

Chemical loading rates from precipitation in the Colorado Rockies

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(Manuscript received November 18, 1980; in final form May 5, 1981)

ABSTRACT

Chemical composition of bulk (= wet + dry) precipitation was measured at two stations in the Colorado Rocky Mountains for each of 150 consecutive weeks. The stations were located at 3000 m elevation approximately 6 km east of the Continental Divide and 40 km north of Denver.

Chemical species routinely measured included particulate C, N, P and H; dissolved organic C, P and N; conductance and total alkalinity; SO_4^{2-} , Cl^- , NO_3^- -N, NO_2^- -N, NH_4^+ -N, Ca^{++} , Mg^{++} , Na^+ , K^+ , H_2PO_4^- -P and H^+ . Particulates were deposited at a rate of 147 kg/ha/yr; C accounted for about 21% of this. The most important anions were total alkalinity expressed as bicarbonate (281 eq/ha/yr), SO_4^{2-} (196 eq/ha/yr) and NO_3^- -N (129 eq/ha/yr). Among cations, Ca^{++} was most important (200 eq/ha/yr) followed by H^+ (106 eq/ha/yr) and NH_4^+ -N (89 eq/ha/yr). Conductance averaged 16 $\mu\text{mho/cm}$.

The composition of dry fallout was collected separately and analyzed for 70 weeks at a single station. Particulates accounted for 129 of the 169 kg/ha/yr total collected. Total alkalinity was by far the most important dry component and, expressed as HCO_3^- , accounted for 506 eq/ha/yr of the total 804 eq/ha/yr for anions. About 75% of the total inorganic phosphorous in bulk precipitation was from dry fallout.

The composition of Como Creek precipitation is rather different from that of other sites reported in the literature. At Como Creek, comparatively low levels of SO_4^{2-} are found simultaneously with comparatively high levels of H^+ . The surprisingly high levels of observed H^+ deposition at the only site in the Rocky Mountain west with a long-term, broad spectrum record signal the need for extended geographic coverage of precipitation chemistry in the western U.S.

1. Introduction

Chemical characteristics of precipitation in the Rocky Mountain region appear to be essentially unstudied except for the data published by Gosz (1975, 1980), brief surveys published by Junge (1958), Junge and Gustafson (1957), Junge and Werby (1958) and the National Center for Atmospheric Research in-house report (Lodge et al., 1968). The number of published studies on the chemical characteristics of precipitation in the Western U.S. as a whole is quite small (e.g., Whitehead and Feth, 1964; Moodie, 1964; Rothacher, 1963; Tarrant et al., 1968; Zeman and Slaymaker, 1978; Cole and Johnson, 1977; Larson, 1975; Liljestrand and Morgan, 1978; McColl and Bush, 1978) compared with the published

studies of the northeastern part of the U.S. and Europe (e.g., see *Proceedings of the international symposium on acid precipitation and the forest ecosystem, 1976*). Precipitation chemistry studies which have been done in the west typically are either of short duration or focus on one or a few components. This is unfortunate in view of the probable importance of precipitation in controlling the chemical mass balance of ecosystems and freshwater chemistry (Hutchinson, 1954; Gorham, 1961, 1976; Likens et al., 1977).

In 1975 we initiated an extended, broad-spectrum study of precipitation chemistry in the Colorado Rockies in order to quantify total loading rates, seasonal variation, and relative amounts of important components of bulk (= wet + dry) precipitation entering a mountain watershed at

3000 m elevation (Fig. 1). We here report results of the first three years of data collection. The study focused on those components of bulk precipitation which are most important in determining buffering capacity, acidity, ionic strength, or which may be of major nutritional significance in ecosystems (e.g., phosphorus). The present paper deals with (1) small-scale spatial heterogeneity, (2) measurement error, (3) average deposition rates, and (4) correlation among deposition components. A subsequent report will deal with temporal patterns of variation, including trends, in more detail.

2. Methods

Bulk precipitation samples were collected continuously over 1-week intervals for 150 weeks beginning in June of 1975. Except for a very few instances in which samples were spilled or equipment was damaged, samples were collected every week at both stations shown in Fig. 2. The bulk precipitation collectors which we used at the two sampling stations have already been described in detail elsewhere (Lewis and Grant, 1978).

We also operated a Wong dry/wet fractionating

sampler for 70 weeks. This device senses precipitation (either rain or snow) and activates a lid which either exposes or covers the collecting bucket as desired. We chose to collect the dry fraction in the Wong collector to avoid problems of melting snow, evaporation, etc. We do not have as many sample points for dry deposition as for bulk because the Wong (1) sometimes did not work properly, in which cases the sample was discarded, (2) was installed 12 months after the bulk collectors, and (3) we had but a single station.

All collectors were mounted on towers such that the collecting surface was approximately 4 m from the ground surface. Elevation of the collector is important for present purposes, since we wish to quantify material entering the watershed rather than locally suspended materials. Coarse particulate material was very seldom found on the nylon screens, indicating that the elevation of the collectors was effective in excluding at least large particles of local origin. The only time noticeable local contamination occurred was in connection with conifer pollen rain.

Both collecting sites are in small clearings surrounded by conifers and/or aspen. Surrounding vegetation serves as an effective wind shield

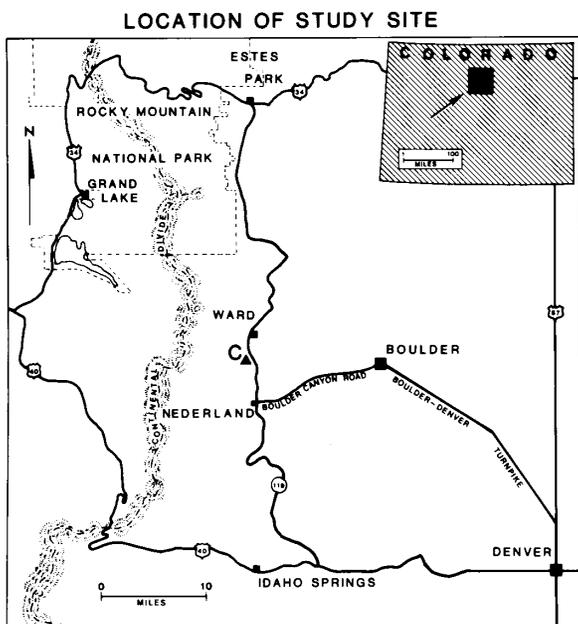


Fig. 1. Location of Como Creek study site (C).

