

Reports

Acid Precipitation in the Western United States

Abstract. *Precipitation chemistry data from a rural area at an elevation of 2900 meters near the Continental Divide in Colorado show unexpectedly low pH values for bulk precipitation. A significant downward trend in pH over the last 3 years is associated with increasing amounts of nitric acid in precipitation.*

High acidity of precipitation was first documented in northern Europe (1). The extended record of precipitation chemistry and pH taken at the Hubbard Brook watershed in New Hampshire has also shown that extremely acidic rainfall, presumably of anthropogenic origin, occurs in the eastern United States (2). The data from northern Europe and the eastern United States suggest that substantial regional changes in the chemistry of precipitation have been caused by the addition of acidic substances to the atmosphere in connection with fossil-fuel combustion. Although there has been some controversy about the exact cause of the increasing acidity (3), it seems most likely at present that the great changes in pH can be largely accounted for in terms of sulfuric and nitric acids derived from the terrestrial release of sulfur dioxide and nitrogen oxides.

Although it is now obvious that industrialization and high population density can change the precipitation chemistry over large areas, it is not presently clear how much of the continent or the biosphere has been affected. Our data give evidence of surprisingly low precipitation pH in the Colorado Rockies, suggesting that changes in the precipitation chemistry may be more widespread than presently realized and that the acid rain phenomenon first noticed in the industrial portions of the eastern United States may be typical of significant portions of the western United States as well.

The study site is located in the Como Creek watershed, Boulder County, Colorado, at an elevation of 2900 m and 6 km east of the Continental Divide. The area in a 850-km radius around the watershed has an extremely low population density except for a strip along the Rocky Mountain front range (Fort Col-

lins-Boulder-Denver), 20 to 50 km east and 1300 m lower in elevation than the station (4). The next closest major urban area is Salt Lake City, 600 km west, and then Phoenix, 900 km southeast. A thorough analysis of weather patterns influencing the Como Creek area has been conducted by Barry (5), whose data show that air movement is predominantly from the northwest over a region of very low population density. Although sporadic upslope air movement from the east does occur, it is common only in the spring and early summer months and even then is interrupted by

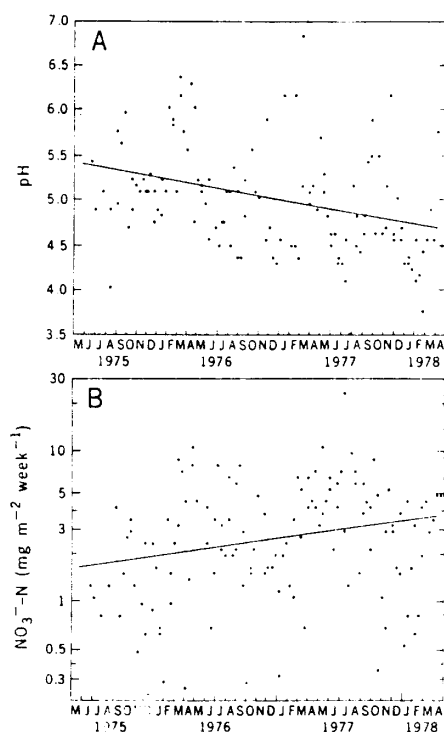


Fig. 1. (A) The pH of bulk precipitation and (B) the loading rate of NO_3^- -N in bulk precipitation over a period of 150 weeks in the Como Creek watershed, Colorado. Significant linear trends are shown by the lines.

long periods of southeasterly air flow over the Continental Divide. We would therefore expect the air to receive only sporadic and limited contamination from nearby urban sources of pollution.

We collected the bulk precipitation (that is, the composite of wet plus dry precipitation) at two stations that were 1 km apart and whose elevations differed by 50 m, over weekly intervals for 150 consecutive weeks (6). The data from the two stations do not differ significantly ($P > .05$) and are averaged for the present purposes. The pH measurements were converted to H^+ concentrations prior to averaging and then reconverted to pH. The pH measurements and chemical analyses were made on the day the sample was collected (7).

Figure 1A shows the pH of the bulk precipitation samples through the 3-year collection period. Many of the pH values are very low. Moreover, there is a clear decline over the 3-year period. The downward trend is highly significant, as indicated by the linear regression of pH against time ($\text{pH} = -0.0053 \cdot (\text{week number}) + 5.43$; $P \leq .01$). The analysis thus indicates that the pH was 5.43 with a standard error of 0.11 at the beginning of the study (week 1, June 1975) and declined at an average rate of 0.0053 unit per week with a standard error of 0.0013 over the succeeding 3-year period. At the end of 3 years, the average pH had declined 0.80 unit, from 5.43 to 4.63, or almost an order of magnitude in H^+ concentration.

