

Acid Deposition in the Western United States

Oppenheimer *et al.* (Reports, 30 Aug. 1985, p. 859) present a provocative argument relating smelter emissions in the American West to observations of sulfate concentration in precipitation on an annual basis in the period from 1980 to 1983. The authors assert that a linear proportionality can be inferred between annual smelter emissions of sulfur dioxide and western precipitation sulfate as far as 1000 kilometers from emission sources. They further state that the derived relation implies support for a linear proportionality between sulfur dioxide emissions and precipitation sulfate concentration in eastern North America.

At first reading, it appears that Oppenheimer *et al.* have presented a simple and cogent analysis that provides support for their suggestions. However, there are several important problems with their approach: (i) the analysis for other chemical constituents in rain chemistry is incomplete; (ii) the validity of the statistical inferences based on the available record of observations is not established; and (iii) it is not shown that these suggestions hold for seasonal or monthly time scales, which are as relevant as the annual periods analyzed by the authors.

Oppenheimer *et al.* examined annual smelter emissions of SO₂ and wet sulfate concentration. By not accounting for other aspects of rain chemistry, however, they do not address the possibility that meteorological factors, not smelter emissions, could control sulfate deposition. The concentration of sulfate in precipitation at western National Acid Deposition Program (NADP) sites has been found to be related to concentrations of nitrate, calcium, and magnesium in the same precipitation (1). But smelter emissions do not include significant amounts of the latter three substances. Because smelters emit only small quantities of nitrogen oxides, emissions from other sources would have to vary in the same way as smelter sulfur oxide emissions for the relation between sulfate and nitrate to be emission-dependent. Yet no evidence is provided by Oppenheimer *et al.* for such emission changes between 1980 and 1983. In addition, there is no evidence provided that the emissions of calcium and magnesium, which are likely to be derived from wind-blown soil, varied in the same way as the smelter emissions. Thus, the smelter emissions can explain only one of the four constituents of rain that have been found to vary together. Regional meteorology may ex-

plain the consistent variations of all four constituents.

In the case of sulfate and nitrate, large-scale meteorological variability in precipitation or wind patterns is known to be a crucial factor in deposition variability in the East (2). Nieman (3) has suggested that widespread annual precipitation changes in the West may explain the observations of Oppenheimer *et al.* if deposition rates are used as an appropriate index for proportionality (3, 4). While one can hypothesize small-scale meteorological mechanisms by which SO₂ smelter emissions could influence nitrate chemistry, such mechanisms are unlikely to be operative. In particular, it could be hypothesized that dissolved SO₂ from smelters accelerates absorption of nitrogen oxides or nitric acid vapor in cloud water. This cannot be a factor because western clouds are not acidic enough. Similarly, highly acidic, airborne sulfuric acid particles scavenged by clouds could also act as a nitrogen oxide absorber. But western aerosol particles generally do not contain high nitrate concentrations.

As for calcium and magnesium, Oppenheimer *et al.* speculate that the relation of soil-derived material (such as calcium carbonate) and sulfate is attributable to increased solubility of such material in acidic water. This is unlikely because western precipitation is not acidic enough (pH ranges between 4.5 and 5.5) to dissolve soil material during the time that condensed water exists in the air.

There is evidence, however, that CaSO₄ · 2H₂O (gypsum) is enriched in soil dust in the West (5). Precipitation data show that calcium is related to sulfate while hydrogen ion is not (unlike conditions in the East). This evidence supports the hypothesis that soil makes a significant contribution to sulfate levels in western precipitation. Thus, smelter emissions or other anthropogenic SO₂ emissions do not appear to be the sole factor influencing atmospheric sulfate behavior in the West.

The second area of concern is the statistical inference in the report. The suggestions of Oppenheimer *et al.* are built on two assumptions: (i) the NADP data are representative of intermountain meteorological conditions, and (ii) the NADP data are uniform throughout the 4 years examined. However, the available NADP stations cited by the authors are not shown to be representative of meteorological conditions generally or of conditions that govern dispersal of emissions in the intermountain region. In addition, the results of the analysis by Oppenheimer *et al.* seem to depend critically on the change found in emissions and wet sulfate between two years, 1981 and 1982.