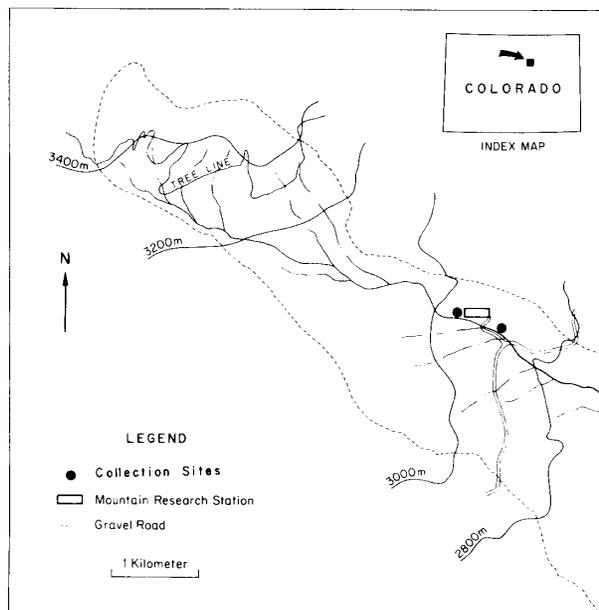


Fig. 2. Location of the two bulk precipitation collectors within the Como Creek watershed.

(Larson, 1971), so no artificial shields were erected around the collectors. Wet precipitation collection experience at the site over the last 20 years has shown that unshielded collectors have the same yield as shielded collectors in forest clearings but not in tundra or cleared areas (J. Clark, personal communication).

Proximity of trees may be relevant to precipitation chemistry measurements because throughfall is often considerably different chemically (e.g., McColl and Bush, 1978). At station 1, no vegetation is present at collector height within an arc of approximately 70° from the vertical. At station 2, the comparable figure is approximately 25° . There are at least two important consequences of these angles: (1) When the angle is too small, the collections can be contaminated by throughfall and debris from the surrounding trees. This effect tends to increase the apparent loading rate estimates of various chemical components, especially K^+ (G. E. Likens, personal communication). The angle at station 2 would appear to be somewhat less than ideal from this point of view, but comparison with the other station shows no evidence of contamination. (2) On the other hand, when the clearance angle is too large the total precipitation collected can be underestimated by as much as a factor of 2 when high winds are common (Larson,

1971). Whether this effect functions differentially on dry and wet fractions is currently unknown. From this point of view, station 2 is nearly ideal in shielding while station 1 is somewhat too exposed. Again, the overall estimates from the two stations were not significantly different, indicating that this effect also is small. Extended meteorological records are available for nearby shielded recording rain gauges; these are compared with the bulk collectors in the results section below.

At the time of sample collection, the bottle containing the accumulated bulk precipitation was removed from the sampler and an auxiliary bottle was hooked up to the hose. A rinse of 500 ml deionized-distilled water was then used to clean the surface of the collector, the small funnel, and the hose. The bulk precipitation and the rinse water were then transported in their separate containers to the laboratory.

Chemical analysis of the bulk precipitation began two hours after sample collection and was for the most part complete by the following day. The rinse water was not combined with the sample itself until measurements of pH, conductance, and alkalinity were made. The rinse water and the precipitation sample were then combined and deionized-distilled water was added as necessary to bring the total volume of the sample up to 1300 ml.

All chemical analysis was done on this diluted sample and subsequent correction was for the use of rinse water, the use of makeup water to bring the total to 1300 ml (if any), and the removal of small amounts of sample for the measurement of pH, conductance, and alkalinity.

Precipitation chemistry can be quantified both in terms of concentration (mass of constituent per volume of water) and loading rate (mass of constituent reaching a unit of collecting area). The difference between these two expressions is straightforward except in the case of conductance, which requires special explanation. When concentration is being discussed, conductance is given in standard units ($\mu\text{mho/cm}$). Such usage parallels concentration values for individual constituents. When conductance is being used parallel with loading rates, however, another approach is required. In this case, we compare the conductance of each sample as if all ionic constituents were concentrated into exactly 10 ml of water. (Since this was done computationally only, chemical effects such as changes in ionic activity do not arise.) Thus for a week that has 1 cm of rain ($= 10,000 \text{ cm}^3/\text{m}^2$) and shows a conductance of 15 $\mu\text{mho/cm}$, the loading rate will be $(10,000/10) \times 15$, or 15,000 $\mu\text{mho/cm}$ in 10 ml.

The measurement of H^+ concentration with glass electrodes can be influenced by a number of things, including ionic strength (Galloway and Likens, 1979). The average ionic strength of our precipitation samples was 3.7×10^{-4} moles/l, which leads to an error of less than 0.1 pH units. The influence of other factors, e.g., temperature and solution stirring was minimized (Galloway and Likens, 1979).

The diluted samples were first filtered through clean glass fiber paper (Whatman GF/C, effective pore size about 2 μm). The filters were then dried at 105° for 24 hours and stored in a desiccator for CHNP (carbon, hydrogen, nitrogen, phosphorus) analysis. Multiple subsamples were taken of each filter with a punch for combustion in a CHN analyzer, which produced estimates of the percentage nitrogen, carbon, and hydrogen in the dry particulate matter. The operation of the CHN analyzer was checked routinely against standard orchard leaves (National Bureau of Standards, Washington, D.C.). Other subsamples from the filters were digested with heat in sulfuric acid and potassium sulfate until they turned clear then

analyzed for soluble reactive phosphorus by the method given below. The digestion efficiency was checked periodically with standard orchard leaves and consistently proved to be highly satisfactory (ca. 95 %).

From the water passing through the filter, an aliquot was removed for ultraviolet combustion to produce estimates of the amount of dissolved organic nitrogen and dissolved organic phosphorus according to the techniques described by Manny et al. (1971). Another aliquot was preserved with 0.01 M HNO_3 for analysis of major cations by atomic absorption (calcium, magnesium, sodium, potassium). Lanthanum was added to suppress calcium interferences. Sulfate was determined by barium precipitation (Golterman, 1969), ammonia by a modified phenolphthalein method (Solozano, 1969; Koroleff, 1976), nitrate and nitrite by the use of the standard azo dye technique in combination with a cadmium-copper reduction system (Bendschneider and Robinson, 1952; Wood et al., 1967), and phosphate-phosphorus by a molybdate method (Murphy and Riley, 1962). Alkalinity was determined by titration with standard acid to a pH of 4.4 using a pH meter (Golterman, 1969) and should be considered a measure of acid-combining capacity rather than a direct measure of bicarbonate alkalinity (Stumm and Morgan, 1970). The results are expressed as bicarbonate even though we will show in the results section that weak organic acids probably were significant contributors also. Selected samples were also titrated to pH 8.3 with NaOH in order to estimate the potential contributions to $[\text{H}^+]$ from weak acid sources (Galloway et al., 1976a, 1976b; Likens et al., 1976). DOC was estimated from the absorbance at 360 nm using the equation of Lewis and Canfield (1977). As the values were not routinely cross-checked by infrared analysis, DOC values should be considered provisional. Chloride was measured using a mercuric thiocyanate method (U.S. EPA, 1979).