The downward trend in pH appears to cut across seasons and across years with very different weather patterns. For example, the winter and spring of 1976-77 were extremely dry and produced very low snowpack at the station. There is no evidence for the exclusive association of declining pH with upslope weather, as would be expected if the pH decline were caused exclusively by the direct movement of pollutants from Denver over the station. Corroborating data from other locations are unavailable. Apparently no systematic, extended study has ever been done of precipitation pH in Colorado or in fact of any location in the western United States, although several government agencies are now interested in beginning such studies.

The increase in acidity can also be expressed in terms of the H^+ input (in milligrams per square meter per week) to the watershed, which in a biogeochemical sense is more important than pH. The results are very similar, however. The regression line based on log-transformed values is given by $\log(\text{H}^+ \text{ input}) = 0.00455 \cdot (\text{week number}) =$

1.43; $P = .001$. The average loading rate thus increased from 0.037 to 0.179 $\text{mg m}^{-2} \text{ week}^{-1}$ over the 150 weeks of the study.

Figure 1B shows the dissolved nitrate nitrogen (NO_3^- -N) delivered weekly to the watershed in bulk precipitation. The data have been log-transformed to reduce the scatter of points. The increase in NO_3^- -N (in milligrams per square meter per week) is statistically significant: $\log(\text{NO}_3^- \text{-N}) = 0.0023 \cdot (\text{week number}) + 0.211$; $P = .003$). The equation implies an average NO_3^- -N loading rate of 1.63 $\text{mg m}^{-2} \text{ week}^{-1}$ at the beginning of the study and 3.60 $\text{mg m}^{-2} \text{ week}^{-1}$ 150 weeks later. This is a difference of 0.141 mmole of NO_3^- per square meter per week.

A mole of NO_3^- derived from gaseous NO_x is presumably associated with a mole of H^+ , as gaseous NO_x compounds combine with water to produce HNO_2 and HNO_3 (8). Thus the increase in NO_3^- -N over the 150-week period would be associated with an increase in H^+ of 0.141 mmole $\text{m}^{-2} \text{ week}^{-1}$. This is exactly sufficient to account for the observed increase in the H^+ loading rates (0.142 mmole $\text{m}^{-2} \text{ week}^{-1}$). The amounts of nitrite nitrogen (NO_2^- -N) in our precipitation samples were consistently below 5 percent of the NO_3^- -N and can therefore be omitted from consideration here.

The average loading rate for sulfate is 18.0 $\text{mg m}^{-2} \text{ week}^{-1}$ over the 150 weeks. There is a suggestive but not statistically significant ($P > .05$) trend toward increasing sulfate loading rates with time (9). Thus, even though sulfuric acid may be a major contributor to total acidity, nitric acid appears to be the component responsible for the observed increase in precipitation acidity.

Our data indicate that the mean acidity of bulk precipitation near the Continental Divide is unexpectedly high and that the acidity of precipitation has increased at a surprisingly fast pace over the past 3 years. The downward trend in pH cannot be extrapolated and may even reverse, but it is suggestive enough to deserve careful observation in the future. The low mean pH is noteworthy even if the downward trend does not continue, however. No local, sizable sources of pollutants are properly situated to account for this trend easily. Two possibilities are that complex and unsuspected mechanisms are moving pollutants substantial distances from the front-range urban corridor contrary to the prevailing patterns of air mass movement or that very widespread changes in precipitation chemistry are presently occurring in the western United States because of significant

increases in the release of nitrogen oxides from multiple sources throughout the West. If the former possibility proves to be correct, our results imply the existence of powerful atmospheric dispersing mechanisms which can move acidic components against strong prevailing weather patterns. If the second possibility proves to be correct, our results imply a very widespread change in precipitation chemistry.

