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Changes in pH and buffering capacity of lakes in the Colorado Rockies

Abstract—A set of pH, alkalinity, and total residue data on lakes in the central Rockies for the period 1938–1960 is compared with a second set of such data taken on the same days of the year in 1979. The total comparison group includes 64 lakes, but some exclusions are made on the basis of water diversions and other complicating factors. A correction is made for variation among years in total runoff. After this correction, there remains a 17% (±2.2%) decline in alkalinity from the early samples to the 1979 samples. The total residue is lower (16%), as is the pH of surface water from the lakes (0.22 units). These changes are attributed to acidification of precipitation, which has been previously documented in the region.

Bulk precipitation at a site in the Colorado Rockies near the Continental Divide is routinely affected by the presence of strong mineral acids (Lewis and Grant 1980a). The trend toward increasing acidification of precipitation at the Como Creek watershed site, the only Rocky Mountain site for which there is a long term record, has been persistent since measurements started in 1975 (Table 1). Although it is not known whether equivalent acidification of precipitation has occurred over the entire central Rockies, it is clear that strong mineral acids may have affected a large portion of the central Rocky Mountain region.

This region contains large numbers of natural lakes, mainly of glacial origin (Pennak 1963). Impoundments are also numerous, especially in the plains (below 2,000 m). The lakes above 2,000 m generally share a low dissolved solids content and low buffering capacity, as the watersheds are underlain by crystalline rock that yields only small amounts of buffering compounds.

Where the acidification of precipitation is combined with the presence of poorly buffered surface water, the potential exists for a reduction in buffering capacity and pH of lakes. The best documented instances are from Norway (Wright and Henriksen 1978), the Adirondack Mountains of the Northeastern U.S. (Schofield 1976), and portions of Ontario (Dillon et al. 1978). Acidification of precipitation in the central Rockies is not so extreme as in these three locations, but it is clearly of sufficient severity that it might have affected the chemistry of lakes above 2,000 m.

The output of bicarbonate from the watershed of Como Creek has declined stoichiometrically in proportion to the increasing hydrogen ion loading (Lewis and Grant 1980b). Here I explore the possibility that similar changes in the buffering capacity of lake waters have occurred in the central Rockies over the last 20–40 years. The study is possible due to the information collected by R. W. Pennak as part of his initial limnological reconnaissance of Colorado lakes. Some of this information is published (*see* Pennak 1963); the rest was obtained by personal communication.

Table 1.   pH data for bulk precipitation in Como Creek watershed since June 1975. Annual intervals are 15 June–14 June; numbers are percent of weeks in indicated pH range.

	3.0–3.5	3.5–4.0	4.0–4.5	4.5–5.0	5.0–5.5	5.5–6.0	6.0–6.5	6.5–7.0
1975–1976	0	0	3	18	42	21	16	0
1976–1977	0	0	21	29	36	5	7	2
1977–1978	2	2	28	38	15	11	4	0
1978–1979	0	8	38	35	10	8	3	0
1979–1980	0	0	35	54	9	2	0	0

Pennak for allowing me to use his records, to E. Gorham and R. Hesslein for critical review, and to N. Knox for the fieldwork.

Pennak's survey data consist of analyses of 152 separate samples spanning the years 1938–1960. Most of the samples were taken in 1938–1942 and 1949–1952. These samples include 64 different lakes, some sampled several times on different dates, others only once. All of the lakes were resampled in the ice-free season of 1979 (Fig. 1).

A factor which might complicate the interpretation of changes over the years is the seasonal change in water chemistry within a year for any particular lake. To minimize this complicating factor, I took the 1979 samples on the same day of the year as those in Pennak's series: a sample taken by Pennak on 5 May 1938 is matched by a 1979 sample taken on or very near 5 May.

Pennak's samples were processed after return to Boulder, usually within 12 h. He determined alkalinity by titration of the sample with 1/44 N HCl to the methyl orange end point, as judged visually against a standard containing methyl orange at the end point. He determined pH by the use of indicators accurate to about 0.2 pH units. For determination of total residue, he evaporated a large quantity of sample (1–3 liters) at 60°C in a porcelain evaporating dish down to about 50–100 ml. This concentrated residue was then transferred to a small evaporating dish and carefully evaporated to dryness. The total dry residue was scraped and brushed from the small dish and weighed.