The data were first analyzed for between-site variation by comparing weekly (1) average loading rates for each measured component at each site along with their standard errors, (2) average absolute difference, (3) relative differences as expressed by the coefficient of variation, (4) skewness, and (5) kurtosis of the differences. These last two statistics provide information about the shape of the frequency distributions of differences

showing, for example, systematic biases between sites. Statistical methods requiring normality of data were used throughout and checks of this and other assumptions were routinely made according to usual testing criteria.

3. Results and discussion

3.1. Aqueous precipitation

We compared precipitation values in mm of water (snow is melted by the collector) from our bulk collectors with the rain gauge data which were independently collected using standard 20 cm recording precipitation instrumentation by the University of Colorado's Mountain Research Station at the Como (C1) weather station site (Fig. 2), approximately 1 km from our collecting sites. The rain gauge station meets recommended shielding standards (Larson, 1971) and has been operating continuously since 1952 (Marr, 1961). Comparison of monthly values indicates excellent consistency: 685 mm to 693 mm in 1976 and 673 mm to 626 mm in 1977 for the rain gauges and bulk collectors, respectively. We have used the amount measured in our bulk collectors for all calculations involving amount of wet precipitation.

There is a substantial seasonality of wet precipitation at the Como Creek site which influences loading rates. Fig. 3 illustrates the seasonality for five year averages from Barry (1973) as well as the observations for the years 1974 through 1977 (J. Clark, unpublished records for C1 station). Early

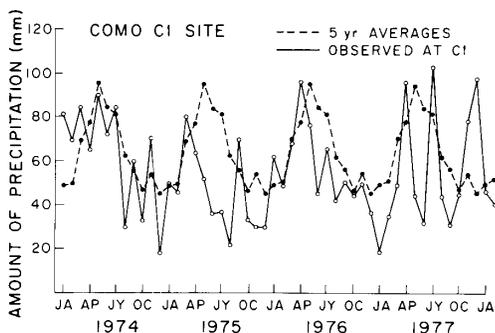


Fig. 3. Precipitation measurements taken at the Como (C1) weather station during the sampling period covered in this paper are shown with open circles and solid lines. Five-year averages for 1972-1977 are shown as closed circles with dotted lines.

spring (April, May, June) is typically the season of heaviest precipitation, while late fall through early winter (October, November, December, January) is the period of lowest precipitation. Actual precipitation amounts vary substantially from these overall patterns in any given month or any given year. June 1977, for example, shows only 32 mm of water while the five year average for June is nearly triple that amount. The most striking instance of departure from average conditions during the study occurred between May 1976 and March 1977, when wet precipitation was below average for 11 consecutive months. There was no significant linear trend in precipitation amount across the entire sampling period. The only other published precipitation chemistry data from this general region were taken at Grand Junction, Colorado (Lodge et al., 1968; Junge and Gustafson, 1957), a site with an average annual rainfall of 213 mm/year and an elevation of 1474 m.

3.2. Spatial variation and measurement error

The two bulk collectors were located approximately 1 km apart (Fig. 2). Differences in chemical loading rates between them reflect the sum of small-scale spatial variation in bulk precipitation input plus all measurement error. We have compared the loading rate data from the two sites in three ways in order to quantify spatial variation and to facilitate comparison of the between-site variation in our data set with variation in other data sets: (1) arithmetic mean loading rates for station 1 and station 2 and their standard errors (Table 1, columns 2 and 3), (2) the average absolute difference between loading rates at the two sites (Table 1, column 4), (3) the relative difference in loading rates, expressed as the coefficient of variation ($CV = (s \times 100)/\bar{y}$), where \bar{y} is the mean of the two stations (Table 1, column 5), and (4) shape estimates of the deviation curves (presented in the last two columns of Table 1).

Average values for the two stations were quite similar. All but one variable of the 20 measured had overlapping 95% confidence intervals for the two stations, indicating no significant differences above what one would expect under the null hypothesis of equal means for 20 such comparisons. On the basis of this between-site consistency, we treat the two stations as replicate measurements for the remainder of this paper. This results in (1) increased reliability of each weekly

Table 1. Comparison of weekly mean bulk precipitation loading rates for upper and lower precipitation sampling stations at Como Creek (mg/m² unless otherwise noted)

Variable	Mean and std. error† station 1	Mean and std. error† station 2	$\frac{1}{N} \sum Y_1 - Y_2 $	Coefficient of variation*†	Skewness	Kurtosis
Particulates	249.2 ± 30.3	339.7 ± 38.2	158.3	50	0.496	20.58
C (%)	23.1 ± 1.2	18.8 ± 1.3	6.92	9	-0.575	0.087
N (%)	1.20 ± 0.09	0.93 ± 0.08	0.45	38	0.456	1.093
P (%)	0.20 ± 0.01	0.16 ± 0.01	0.088	46	0.315	2.26
H (%)	4.20 ± 0.22	3.05 ± 0.21	1.59	40	0.307	0.657
HCO ₃ ⁻	31.5 ± 3.5	33.5 ± 3.6	11.3	43	-1.179	10.31
SO ₄ ⁻	16.30 ± 1.31	15.46 ± 1.64	9.16	51	-2.667	23.62
Ca ⁺⁺	7.66 ± 0.74	7.56 ± 0.63	2.38	28	1.60	11.57
Mg ⁺⁺	0.89 ± 0.07	0.86 ± 0.06	0.32	15	0.245	8.38
Na ⁺	4.20 ± 0.38	3.47 ± 0.27	1.70	40	3.19	15.01
K ⁺	3.04 ± 0.31	3.42 ± 0.54	2.00	55	-4.01	32.65
H ₂ PO ₄ ⁻ -P	0.10 ± 0.02	0.091 ± 0.01	0.062	58	-7.44	76.19
NO ₃ ⁻ -N	3.53 ± 0.29	3.42 ± 0.75	1.00	7	4.76	36.68
NO ₂ ⁻ -N	0.05 ± 0.01	0.060 ± 0.01	0.003	2	-1.27	23.19
NH ₄ ⁺ -N	2.45 ± 0.23	2.41 ± 0.23	0.99	7	1.31	8.17
DOC	8.98 ± 1.55	19.40 ± 1.69	5.77	27	0.543	10.51
DOP	0.066 ± 0.008	0.063 ± 0.012	0.048	66	-4.43	41.23
DON	2.37 ± 0.25	2.77 ± 0.40	1.70	58	-3.67	25.22
pH units	4.79 ± 0.06	4.81 ± 0.06	0.2	4	1.52	10.17
Conductance μmho/cm, 10 ml	22,014 ± 2080	19,741 ± 1278	5.6	32	4.58	36.12

$$* CV = \frac{1}{N} \sum \left\{ \frac{(Y_1 - Y_2)(0.886)(100)}{(Y_1 + Y_2)/2} \right\}$$

