	u	u	u
2664	8.7	4.6	2.1	59.5	0.6	u	5.1	1.3	u	0.5	1.8
	4.2	2.0	1.4	21.9	u	u	2.1	0.7	u	u	0.6
	3.7	1.6	1.4	19.9	u	u	2.4	u	u	u	3.4
	1.6	1.1	1.2	4.8	u	u	u	u	u	u	u
	1.1	1.0	1.0	1.5	u	u	u	u	u	u	u
2664	11.6	4.7	2.5	80.6	u	u	7.0	1.7	u	u	2.6
	2.2	1.1	1.2	21.9	u	u	u	0.5	u	u	u
	2.4	1.0	1.2	19.9	u	u	1.0	u	u	u	0.7
	1.3	1.1	1.0	4.8	u	u	u	u	u	u	u
	1.2	1.0	0.8	1.5	u	u	u	u	u	u	u

Table A7. Desorption of cations from Gelman A/E 47 mm glass-fiber filters determined in sequential leachates of deionized water. Five 50-ml aliquots of Milli-Q water (specific conductance ≤ 1 uS cm^{-1}, 25^{o}C) were filtered sequentially through each of two A/E filters from different lots of filters. Additionally, the first and last leachates were filtered again through a Nuclepore 0.22-um membrane, 47-mm filter. Leachates were analyzed for cations by atomic adsorption spectrophotometry (direct aspiration, air-acetylene) and for anions with a Dionex 2010i ion chromotograph. Data are tabulated in ueq L^{-1} and undetectable levels are designated by u. Levels of Ca^{2+} and Na^+ in re-filtered leachates are in parentheses. Method detection limits for Ca^{2+}, Mg^+, Na^+, and K^+ are 1.0, 0.3, 0.5 ueq L^{-1}, respectively.

Na^+ Lot No. K^+	Aliquot	Ca^{2+}	Mg^+		
1498	1	4.7 (3.3)	2.2	37 (38)	0.6
	2	1.7	1.2	3.6	u
	3	1.3	1.0	4.0	u
	4	1.3	1.0	2.0	u
	5	1.0	0.6	1.7 (1.4)	u
1498	1	6.6 (4.6)	2.2	46 (48)	0.6
	2	1.3	1.2	5.7	u
	3	1.0	1.2	2.7	u
	4	1.0	0.7	1.9	u
	5	1.0 (1.0)	0.7	1.4 (1.3)	u
2664	1	2.8 (2.3)	1.6	39 (39)	0.6
	2	1.0	1.0	3.0	u
	3	1.0	1.0	4.0	u
	4	u	0.5	1.4	u
	5	u (u)	0.5	1.4 (1.4)	u
2664	1	1.7 (1.6)	1.3	34 (36)	u
	2	1.0	1.2	7.6	u
	3	u	1.2	1.7	u
	4	u	0.5	1.4	u
	5	u (u)	0.5	1.4 (1.6)	u