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Chemical Content of Snow and Effect of Melting on Cascade Mountain Lakes

Abstract

Sulfate and nitrate content in snow cores collected in the spring of 1982 indicated that deposition of those ions is greater in the Cascade Mountains, downwind from the Seattle-Tacoma urban-industrial area, than in the Olympic Mountains. Snowmelt and iceout did not result in episodes of low pH and alkalinity in the three high lakes sampled. The minimum pH was 5.8 and neither pH nor alkalinity showed a seasonal trend following iceout, although specific conductance did decrease slightly. The lack of an acidification episode was not surprising because the pH of snow from a site near the studied lakes averaged 5.3. The snow was richer in cations than had been reported earlier in precipitation from the Cascades, even though sulfate concentrations were similar.

Chemical stratification was apparent in the surface 20 m layer of the lower elevation lake, while the upper 50 m of the highest elevation lake was similar in alkalinity content to that observed in snow. The intermediate elevation lake showed a slight tendency to stratify in the upper 50 m. These observations suggest that snowmelt water does not mix with the whole lake volume in these deep lakes with relatively low watershed:lake surface area ratios and low flushing rates as might be expected in lakes with more extreme characteristics.

Introduction

Washington's Cascade Mountain lakes have been classified as some of the most sensitive waters in the United States (Omernick and Powers 1982). Their low buffering capacity is due to the granitic and basaltic bedrock and thin soil development surrounding many of these high elevation lakes. Many have relatively small watersheds, and their basins are steep-sided. Thus, they would be expected to respond rather quickly to even small increases in acid deposition.

The acidity of precipitation reaching the Cascades is greater than might be expected normally. Logan (1980) reported a mean annual pH of 4.66 in precipitation collected at Stampede Pass and, more recently, Logan *et al.* (1982) reported a mean of 4.7 at Snoqualmie Pass for the first half of 1981. Dethier (1979) reported a mean value of 4.8 in an area of the Cascades, north of Stevens Pass. Wasem (1982) has observed even lower values (4.3) for the North Cascades. Powers and Rambo (1981) summarized existing precipitation data.

Some of the acidity in precipitation falling on the Cascades no doubt originates from anthropogenic sources in the Puget sound lowlands (Logan *et al.* 1982). However, there are natural sources also. Mount Saint Helens released nearly three times as much sulfur dioxide, for three months following its eruption in May 1980, as normally originates from anthropogenic sources (PSAP 1980). Emissions had decreased considerably

by 1981 (Casadevall *et al.* 1981). Although the normal pH of precipitation saturated with carbon dioxide is 5.6, sulfate aerosols also exist naturally and, when scavanged by precipitation, can result in lower than "normal" pH. Charlson and Rodhe (1982) have suggested that without anthropogenic sources the precipitation pH could range between 4.5 and 5.6. They suggest that productive parts of the ocean may be a source for natural acidity.

Thus, there is the question of the relative contribution of anthropogenic and natural sources to the acidity of precipitation reaching the Cascades. Also, there are the associated questions of whether there is or has been detectable acidification of any lakes and what the nature of response would be in these lakes to incremental increases in acid deposition. Results reported here are based on the chemical content of snow cores collected in the spring of 1982 in the Olympic and Cascade Mountains and subsequent observations on changing chemical content of three highly sensitive Cascade lakes following iceout. The lakes are Angeline, Big Heart, and Copper and lie in the Alpine Lakes Wilderness area at 1219 to 1555 m elevation between Snoqualmie and Stevens Passes. The objectives were to 1) determine if deposition of acid and the associated ions, sulfate and nitrate, is greater in the Cascades than the Olympics, and 2) determine if there is an episodic effect of decreased alkalinity and pH in the lakes following iceout. Because weather fronts move from west to east across Washington, it was assumed that most of the differences in acidity and ionic composition of snow collected in the Olympics and Cascades would be due to additions from the Seattle-Tacoma, urban-industrial area to the largely natural composition originating over the ocean.

Methods and Materials

Six cores were collected, three at each of two sites, one in the Cascade and one in the Olympic Mountains, during the spring of 1982. Cores were collected with a clean, anodized aluminum, standard core (4.1 cm diameter) from the Minotaur Lake basin (1700 m elevation) in the Cascades, 11 km north of Stevens Pass, and from the Morganroth Lake basin (1258 m elevation) in the Olympics (Fig. 1). These basins were selected for their high elevations and ease of access by helicopter.