† Includes error variance, seasonal, and nonseasonal temporal variance (see text for details).

observation ($s_p = s/\sqrt{n}$), (2) a greater degree of normality (from the central limit theorem) and (3) a very conservative number of degrees of freedom to be used in statistical hypothesis testing. Consequence number 3 is especially important in the analysis of linear trends over time (Lewis and Grant, 1980). Although the average values at the two stations over any substantial period of time were similar, individual samples did often vary substantially, suggesting that small-scale spatial variation sometimes does exist in bulk precipitation and may be worthy of specific consideration in the future.

The 12 positive and 8 negative values calculated for skewness (Table 1) were not significantly different by the runs test, indicating a lack of evidence for consistent overall bias. Although there are significant deviations from normal symmetry in individual components, no overall pattern appears. Potassium, for example, seems to be consistently a bit higher at station 2 (the lower, more shielded site

with a smaller open canopy angle) but Na⁺, Mg⁺⁺, and Ca⁺⁺ appear to be higher at station 1. NO₃⁻-N, and NO₂⁻-N, which are highly correlated with each other in the overall deposition rates, show opposite biases. We conclude that systematic open/closed canopy effects are not large enough to be of concern in this study.

The flatness/peakedness (kurtosis) of the difference curves, on the other hand, shows consistent deviation from normality. In particular, the curves are flatter with more observations in the "shoulders" of the curve and fewer in the tails than for normal curves. This strong and consistent pattern indicates that the values from the two stations are commonly slightly different, but very rarely largely different, and that identical values from the two stations were observed less frequently than expected for a normal curve. We interpret these results to indicate that slight, but real, small-scale (1 km) spatial heterogeneity exists in the precipitation deposition patterns.

Standard errors of the means were calculated as usual (s/\sqrt{n}). Estimation of standard errors in this fashion includes the variation due to seasonal cycles in addition to errors of measurement and sampling. The reader should thus not interpret these variations as due to random error alone. Average temperature provides a clear example in which the magnitude of a standard error is dominated by regular seasonal variation. The coefficient of variation will be similarly affected. We will deal with these important aspects of temporal variation in considerable detail in a subsequent paper.

Table 1 indicates that the standard errors of the weekly arithmetic mean loading rate estimates, averaged over the total 150 week sampling period, are commonly of the order of 10–15% of the mean. This general level of precision is reflected in the ionic balance estimates, which were 0.086 meq/l for cations and 0.096 meq/l for anions. The agreement, within 10.5% of the anion total, is quantitatively what should be expected given the normal variation of the weekly estimates for each component. In our system the bicarbonate anion is particularly crucial. The theoretical titration end point will vary in the neighborhood of 4.4–4.6

depending upon the chemical complexity of a particular sample. We potentiometrically titrate to pH 4.4, although at a pH of 4.6 the concentration of HCO_3^- is so small (approximately equal to 2×10^{-7} moles/liter) as to be almost negligible (Stumm and Morgan, 1970). We believe this particular figure to be most responsible for the anionic surplus in our data. Although we cannot exclude the possibility that unmeasured cations may occasionally be present in unsuspected large quantities, the conductance measurements indicate this is unlikely. On the assumption of infinite dilution the average conductance for our samples should theoretically be $16.0 \mu\text{mho/cm}$, which matches the observed value of $16.1 \mu\text{mho/cm}$ (20°C). This agreement indicates that no major ionic components are being overlooked.

3.3. Relative precipitation composition

Carbon in the form of undissolved particulates and in dissolved organic form (Table 2) was by far the most abundant measured element, by weight, reaching the watershed (oxygen was, of course, likely to be the single most important element but was not directly measured). Calcium was the most important cationic component, accounting for 36%

Table 2. Arithmetic mean bulk precipitation chemistry values and their standard errors for Como Creek based on approximately 150 weekly observations at each of two stations

	kg/ha/yr	eq/ha/yr	mg/l	eq/l
Particulates	147.2 ± 15.91	—	21.8 ± 2.4	—
C (%)	(20.92 ± 0.85)	—	4.73 ± 0.19	—
N (%)	(1.12 ± 0.05)	—	0.25 ± 0.01	—
P (%)	(0.18 ± 0.01)	—	0.04 ± 0.002	—
H (%)	(3.19 ± 0.02)	—	0.72 ± 0.03	—
HCO_3^-	17.2 ± 1.9	281.4 ± 31.8	2.54 ± 0.31	41.7 ± 4.7
SO_4^{2-}	9.43 ± 1.01	196.4 ± 21.0	1.40 ± 0.14	29.1 ± 3.0
Ca^{++}	4.00 ± 0.35	199.6 ± 17.5	0.59 ± 0.05	29.6 ± 2.86
Mg^{++}	0.46 ± 0.03	37.5 ± 5.3	0.07 ± 0.01	5.8 ± 0.8
Na^+	1.97 ± 0.16	85.6 ± 13.0	0.29 ± 0.02	13.0 ± 1.0
K^+	1.57 ± 0.14	40.2 ± 4.6	0.23 ± 0.02	6.0 ± 0.8
H_2PO_4^- -P	0.055 ± 0.009	<0.001	0.008 ± 0.001	<0.0001
NO_3^- -N	1.80 ± 0.15	128.8 ± 10.7	0.27 ± 0.02	19.3 ± 1.6
NO_2^- -N	0.029 ± 0.003	2.0 ± 0.2	0.004 ± 0.001	0.31 ± 0.03
NH_4^+ -N	1.25 ± 0.11	89.4 ± 8.2	0.19 ± 0.02	13.7 ± 1.2
H^+	0.106 ± 0.011	106 ± 11	0.0158 ± 0.0017	15.8 ± 1.7
Cl^-	0.92 ± 0.08	25.8 ± 2.3	0.14 ± 1.26	3.9 ± 0.4
DOC	10.29 ± 0.87	—	1.52 ± 0.13	—
DOP	0.036 ± 0.005	—	0.0053 ± 0.0008	—
DON	1.22 ± 0.15	—	0.18 ± 0.02	—
Conductance ($\mu\text{mho/cm}$)	—	—	16.1 ± 1.2	—

of the cationic equivalents deposited per hectare per year. Hydrogen, ammonium, and sodium ions accounted for 19%, 16% and 15%, respectively. Bicarbonate was by far the most important anion, accounting for 44% of the anionic equivalents; sulfate (31%) and nitrate-nitrogen (20%) accounted for the bulk of the remainder.