The 1979 samples were also returned to Boulder and processed on a schedule
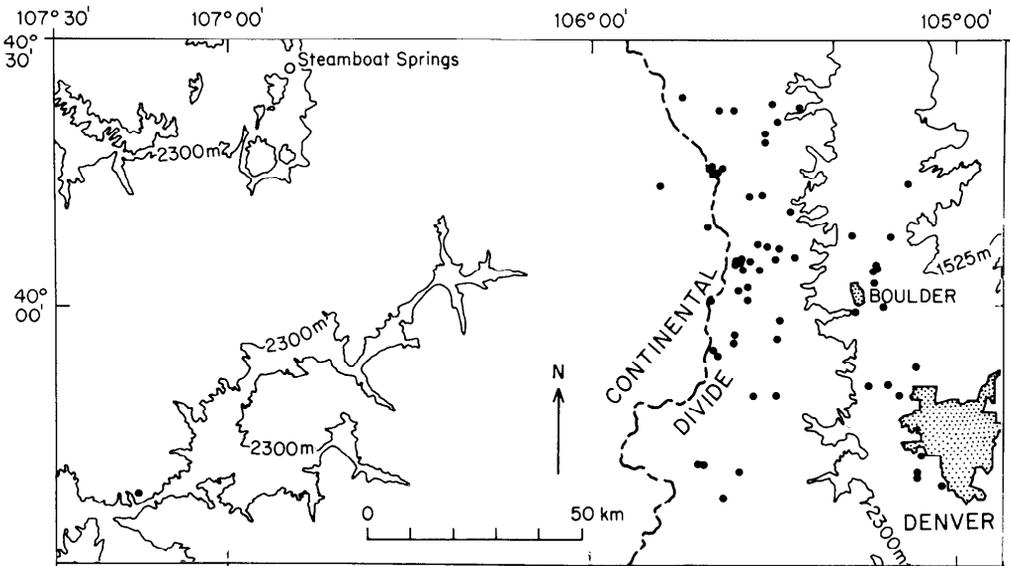

Fig. 1.   Map of region where lake samples were taken. Each dot indicates a lake that was sampled.

similar to Pennak's. The pH was determined with a Radiometer model 26 meter calibrated against buffers at pH 4.0 and 7.0. The meter was checked against Pennak's indicator method and the two found to be in good agreement, although the indicator method is of course more approximate. The samples were titrated with 1/44 N HCl, but the end point (4.4) was determined electrometrically with the pH meter rather than with the methyl orange indicator used by Pennak. The methyl orange end point and the electrometric end point could differ by as much as 2 drops of titrant, but this represents <3% of average alkalinity. For residue determination, 1979 samples were concentrated in a rotary evaporator set at a temperature of 60°C. Concentrate from the evaporator was taken to dryness in a tared porcelain crucible at 60°C.

Random analytical error in the alkalinity determinations was tested in the 1979 sample series by the use of blind duplicates. The chemist titrated one replicate for each of the alkalinity titrations without knowing the identity of the replicate. The average range between the duplicate blind titrations was 9.5% of the mean alkalinity, indicating a standard error for the mean alkalinity determination for each sample in the 1979 series of about 6%. Under the best conditions the error should have been half or a third this size; occasional slight overtitration is probably responsible for inflating the error. Even though the error is higher than expected, it is of little consequence because it is random and its importance will decrease as sample size increases. Similar quantification of analytical variability in Pennak's sample series is not available but is likely to be similar to or lower than for the 1979 series.

Systematic error is of greater concern in a study of this type than random error and is difficult to quantify with certainty. Alkalinity determinations and residue measurements are less likely to be subject to systematic error than pH measurements. As will become evident from the analysis, the pH, alkalinity, and residue provide some redundant indications of the acidification of freshwaters; this redundancy is a guard against systematic error in any one of the three variables.

The samples were taken without particular regard to the location or elevation of the lakes. When the comparative data were available, it was obvious that lakes on the plains and foothills (below 2,000 m) were distinct from the mountain lakes in the extremity of changes which they showed. Changes in the lower lakes are often attributable to changes in water use, which have been major over the last 30 years. For this reason, the lower lakes were considered to be invalid as a comparison group and were excluded from the analysis. Thus the analysis is entirely limited to lakes above 2,000 m.

Even though lakes above 2,000 m are much less likely than the plains lakes to have experienced augmentation or diminution of flowthrough or alteration of watershed characteristics, such changes are known to have occurred for some of them. Since reliable information about these changes was limited, and since changes were of uncertain importance to the present analysis, no attempt was made to evaluate the high lakes on a case-by-case basis with regard to the amount of change they might have undergone. Instead an arbitrary quantitative criterion was chosen as a screening device to remove from the data set any lakes which had been influenced by factors of major importance other than changes in precipitation chemistry since the 1938–1960 period. For alkalinity and total residue, changes of >60% were considered to be evidence of influence other than precipitation chemistry and these lakes were treated as missing values in the analysis. Similarly, for pH, changes of more than 1.5 units were considered to be evidence of the operation of factors other than precipitation chemistry. Thus the final data set on which the statistics were derived excludes radical changes in water chemistry attributable to other factors that might unduly affect the observed mean changes over the years. The trends are

Table 2. Comparative chemical data for Colorado lakes above 2,000 m.