Data for 1980 were available from only two of the eight selected stations, both of which are far distant from the smelter sources; data for the 1982–1983 interval (figure 2 in Oppenheimer *et al.*) reveal a major contradiction: five of the eight stations show a decrease in sulfate concentration, while SO₂ emissions increased.

Analyses of seasonal and monthly NADP data and smelter emissions over the period from 1980 to 1983 (3, 4) show no linear relation between precipitation sulfate and SO₂ emissions. If a linear relation exists, it also should be apparent in airborne sulfate concentration data, since these particles are scavenged in precipitation. Month-by-month changes in summer airborne sulfate and annual precipitation sulfate is not explained in terms of seasonal smelter emission changes (particularly from the Utah smelter) from available data in western Colorado and other locations between 1979 and 1981 (6).

Although Oppenheimer *et al.* present a linear relation between precipitation sulfate and emissions, the fit is limited to a narrow range of emissions and concentrations. Without proof that the linear model is valid beyond this range, extrapolation to extremes of zero emissions or emissions comparable with those in the eastern United States is not defensible. The upper limit of extrapolation gives far higher concentrations than actually observed in the eastern United States. In contrast, the lower limit yields negative concentrations.

Given these conflicting results and the questions raised by the work of Oppenheimer *et al.*, one cannot disregard alternative explanations of sulfate behavior in western precipitation. It follows that acceptance of the proof of a hypothesized linearly proportional relation between smelter emissions and precipitation sulfate is premature until a more complete analysis is reported and discussed.

G. M. HIDY

Desert Research Institute, Reno, NV 89506

REFERENCES

1. R. Williams, personal communication.
2. *Acid Deposition: Atmospheric Processes in Eastern North America* (National Academy Press, Washington, DC, 1983); G. M. Hidy *et al.*, *J. Air Pollut. Control Assoc.* **34**, 333 (1984).
3. B. Nieman, paper presented at the International Symposium on Acid Precipitation, Muskoka, Ont., 15–20 September 1985.
4. P. Lapat and D. Marczyk, "Monitoring acid deposition in the Rocky Mountain West: Illusions and realities" (report presented to the Arizona Department of Public Health, Phoenix, AZ, 1985).
5. C. S. Creager, "Characterization of the influence of soil particulates on precipitation chemistry at five sites in the western U.S." (Kilkelly Environmental Associates, Raleigh, NC, 1985).
6. J. D. Young *et al.*, "Evaluation of the potential for acid deposition effects due to emissions from Kennecott's Utah smelter" (Environmental Research & Technology, Inc., presented to the Utah State Division of Air Quality, Salt Lake City, UT, 1983).

Oppenheimer *et al.* examined sulfur dioxide emission data from nonferrous metal smelters in four western states and conclude that, over a 4-year period, a linear relation exists between these emissions and the sulfate concentrations in rain sampled in neighboring states (1). We were initially impressed that such a linear relation could be uncovered. However, as we must always remind ourselves in environmental science, statistical relations may reflect, but do not demonstrate, causality. So whenever one finds such relations one must be alert for possible alternative explanations. With this in mind, we studied the results of the chemical analysis for all the ions measured in the samples obtained by the National Acid Deposition Program (NADP), as contained in the Combined Precipitation Chemistry Data Base maintained at Brookhaven National Laboratory. We compiled data as micromoles per liter instead of milligrams per liter so that one can more readily assess the significance of the results when comparing the data for various ions (2). Annual volume-weighted average concentrations (Table 1) were calculated by summing the

individual samples instead of averaging the volume-weighted station values. The numbers obtained for sulfate (when compared in the same units) are slightly, but not significantly, different from those reported by Oppenheimer *et al.*

When Oppenheimer (3) provided us with an early version of their manuscript, we examined the data set and observed that a linear relation between concentration and sulfur dioxide smelter emissions was not unique to sulfate and that calcium, magnesium, chloride, and sodium concentrations exhibited equally strong linear relations (4), as shown in Table 1. We were struck with the obvious quandary that these results presented, as these substances are not present in smelter emissions and therefore there is no reason why their concentrations in rainwater should be related to smelter operations. Consequently, we questioned whether there was any mechanistic significance to the relation for sulfate suggested by Oppenheimer *et al.* At that time (5) we informed Oppenheimer of our results, and Oppenheimer *et al.* state in the printed version of their text that "The relation between sulfate and base

cations may arise from increased metal-carbonate solubility with increasing acidity of atmospheric droplets." This argument would require that rain acidity increase in proportion to increased emissions, thereby solubilizing stoichiometric amounts of solid material associated with the rain, a doubtful and highly speculative suggestion.