Column 4, Table 2, shows the average weekly concentrations and standard errors of each measured component in bulk precipitation expressed as mg/l. The reader is reminded that these concentration figures are statistical entities only, to be used for comparative purposes. They do not reflect observed concentrations in a solution in a chemical sense. On a sheer mass basis, the insoluble particulate fraction, especially carbon, contributed most heavily to bulk precipitation. Among the soluble components, the HCO_3^- ion is present in highest concentrations followed closely by dissolved organic carbon, SO_4^- and Ca^{++} .

Finally, column 5 of Table 2 shows the concentrations of bulk precipitation components expressed on an equivalent concentration basis. Among the directly measured ionic constituents, bicarbonate, sulfate and calcium are the most important followed by the nitrate, hydrogen and ammonium ions. The H^+ ion ranks fifth among the components in this category.

The results shown in Table 2 indicate that the chemistry of bulk precipitation in the Como Creek watershed is substantially different from that of any other previously reported site. The differences appear to be best explained by location. The Como Creek site is located in a mountain environment surrounded by large areas of windy and dusty semi-arid plains. Maritime influence appears to be negligible (but cf. Junge and Gustafson, 1957). As a mountain location, the Como catchment receives a much larger amount of wet precipitation than the nearest site for which comparable data are available (Grand Junction, Colorado; Lodge et al., 1968; Junge and Gustafson, 1955). Soil influence is strongly indicated by the very high Ca^{++} to Na^+ ratio in our samples (approximately 2:1) as compared to the Berkeley Hills site (approximately 1:3) where maritime sources are clearly more important. Similarly, the Cl^- to Na^+ ratio of approximately 1:2 deviates sharply from the approximate 1:1 value seen at Berkeley Hills and from the 1.9:1 ratio that would indicate an exclusively maritime source. These ion ratios most

likely reflect terrestrial influence on deposition chemistry.

The SO_4^- deposition rates at Como Creek were lower than at any other sites in the U.S. for which we could obtain bulk deposition values (e.g., Swank and Henderson, 1976; Likens et al., 1977; Tabatabai and Laften, 1976; Cole and Johnson, 1977; McColl and Bush, 1978; Galloway and Whelpdale, 1980). For example, SO_4^- accounted for about 80% of the anionic equivalents at Hubbard Brook (Likens et al., 1977), whereas SO_4^- accounted for about 30% at Como Creek. We interpret the consistently lower SO_4^- deposition as due to the comparatively lower degree of industrialization in the Rocky Mountain and Great Basin areas to the west.

The NO_3^- -N and NH_4^+ -N deposition rates, in contrast, are not consistently lower than all other U.S. sites. Both species were considerably more important at Como Creek than at Berkeley Hills, for example. Our comparatively high NO_3^- to SO_4^- ratios may be the result of two major regional nitrogen sources, the Denver urban corridor (Kelly and Stedman, 1980) and agricultural fertilization, although we do not as yet know what proportion of the nitrogen oxides are of local or regional origin (Lewis and Grant, 1980b). Other western U.S. precipitation measurements have also shown a higher NO_3^- to SO_4^- ratio (e.g., Liljestrand and Morgan, 1978) than that observed in the east (Likens et al., 1977).

Bulk precipitation plays a major role in the nutrient balance of the Como Creek catchment. In particular, quantitatively important amounts of nitrogen, phosphorus and sulfur enter the watershed via this mechanism. Total nitrogen being carried into the watershed amounts to 5.94 kg/ha/yr in all forms (particulate, NO_3^- -N, NO_2^- -N, NH_4^+ -N, and dissolved organic nitrogen). This rather high figure can be compared with 6.7 kg/ha/yr at Hubbard Brook (Likens et al., 1977), 3.0 kg/ha/yr for a site in western Oregon (Frederickson, 1976), 1.49 for a coastal site in Oregon (Tarrant et al., 1968), and approximately 2.0 kg/ha/yr for Berkeley Hills (McColl and Bush, 1978).

Not all of these cited studies included estimates for all major forms of nitrogen, especially particulate and dissolved organics. Our data indicate that these sources provide ecologically important amounts and should not be ignored. By com-

parison, nitrogen fixation is usually of the order of 2–10 kg/ha/yr (Hutchinson, 1954). Nitrogen fixers appear to be rather limited in the Como Creek watershed so the lower figure will probably be nearer the actual value.

3.4. *Precipitation acidity*

In attempting to chart trends in either free acidity, [H⁺], or free alkalinity, [HCO₃⁻, + metal oxides, + weak acids], one must simultaneously consider both components. An increase in pH could be due to a decreasing input of hydrogen ions, to an increasing input in neutralizing components (primarily bicarbonate in our system), or to simultaneous changes in each. In our analyses, we have made the following assumptions:

(1) The primary determinants of free acidity in precipitation are strong mineral acids (H₂SO₄ and HNO₃) in equilibrium with neutralizing components. The pH of our precipitation samples generally was between 4.0 and 5.5, which justifies our attribution of the H⁺ ions (free acidity) to the strong acids in favor of the weak acids (Galloway et al., 1976; Galloway and Likens, 1979). At these pH values the bulk of the alkalinity will be due to the bicarbonate ion; hydroxides will be approximately 1/500 the concentration of bicarbonate ions (Reuss, 1976) and there will be some contribution

to total alkalinity from weak organic acids and metal oxides.

(2) We assume that all of the SO₄⁻ and NO₃⁻ in bulk precipitation is associated with an equivalent amount of H⁺ ion. While we recognize that this is not strictly true (Granat, 1972) deviations from this pattern appear to be small enough to be unimportant for our purposes.

