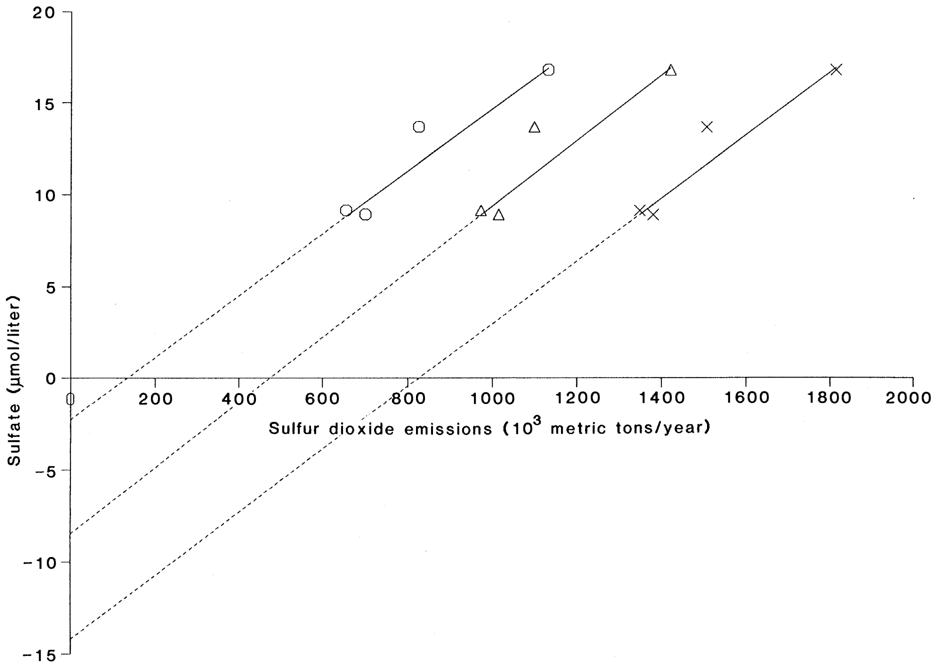

Fig. 1. Sulfate concentrations as a function of sulfur dioxide emissions for nonferrous smelters as estimated by Oppenheimer *et al.* (○), for the sum of these smelter emissions and the nonindustrial emissions estimated by Knudson (*6*) (△), and for the emissions in the seven-state area obtained from 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*).

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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 statistical study. In addition, a recent analysis by others (*4*) of the same data set we used establishes a spatial relation between smelter emissions and sulfate concentrations at remote stations: the slope of the regression of concentration on emissions decreases with increasing smelter-monitor distance, as expected if smelter emissions cause sulfate concentration variations. Finally, the annual analysis is now confirmed by an analysis of monthly data that shows a highly significant relation between smelter emissions and sulfate concentrations at Colorado stations (*5*).

Of the nine measured ions in addition to SO_4^{2-}, four covary with smelter SO_2 on an annual basis. Much of this covariation is fortuitous, particularly for Na^+ and Cl^-. An examination of data from individual stations indicates that from 1980 to 1981, concentrations of Na^+ and Cl^- (unlike SO_4^{2-}, see Table 1) decreased at each of the three stations for which 1980 data are available (*6*). Yet the regional volume-weighted means (VWM's) increased from 1980 to 1981, resulting in correlation with increasing SO_2 emissions, because Newman and Benkovitz included several stations that opened in 1981 and had very high concentrations that year (*7*).

Regression of monthly VWM concentrations of each ion besides sulfate from the combined records of the five Colorado stations on smelter emissions reveals that emissions are significantly related to only Mg^{2+} ($P<0.01$, F test), while Ca^{2+}, Na^+, and Cl^- are unrelated to monthly smelter emissions ($P>0.10$, F tests) (*8*). We can suppose only one reason (aside from simple coincidence) for the correlation of Mg^{2+} with emissions: increasing atmospheric sulfur concentrations affect droplet chemistry and, as a result, soil-borne Mg solubility. Support for this hypothesis comes from the 13-year record of the bulk precipitation chemistry station at Hubbard Brook, New Hampshire, where long-term changes in Ca^{2+}, Mg^{2+}, and other ions, including SO_4^{2-}, were related to regional SO_2 emissions (*9*). Because similar observations are made in studies conducted 2000 miles and several years apart, we suggest that a general chemical phenomenon is at work. Soil material dissolution rates are certainly sensitive to acidity in the relevant *p*H range (*10*), and soil material dissolves rapidly enough to affect concentrations in ambient droplets. Otherwise, how could so much dissolved Ca^{2+} and Mg^{2+} be found in wet precipitation?

Hidy argues that the covariation of sulfate concentration with other ions implies that "meteorological factors, not smelter emissions" control sulfate variability. But it is fundamentally wrong to treat the various possible sources of concentration variation as if they were mutually exclusive. All ionic concentrations in this data set are partially determined by meteorological variation. Multiple regression of sulfate on both emissions and other ionic concentrations (whose variation may represent the effects of meteorology) (*4*) suggests that SO_4^{2-} concentration at specific stations is jointly determined by both emissions and meteorology.