Because mechanized equipment was not allowed in the wilderness area, it was necessary to locate the snow coring site in the Cascades where access was allowed, and at a similar high elevation and as near as possible to the Alpine Lakes Wilderness area lakes where lake chemical content was monitored. The Minotaur Lake basin lies only 30 km northeast of the sampled lakes (Fig. 1), and since most storms move across the Cascades from the southwest (Vong and Waggoner 1983), the deposition of acid in the Minotaur Lake basin would be expected to be rather similar to that near the sampled lakes.

Snow core depth ranged from 3.7 to 7.0 m at the Cascade site on 19 March 1982 and 2.7 to 4.9 m at the Olympic site on 1 April 1982. At each site, cores were collected from the lake surface, on the shore and about 50 m from the lake shore in a meadow area. The deepest snow cover was on the meadow at both sites.

Cores from the Cascades were melted and analyzed for major cations and anions in addition to pH and specific conductance. Samples for alkalinity, pH, and specific conductance were analyzed within a day or two after returning to the laboratory. Cores from the Olympic site were split to determine if a concentration effect had occurred in the lower half of the snow pack through the thawing-freezing process, which is prevalent

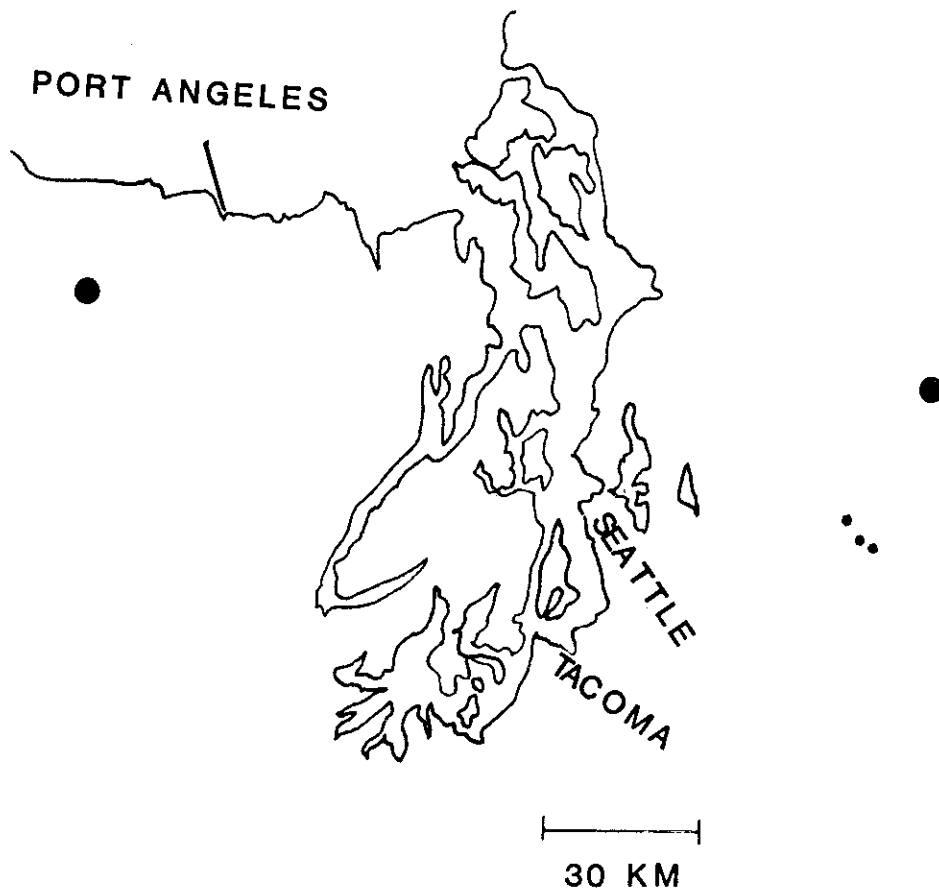


Figure 1. Western Washington showing the locations of alpine lakes (small circles) and snow core sites (large circles).

in Washington's mountain areas. There was no difference detectable in the constituents, so results are reported on the composite cores.

