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CHANGES IN THE OUTPUT OF IONS FROM A WATERSHED AS A RESULT OF THE ACIDIFICATION OF PRECIPITATION

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Abstract. The average hydrogen ion input to a mountain watershed in Colorado increased by a total of 0.142 meq m$^{-2}$ wk$^{-1}$ over a 150-wk study period. Over the same period, the output of bicarbonate ions from the watershed, as determined by weekly stream chemistry measurements, decreased by 0.162 meq m$^{-2}$ wk$^{-1}$ after correction for a slight decrease in bicarbonate input. The output of sulfate, nitrate, ammonia, and dissolved organic matter all increased significantly. These increases are not enough to constitute a major change in watershed mass balance, but the nitrate and ammonia changes in particular could be important to the stream biota because of the low background levels of inorganic nitrogen. Output of calcium, magnesium, sodium, potassium, phosphate, and hydrogen ions showed no significant individual trends, but there is some evidence of a decrease in total cation output. It is postulated that essentially all of the hydrogen ions entering in the form of acid precipitation combine with bicarbonate ions in the soil, and this accounts for the reduction in bicarbonate output of the watershed. This hypothesis is well supported by the match between rates of change in hydrogen ion input and bicarbonate output. Since carbonates are not present in the soil, a combination of acid with bicarbonate would lead to the production and release of free CO$_2$ in amounts equivalent to the acid which is neutralized. Acidification of precipitation thus appears to cause a stoichiometric reduction in bicarbonate output and smaller but potentially important shifts in output of other ions as well.

Key words: acid precipitation; Rocky Mountains; stream chemistry; watershed mass balance.

INTRODUCTION

Recent investigations have shown that the acidification of precipitation by anthropogenetic mechanisms has occurred at a rapid pace in northern Europe (Oden 1976), parts of the eastern United States (Corgill and Likens 1974, Likens and Bormann 1974) and, according to some very recent information, parts of the western United States as well (Lewis and Grant 1980, Table 1). The environmental effects of acid precipitation are only now being investigated and are thus at the present time extremely uncertain (Gorham 1976). Serious effects which seem to be relatively certain are connected with acidification of lakes (Almer 1974, Hendry and Wright 1975, Beamish 1976, Schofield 1976). Alteration of growth rates of vegetation may also occur but still require documentation (Abrahamsen et al. 1976, Cogbill 1976, Tamm 1976, Tamm and Cowling 1976). The effects of acid precipitation on soils are also uncertain. Acidic soils with low exchange capacity and low buffer capacity are likely to be most vulnerable (Wiklander 1974), but several authors have pointed out that the total buffering capacity of soils is high by comparison with the rate of acidification of rainfall (e.g., Frink and Voigt 1976, McFee et al. 1976, Cole and Johnson 1977). The exact fate of hydrogen ions added to soil is difficult to judge owing to the great complexity of soil chemistry, but it would appear that the acid-absorbing capacity of most soils in a strictly chemical sense is quite great. Nevertheless, the addition of acid to soils could easily result in the release of other materials such as ions deriving from ion exchange reactions or acid-base reactions (Oden 1976, Wright et al. 1976, Johnson et al. 1977). Similarly, addition of acids might well reduce the amounts of certain substances liberated from soils.

We have previously shown that the watershed of Como Creek, near the Continental Divide in Colorado, has experienced steady and marked increase in the input of hydrogen ions associated with increasing amounts of nitric acid in precipitation over a 3-yr period, June 1975-May 1978 (Lewis and Grant 1980, Table 1). This increased acid input, which is of unknown but probably anthropogenetic origin, has resulted in a decline in pH of bulk precipitation of 0.8 pH units in the 3-yr interval (from pH 5.4 to pH 4.6, adjusted annual mean). Since the output rates of major chemical substances were documented over the same period, we are able to examine the output data in search of trends which might be related to the acidification of precipitation and thus deduce some of the mechanisms by which incoming acid is processed in the terrestrial system as well as the effect of acid precipitation on the mass balance of the watershed and the chemistry of the stream draining the watershed.