We have now made a more detailed analysis of the basis upon which Oppenheimer *et al.* derived their conclusions. The authors made estimates of smelter emissions, but there is at least one other estimate which appears in an Argonne National Laboratory (ANL) report (6). This estimate also presents emissions from sources other than the smelters given by Oppenheimer *et al.* These data along with those of Oppenheimer *et al.* are presented in Table 2. Industrial emissions taken from the ANL report are not markedly different from the smelter emissions derived by Oppenheimer *et al.*, but the latter might more accurately reflect smelter operations. Because it is not clear why the argument presented by Oppenheimer *et al.* should be delimited to smelter emissions, we also include in Table 2 the estimates for sulfur dioxide emissions from all known sources. We note that these sources are substantial. In addition, we include the emissions not only from the states in which the smelter sources, identified by Oppenheimer *et al.*, are located, but also from the states in which the rain samples were obtained, as we see no reason to dismiss the possibility that these "local" emissions might influence the composition of the samples.

A plot of the average sulfate concentrations and the emissions data (Fig. 1) demonstrates that the apparent relation was derived from essentially three points, since the 1981 and 1983 emission values almost coincide. This linear relation appears even less convincing because the sulfate concentration for the intermediate year, 1980, was determined from only two separate operating stations.

Table 1. Weighted yearly average concentrations of precipitation at NADP stations selected by Oppenheimer *et al.* (1) and change in weighted averages of precipitation as a function of emissions.

Ion	Precipitation ($\mu\text{mol/liter}$)				Slopes [$(\mu\text{mol/liter})/(\text{metric tons SO}_2/\text{year})$]	
	1980	1981	1982	1983	Smelter*	Smelter and nonindustrial†
Sulfate	13.69	16.81	9.16	8.94	17 ± 10	18 ± 13
Chloride	5.05	6.75	4.23	4.86	4.9 ± 2.5	5.2 ± 2.5
Nitrate	22.36	17.56	13.07	13.41		
Phosphate	0.06	0.05	0.09	0.06		
Calcium	8.23	10.16	5.84	5.84	9.5 ± 4.6	10 ± 6.0
Magnesium	1.76	3.43	1.73	1.67	3.8 ± 2.4	4.0 ± 2.0
Sodium	7.12	10.51	4.16	5.29	13 ± 3.9	14 ± 5.7
Ammonium	25.53	16.30	11.29	12.32		
Potassium	0.99	1.26	1.20	1.20		

*Slopes based on Oppenheimer *et al.* (1) emissions for Arizona, Nevada, New Mexico, and Utah. †Slopes based on Oppenheimer emissions (1) plus ANL nonindustrial emissions for the same states (see Table 2). Uncertainties are 95 percent confidence intervals.

Table 2. Estimates of sulfur dioxide emissions (10^3 metric tons per year).

State	Oppenheimer smelters*				ANL utilities				ANL miscellaneous			
	1980	1981	1982	1983	1980	1981	1982	1983	1980	1981	1982	1983
Arizona	579.0	794.1	374.3	445.7	79.4	101.2	99.1	82.4	18.1	17.5	17.5	16.7
Nevada	78.9	114.9	87.7	28.3	35.7	38.4	53.3	48.4	6.4	6.1	6.1	5.8
New Mexico	121.9	144.9	128.9	181.7	76.7	67.7	83.7	100.3	10.8	10.4	10.4	9.9
Utah	45.6	76.8	63.7	44.7	20.0	22.9	22.4	27.1	26.1	25.3	25.8	24.2
Colorado	40.1	39.5	38.7	37.1	70.0	64.9	71.4	71.5	20.9	20.5	20.9	20.0
Idaho	33.2	31.7	24.0	23.2	0	0	0	0	17.9	17.1	17.2	16.1
Wyoming	93.3	88.5	79.8	79.0	109.6	108.9	100.5	96.7	23.0	22.2	22.2	21.0
Four state total	825.4	1130.7	654.6	699.9	211.9	230.2	258.5	258.2	61.3	59.3	59.8	56.6
Seven state total	992	1290.4	797.1	839.2	391.5	403.9	430.4	426.4	123.1	119.2	120.1	113.8

*ANL estimates used for Colorado, Idaho, and Wyoming.