The anions, chloride, sulfate, and nitrate were determined by an ion chromatograph using a Dionex 3 x 500 mm standard anion exchange suppressor column. Bicarbonate was determined by alkalinity titration using the conductometric method (Golterman 1969, pp. 32 and 141). Precision for sulfate and chloride was ± 10 percent and ± 25 percent for nitrate. The alkalinity titration was precise to about ± 5 percent. The cations sodium calcium, magnesium, and potassium were determined with an Instrumentation Laboratory model 353 atomic absorption unit with a precision of about ± 10 percent. An Exttech model 609 digital meter was used to determine pH using a dilute buffer. Comparison of the pH of snowmelt and lake samples determined in the field with two Exttech meters ($n=11$) showed a mean deviation of ± 0.05 pH units, while comparison with two bench scale meters in the laboratory ($n=7$) showed a mean deviation of ± 0.12 units. Specific conductance was determined at $24 \pm 0.5^\circ\text{C}$ with a Barnstead model PM 70 meter.

Lake Samples

Samples were collected on three occasions in Big Heart Lake (1386m) and Copper Lake (1208 m); 23 July, 11 August, 24 August 1982. Angeline Lake was sampled on 23 July and 24 August. Samples were collected from a rubber raft at depths of 0, 5, 10, 20, and 50 m in each lake. Prior to filling, each bottle had been acid washed and thoroughly rinsed and was rinsed again thoroughly with lake water. The bottles were filled completely and capped. An additional five samples, one from each depth, were collected for subsequent pH determination on shore.

The constituents determined and associated methods were the same as those used for snow. Alkalinity was also determined by the Gran method on some samples (Gran 1952). Results were essentially the same as with the conductometric method, mean \pm SD for five replicates of a test sample were 101 ± 3.7 and $101 \pm 1.4 \mu\text{eq l}^{-1}$ for the Gran and conductometric methods, respectively. The change in the slope of specific conductance with added acid proved to be a very precise and relatively rapid determination of alkalinity in those poorly buffered waters. As noted earlier, the precision at such low alkalinities ($<100 \mu\text{eq l}^{-1}$) is at least ± 5 percent.

TABLE 1. Ionic content of snow cores collected at three sites on and near Minotaur Lake in the Cascade Mountains and Morganroth Lake in the Olympic Mountains, Washington, on March 19 and April 1, 1982, respectively. Values are in $\mu\text{eq l}^{-1}$.

Lake and Location	pH	H ⁺	NH ₄ ⁺	Na ⁺	Ca ⁺⁺	Mg ⁺⁺	K ⁺	SO ₄ ⁻	NO ₃ ⁻	Cl ⁻	HCO ₃ ⁻	Σ^-	Σ^+
Minotaur L. (CASCADES)													
Lake Surface	5.2	6.3	3.5	19.2	23.9	5.7	6.9	16.0	5.5	20.6	20.1	65.5	62.2
Shoreline	5.4	4.0	6.0	23.6	30.4	5.0	10.2	12.6	11.2	20.7	26.2	80.6	70.7
Meadow	5.4	4.0	7.0	12.3	15.1	2.6	5.6	6.4	5.2	16.8	20.7	46.6	49.1
Morganroth (OLYMPICS)													
Lake Surface	5.6	2.5	4.7	15.6	7.7	3.1	4.6	3.8	1.1	10.0	17.3	28.2	33.1
Shoreline	5.5	3.2	3.8	13.7	12.4	2.6	2.0	6.4	0.93	11.7	16.9	37.7	35.9
Meadow	5.4	4.0	7.1	13.1	3.0	5.1	3.8	3.0	0.62	10.6	17.2	36.1	31.5

Snow Cores

Results from the cores are shown in Table 1. The differences in pH among all cores are only slight and within the error of determination. However, the sulfate content in the three Cascade cores was about three fold greater than that in cores from the Olympics. Nitrate, on the other hand, was eight fold greater in the Cascade snow. Calcium in the Cascade cores was substantially higher than in those from the Olympics (about $15 \mu\text{eq l}^{-1}$), which could have been responsible for buffering against a lower pH in Cascade snow in spite of more nitrate and sulfate.