Variable	N	1938–1960		1979		Change*		Percent change	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE
pH	104	7.09	0.04	6.87	0.04	−0.22	0.04	—	—
Alkalinity as CO_2 (mg·liter^{-1})	104	22	2.3	18	2.3	−4.2†	0.61	−22	2.2
Σ residue (mg·liter^{-1})	64	35	2.9	29	2.8	−6.1	1.44	−16	2.8

* Change in averages may not equal average change because of missing data.
† Alkalinity is given here in terms of CO_2. As a bicarbonate ion concentration, decline is −5.9 mg·liter^{-1}.

very similar with or without the exclusions, but the exclusions greatly reduce the variance.

Table 2 reports the comparative chemical data, including pH, alkalinity, and total residue, after removal of the lakes below 2,000 m elevation and of lakes which showed evidence of major change not attributable to precipitation chemistry. Figure 2 shows the alkalinity data in terms of a graphical comparison of the 1938–1960 series and the 1979 series.

The relationship between change in alkalinity and change in total residue was tested by regression analysis and proved to be significant ($P < 0.01$). The relationship is: alkalinity (mg·liter^{-1}) = 0.24 × residue (mg·liter^{-1}) − 2.82. The standard error of the slope is 0.08.
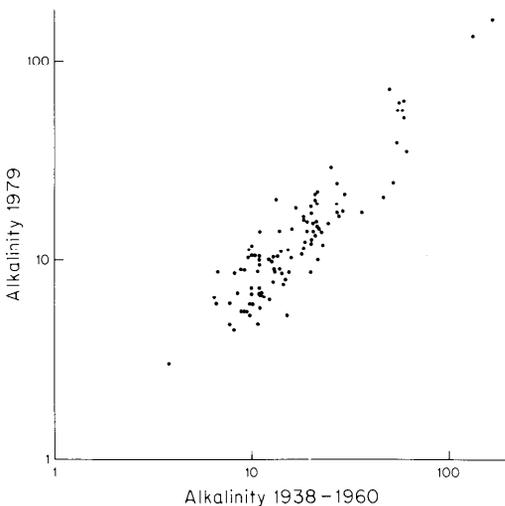
Discharge records (U.S.G.S.) were ob-

tained for all reasonably large streams in the general vicinity of the lakes being considered. These records were used to evaluate variation in discharge between years, which may affect lake chemistry. Sites not represented by data back to at least 1950 were excluded, as were all sites which had been significantly affected by diversions since 1935. There remained four sets of discharge records: the Big Thompson River at Estes Park, the St. Vrain River at Lyons, Middle Boulder Creek at Nederland, and Clear Creek at Lawson. The Big Thompson and Clear Creek have continuous records since 1947 and the St. Vrain and Middle Boulder Creek have records continuously since 1938. For all four of these sites, the mean discharge over all years of record (water years: 1 October–30 September) was obtained. The 1979 year was then expressed as a fraction of this. The 1979 discharges at these four sites were 129% of the long term average. In an alternate method of calculation, the discharges for years in which Pennak made his collections were weighted according to the number of samples collected in each of the individual years and the weighted mean used for comparison with the 1979 year. This led to very similar results, so the simpler method was retained.

The data cannot be interpreted without some attention to the variation among years in total discharge. The water in a mountain lake or stream which feeds it is a combination of the chemical properties of precipitation and soils. As the amount of precipitation increases, the influence of precipitation chemistry in relation to soil chemistry increases. In an especially

Fig. 2. Log-log plot of alkalinity data (mg·liter^{-1} as CO_2) used in analysis (lakes above 2,000 m).

wet year, Colorado mountain waters show lower conductances, buffering capacity, and pH, due to more rapid flushing of water through the terrestrial system (Lewis and Grant 1979; *see also* Pennak 1943). Since Pennak's samples span quite a number of years, his data approach a random selection of wet, dry, and average years. On the other hand, the 1979 year to which this random selection is being compared might have deviated from the average by an amount sufficient to affect the results.

The relationship between streamwater chemistry and the amount of water flushing through the Como Creek watershed, at 2,900 m ASL near the distribution center of the lake samples, showed a yield response of the watershed with respect to bicarbonate of about 80% (Lewis and Grant 1979). This means that a 10% increase in the water flowing through the watershed will result in only an 8% increase in the bicarbonate yield; the bicarbonate concentration of stream water will decline accordingly. This is explained by the higher acidity of rainwater than soils and a consequent reduction in concentration of bicarbonate in runoff as the flushing rate of the watershed increases. This provides the basis for a quantitative correction for the effects of divergence from average runoff on lake chemistry.