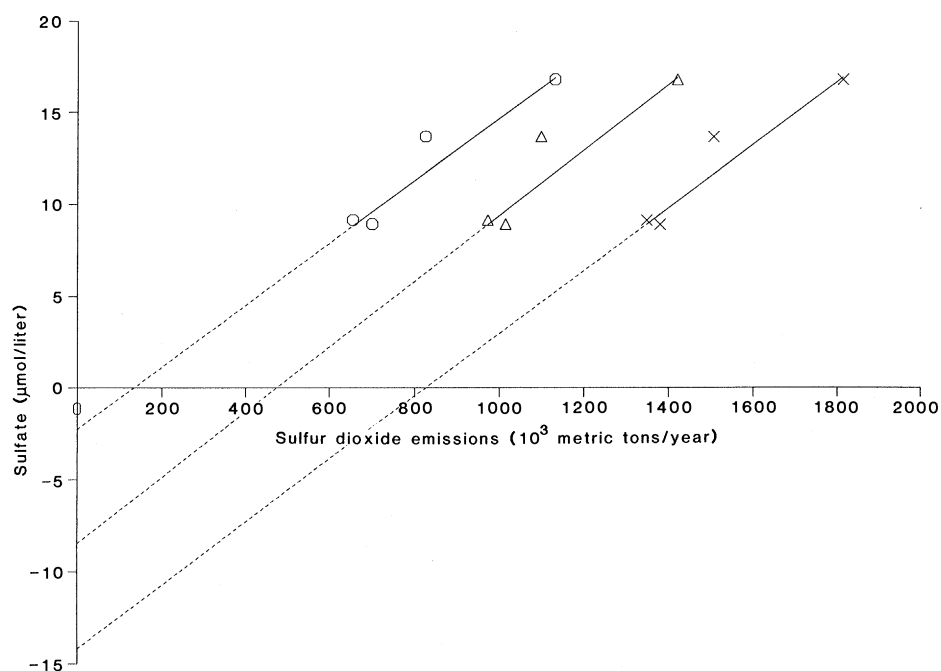


Fig. 1. Sulfate concentrations as a function of sulfur dioxide emissions for nonferrous smelters as estimated by Oppenheimer *et al.* (○), for the sum of these smelter emissions and the nonindustrial emissions estimated by Knudson (6) (△), and for the emissions in the seven-state area obtained from the estimates of Oppenheimer *et al.* of smelter emissions for Arizona, Nevada, New Mexico, and Utah and the ANL estimates of industrial emissions for Colorado, Idaho, and Wyoming plus the ANL estimates for utilities and miscellaneous emissions for all seven states (×).

We also call attention to the values of the linear regression parameters obtained for sulfate, chloride, calcium, magnesium, and sodium not only with the smelter emissions but also those derived after inclusion of all nonindustrial anthropogenic emissions. The results are presented in Table 1. These parameters are all statistically significant at the 5 percent level and are every bit as convincing as those obtained only for sulfate with the smelter emissions selected by Oppenheimer *et al.* Even if the speculative argument from Oppenheimer *et al.* concerning metal-carbonates could not be faulted, it would only address calcium and magnesium. The carbonate argument cannot pertain in the case of sodium, as almost all sodium compounds are readily soluble in water (7), and consequently there is no mechanism for an increased solubility due to higher acidities.