The mean values for sulfate and nitrate in the Cascade cores (respectively 11.7 and $7.3 \mu\text{eq l}^{-1}$) are similar to six-month means in bulk precipitation collections at Snoqualmie pass reported by Logan *et al.* (1982). They found mean concentrations of 14.8 and $8.6 \mu\text{eq l}^{-1}$ for sulfate and nitrate, respectively.

The charge balance showed reasonably good accounting of the ions. The average cation:anion ratios for the Cascade and Olympic cores, respectively, were 1.05 and 1.12.

Nevertheless, Liljestrand and Morgan (1979) have found that the calculated pH from the charge balance can be in error by nearly ± 0.5 units.

TABLE 2. Alkalinity, specific conductance and pH determined at five depths in the top 50 m of three lakes in the Alpine Lakes Wilderness Area, Washington, during 1982.

Lake	pH						Conductivity			Alkalinity		
	7/23		8/11		8/24		$\mu\text{mhos cm}^{-1}$			$\mu\text{eq l}^{-1}$		
	Field	Lab	Field	Lab	Field	Lab	7/13	8/11	8/24	7/12	8/11	8/24
ANGELINE												
Surface	6.4	5.9	—	—	5.8	5.9	8.7	—	4.4	26.7	—	16.7
5 m	6.5	5.9	—	—	5.8	5.9	7.2	—	4.3	24.0	—	16.6
10 m	6.4	5.8	—	—	5.7	5.8	5.2	—	3.9	25.1	—	16.8
20 m	6.3	5.9	—	—	5.9	5.9	4.9	—	3.9	17.3	—	17.1
50 m	6.3	5.9	—	—	5.8	5.8	5.1	—	4.9	19.7	—	19.3
BIG HEART												
Surface	6.4	5.9	6.3	5.8	6.0	6.0	5.9	5.6	5.0	23.4	22.0	24.0
5 m	5.6	5.9	6.3	6.0	6.0	5.9	7.2	8.0	5.0	33.3	21.7	25.3
10 m	6.2	6.0	6.2	5.9	5.9	5.9	5.3	5.2	4.5	30.0	29.7	30.3
20 m	6.2	5.7	6.3	5.8	6.0	5.9	9.1	7.6	4.3	10.1	17.9	24.3
50 m	6.2	6.0	6.2	5.9	5.9	6.0	6.6	5.0	4.5	30.4	38.1	37.3
COPPER												
Surface	6.2	6.4	6.2	6.3	6.6	6.5	11.0	10.9	8.9	70.4	70.9	62.1
5 m	6.3	6.5	6.5	6.5	6.6	6.5	13.3	14.7	8.2	68.4	69.7	71.8
10 m	6.4	6.6	6.6	6.4	6.6	6.4	14.3	12.9	11.0	88.3	89.7	92.7
20 m	6.3	6.6	6.5	6.5	6.6	6.6	18.1	19.7	14.1	126.7	151.7	160.1
50 m	6.5	6.6	6.6	6.7	6.4	6.5	33.5	25.9	26.9	300.4	329.7	333.7

Lake Quality

Results from sampling the three lakes at three different times during the summer following iceout are shown in Table 2. Minimum pH was about 5.8, which occurred in Angeline Lake about a month after iceout. Values were slightly higher in Big Heart and 0.5 to 0.6 higher in Copper Lake. Field determinations of pH in Angeline and Big Heart gave higher values than laboratory determinations by about 0.2 to 0.5 units, except for the last samples. The agreement between field and laboratory measurements was good for Copper Lake. Alkalinity and specific conductance, as well, were higher in Copper than the other two lakes. Cation-anion balances for the three lakes are shown in Figure 2.

A consistent seasonal trend in alkalinity and pH was not apparent in any lake, although specific conductance values were lower in the three lakes at all depths in late summer compared to those observed earlier right after iceout. The means of the five depth samples (Table 2) changed during the summer from 6.2 to 4.3 $\mu\text{mhos cm}^{-1}$ in Angeline, from 6.8 to 6.3 to 4.7 in Big Heart, and from 18.0 to 16.8 to 13.8 in Copper. Except at Copper, there was no stratification of the concentration with depth.