(3) Total alkalinity is assumed to be the sum of measured alkalinity plus the difference between the hydrogen ion concentration estimated on the basis of the major anions and the hydrogen ion concentration actually observed. Total acidity (H⁺) in the sense of Galloway et al. (1976b) was not measured weekly but was estimated for several samples by titrating to pH 8.3 with a strong base. Because of the difficulties involved with the atmospheric H₂O + CO₂ ⇌ H₂CO₃ reaction (Galloway and Likens, 1979), we titrated for total acidity only those samples in which the original pH was less than 5.0. Our results indicate a range of H_F (= free acidity) of between 15 and 35% with a mean of approximately 20%.

The H⁺ loading rate estimated from the sum of the equivalents of sulfate and nitrate was 325 eq/ha/yr (Table 3). Measured H⁺ was 106 eq/ha/yr, implying that 219 eq/ha/yr of H⁺ was neutralized. These figures indicate that 67% of H⁺,

Table 3. *Simple linear correlation coefficients (× 100) among bulk precipitation components. The upper right triangle uses loading rates, the lower left uses concentrations. Correlations which were significant at p ≤ 0.05 are in italic type*

	Amt. Prep.	Part.	HCO ₃	SO ₄ ⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H ₂ PO ₄ -P	NO ₃ -N	NO ₂ -N	NH ₄ -N	DOC	DOP	DON	H ⁺	Conduct.
Amount precipitation	31	60	19	44	40	46	22	19	52	58	39	99	35	24	42	71	
Particulates		0	7	53	60	18	33	36	38	39	30	33	65	33	-5	36	
HCO ₃			-22	35	27	22	5	-5	2	28	13	65	17	-3	-1	33	
SO ₄ ⁻			-11	13	14	4	14	19	-36	28	29	18	15	28	46	41	
Ca ⁺⁺			23	40		82	46	32	36	54	54	30	51	41	35	-8	40
Mg ⁺⁺			15	35	95		43	42	41	46	45	28	45	50	44	-8	44
Na ⁺			35	48	79	80		46	12	23	20	9	53	21	9	13	34
K ⁺			24	55	85	87	76		16	7	21	6	29	51	20	-9	32
H ₂ PO ₄ -P			10	22	55	42	45	54		43	39	30	21	28	32	15	32
NO ₃ -N			-10	42	49	54	59	51	75		76	66	56	39	56	37	62
NO ₂ -N			-4	16	45	52	60	40	72	71		62	64	46	50	37	71
NH ₄ -N			9	29	60	61	67	59	77	79	72		45	36	57	-21	49
DOC			40	32	91	93	79	87	45	61	41	73		39	29	40	71
DOP			15	35	81	85	69	78	58	64	50	67	62		34	9	58
DON			-23	26	44	22	18	22	69	65	28	59	21	56		21	43
pH			20	43	-37	41	30	20	25	-7	-14	1	7	19	3	-6	-5

as estimated from SO_4^{2-} and NO_3^- , was neutralized by bulk precipitation bases. Conversely, we estimate the total alkalinity as the observed 282 eq/ha/yr plus the neutralized 219 eq/ha/yr = 501 eq/ha/yr, of which 44% had been neutralized by H^+ . The average $[\text{H}^+]$ yielded a pH of 4.80. Because some of our samples had pH's greater than 5.65, we also averaged CO_2 -acidity as given in Stumm and Morgan (1970) rather than $[\text{H}^+]$. This method indicated an average acidity of 23.1 $\mu\text{eq/l}$ which translates to a pH value of 4.67, only slightly different from average $[\text{H}^+]$ (pH = 4.80).

The 4.80 value compares with 6.15 for Iowa (Tabatabai and Lafen, 1976), 5.0 and 6.3 for northern and lower Michigan, respectively (Richardson and Merva, 1976), 6.5 for central Texas (Cooper et al., 1976), 4.14 for the northeastern U.S. (Likens et al., 1977), 5.0 for Berkeley Hills, California (McColl and Bush, 1978), and 4.06 for Pasadena, California (Liljestrand and Morgan, 1978). Pack (1980) reports pH values between 4.07 and 4.46 for several sites in the eastern U.S., while Brezonik et al. (1980) report average values between 4.7 and 5.5 for the Florida peninsula. Lewis (1981) indicates a value of 5.96 for a watershed in Venezuela. The values in the literature are sometimes based on different sampling techniques (e.g., wet only vs. bulk samples) and often span different lengths of time. As values less than pH = 5.65 are indicative of influence by human activities (Galloway et al., 1976a), our data provide strong evidence that the precipitation falling into the Como Creek watershed is routinely influenced by human activities (Lewis and Grant, 1980a). Although Barry (1973) showed that the vast majority of air mass movements over the collecting site come across the Continental Divide from low population density regions to the west and northwest, the Como site does experience up-slope conditions which can bring substantial amounts of nitrogen to the area, at least during some periods of the year (Kelly and Stedman, 1980). We are not yet in a position to identify the geographic sources of the acidifying components in a quantitative way. In any case, our data indicate that at least one site in the Rocky Mountain west is routinely receiving precipitation which is decidedly acidic.

The major buffering compound in our system is bicarbonate, in marked contrast to the Hubbard Brook watershed, where bicarbonate is present in

trace amounts only (Likens et al., 1977). The bicarbonate ion is the single most important measured ionic component on an equivalent basis, indicating that substantial amounts of alkaline earths such as CaCO_3 are important contributors to bulk precipitation in this region. These data are consistent with Gosz's findings (1975) that particulate input is more important in the Sangre de Cristo mountains of New Mexico than in the White Mountains of New Hampshire. The extent to which terrestrial components are influencing the character of Como Creek precipitation has already been shown by the results of the total alkalinity and total acidity calculations. Further, the results of the titration to pH 8.3 on selected samples shows a much greater proportion of weak acids in Rocky Mountain precipitation than in precipitation at Hubbard Brook. These act as a reserve buffer system and tend to counteract increases in pH. Consideration of the overall average values of each of these components indicates that roughly 50% of the normal acid buffering capacity of precipitation at Como Creek has been exhausted.

We calculated the theoretical pH of our samples using Granat's (1972) model, which treats sea salt as neutral and corrects for sea salt contributions to precipitation by subtracting the appropriate equivalent amounts for each component. This model has been shown to be effective in predicting pH values for several sites in the eastern U.S. (Cogbill and Likens, 1974). The Granat model as given in Granat's 1972 paper predicts a pH of 6.02 for Como Creek precipitation, 1.22 pH units higher than the observed value of 4.80. This large discrepancy is further evidence that the composition of bulk precipitation at Como Creek is strongly influenced by terrestrial sources which make the Granat maritime model inappropriate for this region.