The average deviation of discharge for the 1979 water year from the long term average and the yield response of bicarbonate at a representative watershed in the area where the samples were taken are combined to produce the quantitative estimate of the effect of discharge on alkalinity. Since the discharge was 29% above average in 1979, the bicarbonate yield will be 0.8 (29) or 23% above average. The composite bicarbonate concentrations should thus be 123/129 or 95% of average: the expected alkalinities of the lakes would be 5% lower in 1979 than in Pennak's series if no factors varied other than discharge.

The 22% observed decline in alkalinity, when corrected by 5% to account for the effect of increased runoff, yields a corrected percentage change in alkalinity of 17% to be accounted for by factors other than discharge variations. In view of the standard error (about 2%), it seems doubtful that the 17% decline can be explained by any reasonable mechanism other than acidification of the water reaching the lakes.

Reduction of total residue is consistent with removal of bicarbonate by strong acids. Bicarbonate is the dominant anion of these waters. Although the addition of strong acid might be viewed as substitution of a sulfate or nitrate anion for bicarbonate, demand for both of these anions, and particularly for nitrate, is strong in the terrestrial and aquatic systems of the central Rockies. There is also some direct empirical evidence for lower anion output following acidification of soils (Johnson et al. 1979). Consequently some reduction in residue is expected, although the exact reduction cannot be predicted with confidence because of the complexity of chemical interactions, especially in soils. Reduction in ionic solids accompanying acidification has been documented empirically for the Como Creek watershed (Lewis and Grant 1980*b*).

Reduction of pH is also consistent with reduction of bicarbonate concentrations by strong acids, although the pH effect will of course be subtle while significant bicarbonate remains.

William M. Lewis, Jr.

Department of Environmental,
    Population and Organismic Biology
University of Colorado
Boulder 80309

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Concentration of *Serratia* in the surface microlayer[1]

Abstract—Concentrations of *Serratia mar-
cescens* and *Serratia marinorubra* were mea-
sured in the surface microlayer by a floating
Nuclepore filter technique. Controlled remov-
al of the filters permitted comparisons of bac-
terial concentrations in various thicknesses of
the microlayer from 8 to 100 μm. *Serratia* be-
came enriched in the microlayer by a factor
>4 during the process of preparing suspen-
sions by dilution and vortex mixing. Enriched
concentrations were found only in the upper
20 μm and reached enrichment factors >15
within 1 h, but EF values >120 were obtained
from the upper 10 μm of suspensions aged
undisturbed for 18 h. Rates of increase of EF
were greater for uncleaned water surfaces
than for cleaned surfaces, indicating a rela-
tionship between microlayer concentration
and surface films.

The surface microlayer (SM) is a thin
layer of water at the air–water interface
where both living and nonliving mate-
rials may be present in concentrations
different from those of the subsurface
water. Its thickness depends on the ma-
terial in question, but generally it is of
the order of 300 μm or less. The many
techniques used to sample the SM of nat-
ural water surfaces have been reviewed
by Van Vleet and Williams (1980). One
of these, a membrane adsorption tech-
nique, used Nuclepore filters to deter-
mine the enrichment of microbial popu-
lations in the SM of coastal marshes
(Crow et al. 1975); I have used this float-
ing filter technique for controlled remov-
al of the SM in laboratory bacterial sus-
pensions.

Experiments were done in glass tanks
(15-cm diameter × 7.5 cm high). *Serratia
marcescens* and *Serratia marinorubra*
were grown in Difco nutrient broth or
ZoBell media 2216E (Difco Bacto pep-
tone 5.0 g, Difco Bacto yeast extract 1.0
g, FePO$_4$ 0.01 g, aged seawater 1,000 ml),
incubated at 30°C unagitated for 18 h.
Cell suspensions were then prepared by
mixing with a magnetic stirrer a 1/300
dilution of the broth cultures in unster-
ilized pond or seawater. The resultant
bulk concentrations used in these exper-
iments were generally of the order of
$10^6 \cdot ml^{-1}$. The glass tanks were filled and
many milliliters allowed to overflow.

Sterilized, dry Nuclepore membrane
filters (polycarbonate, hydrophilic, 13-,
25-, and 47-mm diameter, 0.4-μm pore
size) were preweighed in sterile, dry
plastic Petri dishes. All filters were han-
dled with sterile No. 7 stainless steel for-
ceps. A filter was slowly lowered to the
water surface until it was floating. After
30 s it was peeled off, placed in its Petri
plate, and weighed within 10 s on a Mett-
ler balance (type H16) with a measure-
ment accuracy of $1.0\pm0.4 \times 10^{-4}$ g. Sam-
ple volumes were determined by
subtracting dry weights from wet weights.
Evaporative loss was $<2 \times 10^{-4}$ ml ·
min^{-1}; in the 10 s needed for a weighing
these losses are negligible, being <0.8%