An exception to this lack of trend in alkalinity and pH during the summer was in Angeline, where alkalinity in the upper 10 m did decrease with time, and an anomalously low alkalinity occurred at 20 m in Big Heart in the earliest samples. Overall, however, alkalinity values determined in the upper 10 m (six values in Angeline and nine each in Big Heart and Copper) varied rather consistently in the three lakes with means and standard deviations of 21.0 ± 4.8 , 26.6 ± 4.2 , and $76.0 \pm 11.1 \mu\text{eq l}^{-1}$ for Angeline,

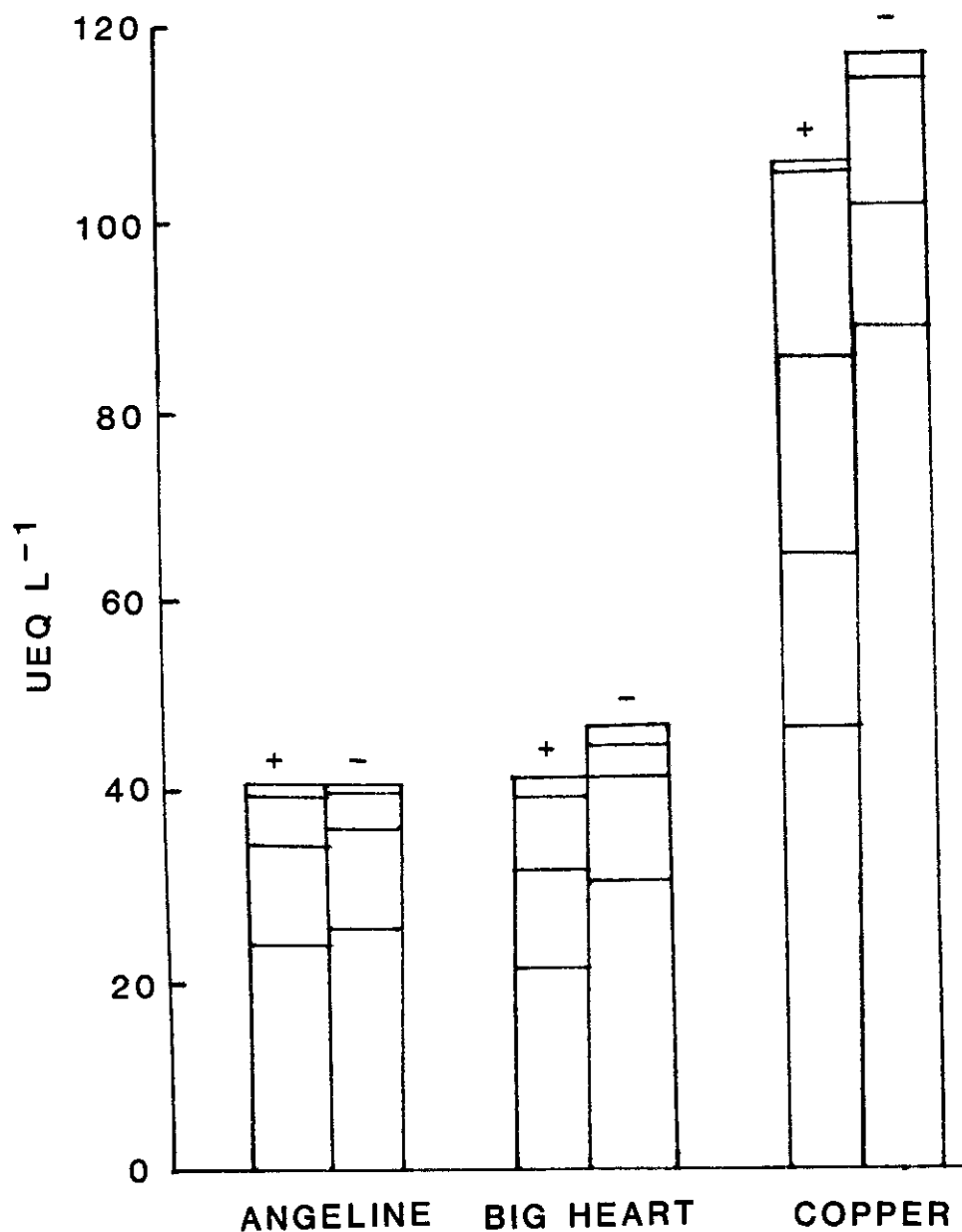


Figure 2. Cation-anion balance for three Alpine Lakes Wilderness Area lakes, 23 July 1982. Ascending order: cations—Ca, Na, Mg, K, H; anions—HCO₃, SO₄, Cl, NO₃.