Liljestrand and Morgan (1979), in an analysis of random error associated with pH measurements, used a charge balance model to estimate pH from the data published by Lodge et al. (1968). Their analysis indicated that the pH of precipitation at Grand Junction, the site closest to Como Creek, was likely to have been between 7.15 and 7.34. Whether the enormous difference between that estimate and our observed 4.80 figure at Como Creek is due to regional, topographic, or temporal variation (downward trend in pH over time) or some combination of the three cannot at present be

determined. It is also possible that the original limited suite of variables measured by Lodge et al. (1968), which did not include alkalinity or pH, was inadequate to characterize the H^+ composition.

3.5. Correlation analysis

In order to measure the degree of linear association among all the components pairwise we calculated the Pearson product moment correlation coefficient for all pairs of the bulk precipitation components. Because this statistic is so sensitive to extreme or outlying values, we filtered all the data by automatically excluding any outlier more than 1.96 standard deviations from the mean. This filter was applied uniformly to all variables and usually resulted in exclusion of 1 to 7 points. In general, application of this filter led to slightly lower correlation coefficients. The mean values for the filtered data set are given by Lewis (1981), whereas the means for the unfiltered data have been given here in Tables 1 and 2.

The results are shown in Table 3, where the upper right triangle shows the correlation coefficients among loading rates and the lower left triangle shows the correlations among concentrations where such units are appropriate. To read the matrix of correlation coefficients, choose the triangle which contains the information of interest and find the intersection point for any particular component pair. For example, the estimate of correlation between loading rates of Ca^{++} and SO_4^- is a non-significant 0.13 (roman figures), while the corresponding estimate of correlation between concentrations of Ca^{++} and SO_4^- is a highly significant 0.40 (italic figures). We will examine the correlations among precipitation components in more detail elsewhere and restrict our attention in this paper to the most obvious patterns.

There is a much stronger interrelationship among concentrations than among loading rates. The average (absolute value) correlation estimate among components from the standpoint of concentration was 0.51 while the average among loading rates for these same variables was 0.33. Correlations higher than 0.9 were rare in the loading rate set but there were several in the concentration set. These results illustrate the multiplicative nature of loading rate (concentration \times volume) as well as the relatively high degree of statistical independence between con-

centration and amount of precipitation, when measured weekly.

The degree of correlation between loading rate and amount of precipitation was surprisingly small. DOC was the only component with a near-perfect linear relationship. Most components showed a positive correlation with most other components. In loading rates a part of this relationship is likely due to the seasonality of precipitation and concomitant seasonality of loading rates. With respect to concentrations, it seems that precipitation which was high in some components tended to be high in many others as well.

H^+ loading rate was most strongly correlated with amount of precipitation, SO_4^- , NO_3^- -N, NO_2^- -N and DOC loading rates. The strong positive association with sulfate and nitrate is easily understood, as these are the anions of the strong acids believed to be contributing the vast majority of H^+ ions.

Bicarbonate loading rate was most strongly associated with DOC and was also positively associated with Mg^{++} and Ca^{++} . These results suggest that much of the bicarbonate ion may be derived from $MgCO_3$ and $CaCO_3$ dust. The SO_4^- ion was not particularly strongly correlated with any other ion except H^+ . The nitrogen-containing compounds NO_3^- , NO_2^- and NH_4^+ were fairly strongly interrelated, suggesting common sources as well as interconversions.

Precipitation pH was positively correlated with the concentration of the bicarbonate ion, negatively correlated with the sulfate ion, and positively correlated to a substantial degree with the NH_4^+ ion. These patterns are consistent with our assumptions about the substances controlling precipitation acidity. McColl and Bush (1978) report few significant correlations among their measured components, whereas we found significance to be more the rule than the exception. This variance between studies is at least partly due to our larger sample size, which permits detection of weaker associations.

At first glance the marked seasonal patterns in loading rates, observed in many of the components of bulk precipitation, appeared to be explained by the underlying seasonality of aqueous precipitation. A second cause of changes in loading rates, however, could be changes in concentration which either exaggerate or damp the influence of varying amounts of aqueous precipitation. In order to

quantify the influence of each of these components independently, Model II multiple regression of loading rates versus amount of aqueous precipitation and concentration was performed on all components. The results are shown in Table 4 expressed in terms of the coefficient of determination (r^2) which can be interpreted as the proportion of the variation in loading rates "explained" by linear relationships between the amount of aqueous precipitation and concentration, separately.

The first pattern shown in Table 4 is that, in general, much of the variance is unexplained by amount of aqueous precipitation and concentration. This was the result of strong patterns of nonlinearity between both concentration and amount of precipitation.

A second pattern in Table 4 is that five of six components which show an r^2 value larger than 40% in column 4 derive a larger share of that explanatory power from the amount of aqueous precipitation. Dissolved organic nitrogen is the single exception. Dissolved organic carbon, in

Table 4. Proportion of variation in loading rates explained by amount of aqueous precipitation and by concentration in Como Creek bulk precipitation as measured by the coefficient of determination in (r^2) in %

Component	r_1^2 amount of aqueous precipitation	r_2^2 concentration	$r_1^2 + r_2^2$ total
Particulates	9	3	12
% C	23	1	24
% N	38	0	38
% P	2	0	2
% H	18	0	18
HCO ₃ ⁻	48	33	80
SO ₄ ⁼	3	23	26
Ca ⁺⁺	24	20	45
Mg ⁺⁺	18	19	37
Na ⁺	22	1	23
K ⁺	6	5	11
H ₂ PO ₄ ⁻ -P	6	12	17
NO ₃ ⁻ -N	39	26	62
NO ₂ ⁻ -N	41	9	49
NH ₄ ⁺ -N	13	25	39
DOC	97	0	97
DOP	15	13	28
DON	7	36	43
H ⁺	43	7	50

particular, follows the aqueous pattern almost perfectly. In contrast, DON, H₂PO₄⁻-P, NH₄⁺-N and SO₄⁼ loading rates follow changes in concentration more closely than amount of aqueous precipitation.

3.6. Dry fallout

Table 5 provides a comparison between the bulk precipitation and the dry deposition fraction, each of which was measured directly. The methodology of dry fallout collection is not well established and, for the reasons given earlier, the reliability of the data for dry values is somewhat lower than for bulk precipitation. These caveats notwithstanding, several very interesting patterns can be seen in Table 5.