We conclude that the data presented by Oppenheimer *et al.* do not demonstrate that the linear relation between sulfate concentrations in rain and smelter emissions can be regarded as a causal relation. Extrapolation to zero smelter emissions is of course not warranted until the model is shown to be correct. Nevertheless, the data plotted in Fig. 1, extrapolated to zero emissions, appear to yield negative sulfate concentrations, especially when we include the seven-state area and all the anthropogenic emissions from it. Therefore, even the sense of the relation the authors present appears to be

questionable. The proper model must take account of the fact that in this geographic region the composition of rainwater samples is strongly influenced by soil-derived constituents and that yearly differences in meteorology must play an important role in governing the average ion concentration in rain. We do applaud Oppenheimer *et al.* for their attempt at performing this analysis and hope that others will be stimulated by the possibility that a relation can be derived by looking at such data. Possibly if future investigators address both the temporal and spatial components of the data and include studies of meteorological conditions and perhaps air mass back trajectories associated with each rain event, a relation, if it exists, might be discerned (8).

LEONARD NEWMAN
CARMEN M. BENKOVITZ
Department of Applied Science,
Brookhaven National Laboratory,
Upton, NY 11973

REFERENCES AND NOTES

1. Actually one of the rain-measuring stations included in the analysis by Oppenheimer *et al.* was in the state where most of the smelters are located. This station, in Organ Pipe, Arizona, and numbered 8 in their figure 1, had a sulfate concentration in the peak emission year that was unequalled by any except the Pawnee, Colorado, station (see their table 1 and figure 2).
2. We did not examine hydrogen ion concentrations because we accept the fact that this concentration can be modified by neutralization reactions.
3. M. Oppenheimer, private communication, 8 January 1985.

4. The nitrate, ammonium, and potassium concentrations did not show a significant regression with sulfur dioxide smelter emissions. The phosphate concentrations were too low and near the detection limit of the chemical methods employed for the analysis, so that a correlation, if it existed, could not be discerned.
5. L. Newman, private communication, 15 March 1985.
6. D. Knudson, "An inventory of monthly sulfur dioxide emissions for the years 1975-1983" (ANL/EES-TM-277, Argonne National Laboratory, Argonne, IL, 1985). Annual emissions estimates for each year were obtained by adjusting the state-level National Acid Precipitation Assessment Program (NAPAP) 1980 base-year emissions for each source category according to a year-specific fractional change calculated from the Environmental Protection Agency (EPA) National Air Pollutant Emissions Estimates for 1970-1983. Emissions we have labeled as ANL utilities include ANL categories utility coal and utility oil; ANL industrial emissions include ANL categories industrial processes, industrial coal combustion, and industrial oil combustion; ANL miscellaneous category includes commercial and institutional fuel combustion, industrial, commercial, and institutional space heating, stationary source internal combustion, solvent use, solid waste disposal, and area sources. Information on the NAPAP 1980 base year can be found in D. A. Toothman, J.C. Yates, E. J. Sago, "Status report on the development of the NAPAP 1980 emission inventory for the 1980 base year and summary of preliminary data" (EPA-600/7-84-091, Environmental Protection Agency, Washington, DC, 1984).
7. The presence of refractory minerals is unlikely and, even if present, they would not be solubilized by the mild acidity present in rain.
8. We appreciate the many helpful and critical discussions with Stephen E. Schwartz. This research was funded as part of the National Acid Deposition Program through the Processing of Emissions by Clouds and Precipitation program at Brookhaven National Laboratory and performed under the auspices of the U.S. Department of Energy contract DE-AC02-76CH00016.

Response: Hidy and Newman and Benkovitz raise interesting questions about our study of precipitation sulfate concentrations and copper smelter sulfur dioxide emissions in the western United States. Our primary conclusions were that smelter emissions contribute significantly to sulfate concentrations at remote stations and that available data support a linear relation between concentration and emissions. The following questions are raised in the letters. Why do concentrations of Na^+ , Cl^- , Ca^{2+} , and Mg^{2+} also have linear relations to sulfur dioxide emissions on an annual basis? Why do sulfate concentrations covary with concentrations of Ca^{2+} , NO_3^- , and other ions? Does the sulfate- SO_2 relation exist on other time scales, and is it geographically structured and sensibly related to meteorology? Does the statistical relation reflect a causal response of sulfate concentrations to smelter emissions variation?

Smelters are the dominant source of sulfur dioxide in the intermountain region covered by the study (1), and sulfur transport is a regional phenomenon (2). A meteorological model based on upper- and ground-level wind trajectories establishes the smelters as a major source of sulfate in Colorado precipitation in 1981 (3). These physical properties underlie the inference of causality from our