Big Heart, and Copper, respectively; this is an average deviation of 18 percent. Considering that the analytical precision is ± 5 percent, an expected inlake/sampling variability in the surface waters may be about ± 13 percent.

Chemical stratification was pronounced in the upper 50 m in Copper Lake, but this was not the case in Angeline and was less apparent in Big Heart, the two higher eleva-

tion lakes. Figure 3 shows mean bicarbonate content with depth in the three lakes. Concentrations at depth in Copper Lake were consistently three to four times greater than those in the upper 10 m. Concentrations were rather uniform in Angeline, but except for the consistently lower values at 20 m, alkalinity tended to increase with depth in Big Heart, showing a greater tendency for stratification as in Copper. The lakes are all deeper than the sampled 50 m; Copper, Big Heart, and Angeline, respectively, have maximum depths of 104, 168, and 155 m (Dethier *et al.* 1979).

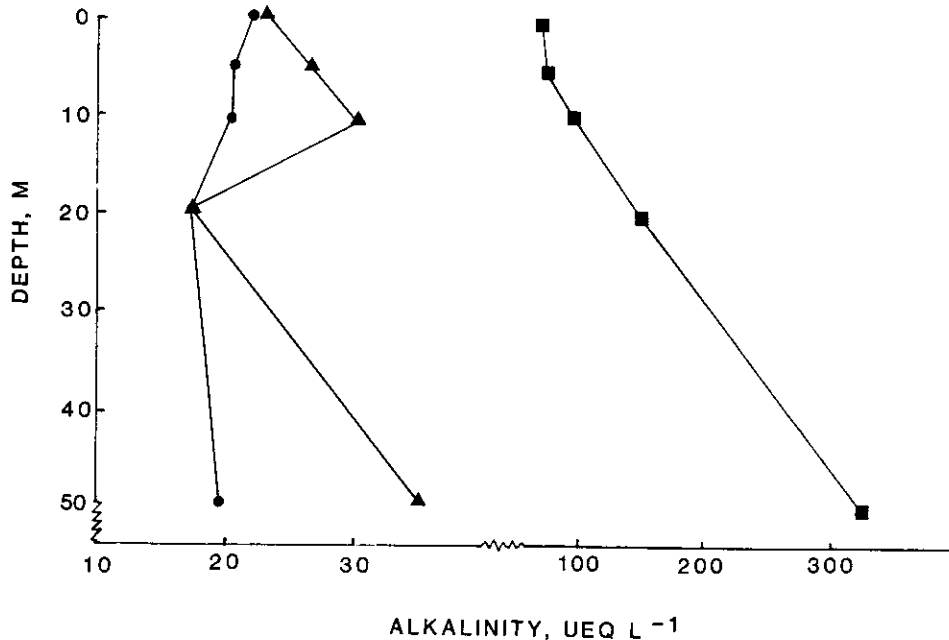


Figure 3. Distribution of alkalinity (HCO_3^-) with depth in the upper 50 m of Angeline (circles), Big Heart (triangles) and Copper (squares) Lakes during the summer of 1982. Values are means of two samples in Angeline and three each from Big Heart and Copper.

Discussion

Deposition of sulfate and nitrate appears to be greater in the Cascades downwind of the Seattle-Tacoma, urban-industrial area, than in the Olympics. Admittedly, this indication is based on only one set of three cores from one site in each area. However, the mean concentrations of sulfate and nitrate from the Cascade cores were similar, although 21 and 15 percent lower, than mean six-month values reported in precipitation from Snoqualmie Pass in 1981 by Logan *et al.* (1982). Their six-month mean sulfate concentration of 14.8 ueq l^{-1} from January through July, 1981, indicates that the rate of sulfate deposition was about 15 kg ha^{-1} during that period. About 10 percent of the strong acid content was due to nitrate and 60 percent to non-marine sulfate. Their mean precipitation pH was 4.7 while that from 1982 snow cores was 5.3. This comparison of the 1981 precipitation results of Logan *et al.*, with the snow content from 1982, is not entirely valid because Mount Saint Helens was still discharging significant amounts of sulfur dioxide in 1981, which no doubt had subsided more by the time the 1982 snow cores were collected.