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References and Notes

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3. G. E. Likens, N. M. Johnson, J. N. Galloway, F. H. Bormann, *Science* **194**, 643 (1976).
4. The density of roads and the amount of traffic near the station are extremely low. The nearest hard-surface road (a two-lane highway) to the sampling station is 5 km away. Seasonal surges in traffic do not appear to be related to H^+ input.
5. R. Barry, *Arct. Alp. Res. Occas. Pap.* **3** (1972); *Arct. Alp. Res.* **5**, 89 (1973).
6. Wet precipitation includes snow and rain with its dissolved and particulate chemical components. Dry precipitation includes all materials accumulating on the collectors during periods when there is no wet precipitation. Large Plexiglas collectors (0.25 m^2) were used so that accurate analysis could be made even for weeks with very limited amounts of wet precipitation. The collectors were mounted 4 m off the ground in

clearings shielded by trees and were heated to prevent freezing in winter. The collectors were connected to borosilicate glass bottles with surgical rubber tubing incorporating a vapor barrier. Exposure of distilled water to the collector for extended periods indicated no significant contamination of the sample by the collector. The collecting surface was rinsed weekly and the bottles and tubes were replaced weekly with cleaned, sterilized bottles and tubes. Additional details are given in W. M. Lewis, Jr., and M. C. Grant, *Water Resour. Res.* **14**, 1098 (1978).

7. The pH was measured with a Radiometer model 26 meter equipped with a combination electrode and standardized against pH 4.0 and 6.0 buffers just prior to use. The sample was then filtered through glass-fiber paper (mean pore size, $2 \mu\text{m}$), and the particulate and dissolved components were analyzed separately. Most important to the present discussion are the nitrate and sulfate analyses, but all major cations and anions were included in the analysis (total measured cation input, $1.08 \text{ meq m}^{-2} \text{ week}^{-1}$; total measured anion input, $1.17 \text{ meq m}^{-2} \text{ week}^{-1}$; number of samples = 150). Nitrate analysis was done by reduction of nitrate to nitrite and formation of an azo dye (K. Bendschneider and R. J. Robinson, *J. Mar. Res.* **11**, 87 (1952); E. D. Wood, F. Armstrong, F. Richards, *J. Mar. Biol. Assoc. U.K.* **47**, 23 (1967)). The sulfate analysis was done by a barium chloride precipitation method [H. L. Golterman, *Methods for Chemical Analysis of Fresh Waters* (International Biological Program Handbook No. 8, Blackwell Scientific, Oxford, 1969)].
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9. This amount of sulfate is equivalent to $0.376 \text{ meq m}^{-2} \text{ week}^{-1}$. The standard error for weekly measurements is $0.041 \text{ meq m}^{-2} \text{ week}^{-1}$, and the coefficient of variation is 121 percent (number of samples = 129).
10. This research was supported in part by the Forest Service, U.S. Department of Agriculture, through the Eisenhower Consortium for Western Environmental Forestry Research (published as Eisenhower Consortium Journal Series Paper No. 29) and by the University of Colorado through Biomedical Research Support grant 153-2281.

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Direct Measurement of Solar Luminosity Variation

Abstract. *Two rocket flights of an absolute pyrheliometer, separated by 30 months, indicate an increase in solar luminosity (solar constant) of 0.4 percent. The significance of this result is considered in light of the instrument performance during the rocket flights and of pre- and postflight intercomparisons with independently maintained pyrheliometers. There is a high probability that the measured difference is real. Additional observations are required to determine whether the difference results from random fluctuations in solar luminosity, a nonrandom change of short duration, or a sustained change that has climatological significance.*

The energy that determines the earth's climate is derived from solar optical radiation through interactions with the terrestrial ocean, landmass, and atmosphere. Recent models of climate indicate that small, persistent changes in solar luminosity have substantive climatological impact. The magnitude of the effect depends on the model used, but most predict pronounced sensitivity of the climate to changes in solar luminosity (1-3).

Evidence from many sources (4-7) depicts the earth's climate during the past billion years as nominally tropical, with numerous cyclic excursions to colder periods, some of which were severe enough to cause extensive glaciation from the poles to the middle latitudes.

Models predict that such climatological changes can be produced by systematic variation of the earth's insolation by as little as 0.5 percent per century (8).

The high sensitivity of the earth's climate to insolation and the probable relations between solar magnetic activity and solar luminosity (9) are compelling arguments for long-term monitoring of solar luminosity. This task requires experiment platforms outside the atmosphere and pyrheliometric instrumentation capable of measuring solar flux accurately [that is, with uncertainties in long-term precision (if not accuracy) of no more than 0.1 percent]. The platforms have been available for some time, but the required instrumentation is a recent development (10). The experimental re-