SITE CHARACTERISTICS

The Como Creek Watershed is located at 2900 m altitude 6 km east of the Continental Divide in north-central Colorado (Fig. 1). The stream above the sam-

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1 Manuscript received 21 August 1978; revised 15 March 1979; accepted 12 April 1979.
pling site drains an area of 664 ha that has been subjected to minimal human activity over the past 40 yr. The area is covered primarily with conifers (Abies lasiocarpa, Picea engelmannii, Pinus contorta, Pinus flexilis), but also has some aspen (Populus tremuloides) and Salix. Approximately 20% of the watershed is not forested because it is above tree line, too boggy, or was cut some 60–75 yr ago and never reseeded. These areas are covered with alpine herbs, grasses, sedges (Carex), and willows (Salix).

The discharge of Como Creek varies from 3.5 l/s in late summer to a maximum of ~360 l/s during the runoff period (June) of a wet year. Total wet precipitation reaching the watershed averages ~770 mm/yr, and there is a slight increase in the amount of precipitation from the bottom to the top of the watershed. Weather comes principally over the Continental Divide from the west, although upslope storms from the east are not unusual in spring or early summer (Barry 1973).

The watershed soils, which are presently under intensive study (S. Burns, personal communication), are typically quite thin (mean ~ 60 cm; maximum ~ 200 cm) and overlie granitic parent material. The cation exchange capacities range between 5 and 30 meq/100 g and average ~ 20 meq/100 g. Surface pH values range mostly between 4.5 and 6.0. No carbonates are present. The soils are of the podzol type, but according to revised taxonomy would be classed as podosols with intermixed alfisols undergoing podosolization (Soil Survey Staff 1975: Burns, personal communication).

Como Creek has a very low dissolved-solids content (average specific conductance, 32 µS/cm at 25°C) and very low dissolved-nutrient levels. Although the pH of the stream changes seasonally, the median pH is slightly below 7.0. Substantial amounts of dissolved organic carbon derived from the terrestrial system (2.7 mg C/l, weighted mean) are typical of the stream.

**Methods**

Stream water and bulk precipitation were sampled on a uniform schedule for 150 wk. Stream samples were taken weekly with a hard plastic bottle over a period of ~2 min at a single location. Bulk precipitation was collected continuously at two stations 1 km apart along the stream. The precipitation collector was emptied and rinsed at weekly intervals. The methods of collection and analysis for bulk precipitation samples have been given elsewhere (Lewis and Grant 1978) and need only be outlined here.

Analysis of all samples was initiated within 3 h of the time of collection. The samples were filtered through Whatman GF/C glass fiber paper (effective pore size ~2 µm) so that the particulate and dissolved fractions could be analyzed separately. For present purposes, only the analyses of pH and the major dissolved cations and anions are relevant.

The amount of hydrogen ion was determined from the pH of a fresh sample. Major cations (calcium, magnesium, sodium, potassium) were determined by atomic absorption on acidified samples (1% of 1.0 normal HNO₃). Alkalinity was determined by titration of a 100-ml aliquot with standard acid to a pH of 4.4. All of the alkalinity in the sample is assumed to be due to the CO₃/HCO₃⁻ system, although in fact ~5% was due to the presence of other bases. Sulfate was determined by a barium precipitation technique (Golterman 1969) and phosphate by an ascorbic acid method (Golterman 1969). The ammonia concentrations were determined by a phenolhypochlorite method (Solorzano 1969) and the nitrate concentrations by cadmium-copper reduction followed by formation of an azo dye (Bendschneider and Robinson 1952, Wood et al. 1967).

Discharge from the watershed was estimated weekly by means of a Parshall flume which was empirically calibrated with pumps. In the computation of output rates for the watershed, the amount of each dissolved substance on a particular week was multiplied times the discharge for that week. Output in particulate form was quantitatively unimportant for the present analysis and is therefore not included here. The computation of chemical input was accomplished in a similar manner from the weekly amount of each of the substances in bulk precipitation reaching the watershed. The weekly input and output data were then studied as a function of time by means of regression techniques.