Water sampling followed iceout in three lakes in the Alpine Lakes Wilderness area, about 30 km southwest of and at a similar elevation as the snow core site, did not reveal an episode of low pH and low alkalinity. The minimum pH observed, determined under laboratory conditions, was 5.8. Values were about 0.5 units higher in the lower elevation lake. It is not clear why field determinations on the first two occasions were 0.2 to 0.5 pH units higher than those measured in the laboratory. However, strong peaks in photosynthesis were observed to occur following iceout in another high Cascade lake (Hendrey and Welch 1974). Even modest photosynthetic rates could significantly raise pH in such poorly buffered waters. The discrepancy between field and laboratory pH determinations was in fact greater after iceout than later in the summer, which tends to support this hypothesis.

Considering that the pH of the snow may have been near 5.3, it was not surprising that a definite iceout episode did not occur. If the pH in the snow pack had been as low as the mean precipitation pH determined by Logan *et al.* at Snoqualmie Pass (4.7), a low pH episodic effect probably would have occurred, at least in the surface waters of these lakes. Except for ammonium, all cations were considerably higher in the Cascade snow cores than in the Snoqualmie Pass precipitation collected by Logan *et al.* This was especially true for calcium. There appears to have been some additional buffering in the snow pack with cations, as indicated from the cores, that was not found in precipitation reported by Logan *et al.* However, cores were collected in open areas in a lake basin with little vegetation and, therefore, should have represented precipitation only. Another possibility is that snow in the Cascades may not represent the most acidic precipitation falling on those high lake watersheds. Recent precipitation sampling at a lower elevation (180 m) west of the Alpine Lakes Wilderness area lakes shows that the annual mean pH was 4.6, but during spring and summer it was much more acid at pH 4.15 (Vong and Waggoner 1983).

Although acidity of the snowpack was not sufficient to cause an episode, the more dilute waters entering the surface waters of the lakes following iceout apparently produced some chemical stratification. This phenomenon was indicated in all three lakes by specific conductance, which decreased consistently over the one-month period. Dilution of the surface waters producing chemical stratification was most apparent in Copper, the lowest elevation lake sampled, where bicarbonate in the upper 10 m was one-fourth to one-third the bicarbonate content of the deeper water. There was a more subtle indication of this phenomenon in Big Heart, the next higher lake, but in Angeline, the highest in elevation, bicarbonate was relatively constant with depth and was similar to levels determined in the snowpack. The surface content of bicarbonate in Copper was only about two tenths that at 50 m; the ratio for specific conductance was one third. Stratification may exist at greater depths in the higher lakes also; nevertheless, lake alkalinity seems to be more affected by other sources of alkalinity (probably groundwater and weathering), as elevation decreases, than only the contents of snowmelt water.

This pattern of chemical changes due to snowmelt being restricted to the surface waters of lakes is probably typical of relatively deep lakes with low watershed area: lake area ratios. The two higher elevation lakes, which are over 150 m in depth, have watershed:lake surface ratios of about 5, and flushing rates crudely estimated at around 0.1 yr^{-1} . In such systems it can be assumed that the snowmelt water will move largely through the surface waters, even before iceout, as the constituent profiles in these lakes

may suggest. Hendrey *et al.* (1980) observed that snowmelt water in two Adirondack lakes with relatively small watershed : lake surface ratios (6.9 and 9.0), lowered the pH in the upper 1 m only, while the lake with a large ratio (69) became well mixed. The latter lake was deeper, but its flushing rate was 5.6 yr⁻¹, about threefold greater than the other two lakes.

In such systems that remain stratified during the snowmelt episode there would tend to be a refuge for mobile animals, such as fish, in the deeper waters, which would be relatively unaffected by the lowered pH of the snowmelt water. In shallower lakes with higher watershed:lake surface area ratios and consequent faster flushing rates, such stratification may not persist and there would be no refuge. Lakes with the latter morphometric and hydrologic characteristics would tend to be more sensitive biologically.

Acknowledgments

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