Dry fallout contributed about 87% of insoluble particulates. More than 75% of the inorganic phosphate which entered the watershed from the atmosphere did so in the form of dry fallout. Most of the magnesium and sodium also settled out in the dry fraction while roughly 50% of the calcium was so deposited. Most of the other constituents such as SO₄⁼ and NO₃⁻, were deposited in a ratio of about 1:5 dry to bulk.

Estimation of the relative partitioning for the H⁺, NH₄⁺, and HCO₃⁻ is somewhat more complicated because of the interdependency of these constituents. In our bulk collection samples these components will have equilibrated with each other (and atmospheric CO₂) as described earlier. The dry sample, however, was never mixed with any other sample but was directly solubilized in distilled

Table 5. Arithmetic mean dry fallout estimates, standard errors, and proportion of bulk values for 70 weekly observations at a single station

	kg/ha/yr	eq/ha/yr	% of bulk precipitation loading rate
Particulates	128.6 ± 17.3	—	87.4
HCO ₃ ⁻	30.83 ± 1.78	505.5 ± 29.1	180
SO ₄ ⁼	1.95 ± 0.59	40.6 ± 12.1	20.7
Ca ⁺⁺	1.55 ± 0.26	77.4 ± 12.8	38.8
Mg ⁺⁺	0.29 ± 0.07	23.8 ± 5.6	63.0
Na ⁺	1.47 ± 0.16	63.9 ± 7.0	74.6
K ⁺	0.75 ± 0.14	19.1 ± 3.7	47.8
H ₂ PO ₄ ⁻ -P	0.04 ± 0.01	0.4 ± 0.6	75.6
NO ₃ ⁻ -N	0.40 ± 0.03	28.4 ± 2.0	22.2
NO ₂ ⁻ -N	0.003 ± 0.001	0.2 ± 0.03	10.3
NH ₄ ⁺ -N	0.29 ± 0.03	2.1 ± 0.23	23.2
Soluble organic C	0.67 ± 0.09	—	6.5
Soluble organic P	0.02 ± 0.003	—	55.6
Soluble organic N	0.20 ± 0.03	—	16.4
H ⁺	0.04 ± 0.01	43 ± 10	37.7

H₂O. This is why the dry fallout HCO₃⁻ fraction alone had more HCO₃⁻ than bulk precipitation.

Dry fallout contributed major amounts of several bulk precipitation components. From an element cycling point of view, exclusion of dry deposition would lead to serious systematic biases. Ecologically, we view bulk loading rates to be a reasonable assessment of naturally occurring deposition.

4. General comments

The composition of bulk precipitation at the high mountain Como Creek site was found to be considerably different from that of any previously published data. The precipitation was unique in showing comparatively low levels of SO₄⁻ while simultaneously being decidedly acidic. Comparatively large amounts of Ca⁺⁺ and Na⁺ plus the quantitatively important role of dry fallout strongly indicate that terrestrial sources were a major source of deposition in the Como catchment.

If the data presented in this paper on precipitation acidity prove to be typical of the Rocky Mountain west and if the trend of increasing acidity continues (e.g., Lewis and Grant, 1980a), substantial changes in the recipient mountain

ecosystems can be expected (Lewis and Grant, 1979). High mountain lakes of the Rockies tend to be poorly buffered because of the predominantly granitic substratum and thus are likely to be comparatively sensitive to changes in precipitation pH. Aquatic systems, especially lakes, will probably be affected first and most adversely (e.g., Beamish, 1974), much in the fashion of the Adirondacks (e.g., Cronan and Schofield, 1979). The difficulties presented by acid precipitation in the Rocky Mountain region may well be intensified by the anticipated development of fossil fuel reserves, especially coal and oil shale, in this region. The potential for change is large. We believe the chemistry of precipitation in this region warrants continued close empirical study.

5. Acknowledgements

This research was partially supported by: the U.S. Forest Service, Eisenhower Consortium for Western Environmental Forestry Research; the University of Colorado through Biomedical Research Support grant No. 153-2281; the Council for Research and Creative Work and the University of Colorado Mountain Research Station through use of its facilities. This paper is number 054 in the Eisenhower Consortium Journal Series.

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ХИМИЯ ОСАДКОВ В ШТАТЕ КОЛОРАДО, США

Химический состав количества осадков (жидких и сухих) измерялся на двух станциях в Скалистых Горах штата Колорадо, на каждой станции по 150 последовательных недель. Станции Комо Крик (Ручей Комо) находятся на высоте 3000 м, примерно в 6 км к востоку от Континентального водораздела (так же перевала в Скалистых Горах) и в 40 км к востоку от Денвера.

Химические разновидности измеряемые обычным образом включали частицы ("партикулаты") С, N, P и H; растворенные органические С, P и N; проводимость и суммарную щелочность; SO_4^- , NO_3^- -N, NO_2^- -N, NH_4^+ -N, Ca^{++} , Mg^{++} , Na^+ , K^+ , H_2PO_4^- -P и H^+ . Частицы осаждались в водораздел с количеством в 147 кг/гектар/в год с тем что, С составляло около 21% всего этого количества. Самые важные анионные компоненты были: суммарная щелочность выраженная в форме двууглекислого (281 экв/гек/в год) SO_4^- (196 экв/гек/в год) и NO_3^- -N (129 экв/гек/в год). Среди катионов Ca^{++} был самым важным (200 экв/гек/в год), затем следовал H^+ (106 экв/гек/в год) и NH_4^+ -N (89 экв/гек/в год). Проводимость в

среднем 16 микромосм.

Состав сухого выпадения (осадков) собирался и анализировался в течение 70 недель на одной станции. Частицы составляли 129 кг/гек/в год из 169 кг/гек/в год всех собранных. Суммарная щелочность была решительно самым главным сухим компонентом и выраженная как HCO_3^- , составляла 506 экв/гек/в год из всех измеренных суммарных 804 экв/гек/в год. Около 75% общего неорганического фосфора загрязненного в водораздел было из сухих осадков.

Состав осадков Комо Крик значительно отличается от других образцов описанных в литературе, и собственно тем, что сравнительно низкие уровни SO_4^- были найдены одновременно с сравнительно высокими уровнями H^+ . Удивительно высокие и увеличивающиеся уровни отложений изученного H^+ на единственном участке западных Скалистых Гор с данными длительного срока и широкого спектра, указывают на потребность обширного географического освещения химии осадков в западной части Соединенных Штатов.