One complicating factor in the determination of trends across years in the output data has to do with the heavy pulsing of output in connection with spring runoff. Variation in amount of discharge can change the output rates because the nutrient pool in the terrestrial system responds to additional flushing with increases in output. This seasonal change might not affect a statistical examination of trends across years if large numbers of years were included in the data base. For a small number of years, however, a fortuitous
Table 1 shows no significant change in the output of calcium, magnesium, sodium, potassium, phosphorus, or hydrogen from the watershed. The amount of bicarbonate leaving the system declined significantly over the 150-wk study period, but the output of ammonium, nitrate, and sulfate ions increased significantly. The magnitudes of change in ammonium, nitrate, and sulfate are trivial in terms of mass balance, although they could be of considerable biological importance in the stream itself. In contrast, the bicarbonate change is major in terms of mass balance. On the whole, the output data indicate a drastic change in the regulation of bicarbonate output and secondary changes in ammonium, nitrate, and sulfate output.

**INTERPRETATION AND DISCUSSION**

Since increase in hydrogen ion input is not matched by a significant increase in hydrogen ion output, it is safe to conclude that the increasing amounts of hydrogen ion entering the system are taken up almost entirely by the terrestrial component. If the incoming hydrogen ions were taken up by the mechanism of ion exchange, one would expect to see an increasing trend in some or all of the cations. The data show no such trend.

Another possible fate of incoming hydrogen ions is combination with bases in the soil system. Since the soil in the Como Creek Watershed has a relatively low pH and is of granitic origin, the amount of carbonate present is essentially zero. This means that bicarbonate is the most likely inorganic base to combine with the incoming hydrogen ions and thus account for their failure to appear in the output from the system. This mechanism is consistent with the data, as the bicarbonate output of the watershed shows a significant downward trend corresponding to the upward trend in hydrogen ion input (Table 1). One might expect some decline in bicarbonate solely as a by-product of the declining input of bicarbonate (0.040 meq m⁻² wk⁻¹),
but the decline in output of bicarbonate is considerably
greater than this (0.202 meq·m⁻²·wk⁻¹). Thus a total
decline in output of bicarbonate equal to 0.162
meq·m⁻²·wk⁻¹ cannot be accounted for except by
means of the increased input of hydrogen ion. The
increase in hydrogen ion input is in fact remarkably
well matched to the unaccountable decrease in bicar-
bonate output (0.142 vs. 0.162 meq·m⁻²·wk⁻¹). We
therefore postulate that hydrogen ions equal to 0.162
meq·m⁻²·wk⁻¹ combine with bicarbonate ions to pro-
duce free CO₂:

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2. \]

This implies that 0.162 meq·m⁻²·wk⁻¹ of CO₂ are pro-
duced simply as a result of acidification of the soil,
and that the full increase in hydrogen ion input can be
accounted for by the bicarbonate buffer system. The
increase in nitrate input is undoubtedly taken up for
the most part by the biota.

An independent check on the proposed soil bicar-
bonate titration by strong acids in bulk precipitation
is possible through a corollary hypothesis. If increas-
ing precipitation acidity does indeed reduce annual
bicarbonate yield by titration of soil bicarbonates, a
seasonal effect should also be evident, as the flushing
of soils by precipitation varies seasonally. The data
show that bicarbonate yield increases at a rate signifi-
cantly less than the increased rate of discharge within
any 1 of the 3 yr of the study (\(P < .05\)). Furthermore,
the slope of yield on discharge for bicarbonate is lower
than for any major cation, indicating that mere dilution
of soil water by precipitation cannot explain the re-
results. We have developed this and more complex as-
pects of seasonal changes in yield elsewhere (Lewis
and Grant 1979). The essential point here is that sea-
sonal changes in yield are as expected if the mecha-
nism we have proposed to account for long-term
 trends in bicarbonate output is valid.

The ionic balances of all but the last column in Table
1 are well within analytical limits. The last column,
which reports changes in output, is unsatisfactory in
this respect, as net change in anions exceeds net
change in cations by 0.180 meq·m⁻²·wk⁻¹ over the
150-wk period. Assuming that anion and cation loss
should be similar, this degree of imbalance seems un-
likely. We therefore considered additional factors
which would be likely to account for the difference.

1. Although individual cations do not show a down-
ward trend, it is possible that total cations would. We
did the regression analysis for total cations and dis-
covered a negative relation that was not significant
statistically but was highly suggestive (\(P = .14\)). If
accepted as valid, this relationship would account for
≈0.050 meq·m⁻²·wk⁻¹ as a cation decrease brought
about by bicarbonate decrease. (2) Organic anions are
not considered in Table 1. A regression study of the
DOC (dissolved organic carbon) output shows a highly
significant increase (\(P < .001\)) from 6.63 mg
C·m⁻²·wk⁻¹ at the beginning of the study to 9.00 mg
C·m⁻²·wk⁻¹ at the end, or a total change over the 150
wk of 2.37 mg C·m⁻²·wk⁻¹. The cause of this change
is unknown, but changing rates of decomposition in
the terrestrial system may be involved (G. E. Likens,
personal communication). Although the ionic strength
of these organic compounds cannot be estimated reli-
ably, this major change in carbon output also con-
tributes to the resolution of the ionic balance problem
in column four of Table 1. (3) Chloride, which is a
minor constituent in this system, was not analyzed
systematically and may therefore account for part of
the apparent imbalance.

The data indicate that the Como Creek Watershed
is strongly responsive to increases in the acidity of
precipitation as a result of the titration of bicarbonate
by strong acids in the soil system. This in turn implies
that stream chemistry is responsive to watershed acid-
ification insofar as stream chemistry is regulated by
watershed output. Although the total inventory of
buffering substances is definitely not exhausted by the
increased input of mineral acids in precipitation, the
output characteristics of the watershed are changed as
a result of the titration of the main buffering compound
(bicarbonate) by the hydrogen ions. An effect of this
type would be limited to soils containing negligible
carbonate, as addition of hydrogen ions to a system
containing carbonate would be expected to produce
additional bicarbonate rather than reduce the amount
of bicarbonate (Stumm and Morgan 1970).

The mechanism we have proposed for the fate of
increasing acidity in the Como Creek system requires
the production of CO₂ from bicarbonate as it is titrated
with strong acid. If this CO₂ escapes from the soil,
present total release of carbon dioxide attributable
specifically to the titration effect would amount to
some 101 mg C·m⁻²·yr⁻¹, which is small by compari-
son with fossil fuel sources (= 10 000 mg C·m⁻²·yr⁻¹,
Adams 1977) but could become larger with continued
acidification. Any increment in CO₂ release caused by
the titration mechanism must be considered anthro-
poegenetic because the increasing acidity itself is an-
thropoegenetic.

The increases in output of inorganic nitrogen, al-
though of negligible importance to mass balance, are
worthy of note in another context, as fixed inorganic
nitrogen is of great potential nutritional significance to
the freshwater biota. The increase in stream concen-
trations of nitrate, after adjustment for variation in
discharge by the multiple regression procedure, is
248% over the 150-wk period (change in weighted av-
erage of stream concentrations from 2.0 μg/l NO₃-N
to 4.9 μg/l NO₃-N over the 150-wk period). The
comparable figure for ammonia is 375% (change in weight-
ed average stream concentrations from 3.8 to 14.2
μg/l NH₃-N). The mechanism by which these increases
occur is not clear, but if acidification of precipitation is
responsible, the trend can be expected to continue and
will thus increase significantly the availability of a potentially limiting nutrient for the biota of the freshwaters draining the watershed.

The conclusions drawn here can only be tentative, as the period of data collection, although long in absolute terms, is insufficient for unqualified conclusions concerning trends. The Hubbard Brook Ecosystem Study has shown that it is highly advantageous to study nutrient cycling in natural ecosystems from the perspective of some 10 yr of data (Likens et al. 1977), but it is excessively restrictive and costly to limit interpretation to such conditions. Moreover, statistical correction for confounding trends greatly reduces the likelihood of erroneous conclusions.

Acknowledgments

This research was supported in part by the Forest Service, United States Department of Agriculture, through the Eisenhower Consortium for Western Environmental Forestry Research (published as Eisenhower Consortium Journal Series Paper Number 30) and by the University of Colorado through Biomedical Research Support Grant Number 153-2281. We are indebted to the University of Colorado Mountain Research Station for use of its facilities. We are grateful to Scott Burnk for information on soils, to Gene Likens and another reviewer for helpful comments on the manuscript, and to Donald Runnells for an evaluation of the feasibility of our main thesis about the fate of increased hydrogen ion loading on the soil system.

Literature Cited