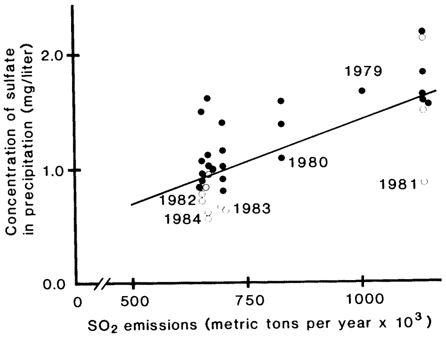

Figure 1. The least-squares regression line is drawn through combined annual volume-weighted means based on all 34 annual points. Regional means are weighted by the number of stations available in the corresponding year, as suggested by Sokal and Rohlf (*12*). The slope is significant (95% CL's: 0.77, 2.09 mg/liter/10^6 tons SO_2/year; 95% CL's on intercept: −0.56, 0.53). The line is drawn only for the region of the *x*-axis where the 95% confidence interval in the estimate of regional average concentration is less than ±0.25 mg/liter. ●, Colorado station; ○, non-Colorado station.

Hidy also argues that the correlation between calcium and sulfate concentrations provides evidence that the sulfate originates as gypsum dust. But the covariation of ions reflects the partial determination of concentration by meteorology and as a matter of fact, on a monthly basis at western stations SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NO_3^-, and NH_4^+ are statistically related to each other in *all* pairwise correlations. There is no significant evidence for a special role for gypsum dust in these data. Furthermore, Ca^{2+} and SO_4^{2-} covariation has been observed (*9*) where gypsum dust is a negligible factor in precipitation chemistry. Thus, Hidy's inference from ionic correlations that "soil makes a significant contribution to sulfate levels in western precipitation" seems unfounded. Only indirect evidence (Hidy's reference *5*) exists for a soil gypsum contribution to wet sulfate concentrations, while two direct studies in this specific region do not support the suggestion of a substantial soil contribution to precipitation sulfate (*11*).

We refrained from extrapolating the regression line to zero emissions because of the large uncertainty in the estimate of the *y* intercept [95% confidence limits (CL's), 1.37, 0.97]. Similar uncertainties exist in the regression of Newman and Benkovitz. Even if the statistical uncertainty were reduced, as it is in our Fig. 1, with the combination of sources and receptors we used, the intercept would not represent a background concentration at a particular station. The intercept can be physically interpreted as the concentration resulting from background emissions only when the regression is based on a geographically coherent group of receptors, where all substantially varying sources accounting for deposition are included in the source category and all other sources are excluded. Large negative intercepts, such as those in figure 1 of the comment by Newman and Benkovitz, indicate that some of the included emissions contribute little to concentrations observed at some of the monitoring stations. Varying distances from sources suggest that emissions are not equally relevant to concentration at all receptors.

Table 1. Annual average sulfate concentrations at intermountain NADP stations (mg/liter). Small differences in station-specific and regional mean values between our original report and this table result from differences between our averaging methods and those used by the NADP. "Manitou 1980" was inadvertently omitted from our report, and by criteria stated there, "Yellowstone 1983" should not have been included. Asterisks indicate that the station was in operation, but coverage included fewer than 30 weeks of chemical data or data from fewer than 10 months of the year.

NADP station	Year					
	1979	1980	1981	1982	1983	1984
Alamosa, CO			1.82	1.49	1.39	*
Sand Spring, CO		1.07	1.58	0.96	1.02	1.00
Manitou, CO	1.66	1.38	1.62	1.07	0.91	1.12
Pawnee, CO		1.57	2.17	0.83	1.15	1.62
Rocky Mtn. NP, CO			1.55	0.91	0.80	0.98
Yellowstone NP, WY			1.49	0.77	*	0.58
Craters of the Moon, ID			0.86	0.72	0.65	0.61
Organ Pipe, AZ			2.14	0.83	0.64	0.97
Combined volume-weighted mean	1.66	1.35	1.56	0.89	0.88	1.00
Total smelter emissions (metric tons × 10^3)	1004.53	823.01	1130.35	654.60	699.77	663.55

Deposition and concentration are confused in Hidy's citing of monthly and seasonal analyses. Statistical analysis (*5*) of monthly data supports our original contention of a relation between sulfate concentration and smelter SO_2. The other studies cited (Hidy's references *3* and *4*) deal largely with deposition, the product of VWM concentration, and precipitation amount. The relation between deposition and emissions is obscured by fluctuations in precipitation amount because combined VWM sulfate concentration is independent of precipitation amount in this data set. Seasonal concentration variations further obscure the relation of emissions to deposition in quarterly data.

Newman and Benkovitz incorrectly assert that our regression is "derived from essentially three points." As our Fig. 1 and Table 1 demonstrate, the annual relation over the period from 1980 to 1983 is based on 26 points and has now been extended to include 1979 and 1984, for a total of 34 points. Figure 1 shows that during the period from 1982 to 1984, when annual emissions varied little, annual regional average sulfate concentrations were indistinguishable from year to year, as would be predicted from a cause-and-effect relation between emissions and concentration. The regionally combined VWM's on which the regression is based are subject to less error than station-specific observations. The observations that make up the combined average provide important additional information, however, in that they allow an estimate (independent of that obtained from the standard error of the slope) of within-year concentration variability (*12*).

Hidy observes that from 1982 to 1983, while annual smelter emissions increased by about 5% of total 1982 emissions, concentration fell at five out of eight stations. In view of the large variation from station to station (see Fig. 1) and the fact that emissions do not uniquely determine concentrations, these fluctuations do not, in Hidy's words, "reveal a major contradiction" so much as they underscore the efficacy of using regional means to elucidate source-receptor relations.

Extrapolation of the regression line to high emissions values to predict eastern U.S. concentrations is unwarranted: wet (and probably dry) removal is much faster in the East, so that long-range source-receptor slopes are inherently smaller. However, sulfate and hydrogen ion concentrations in these data resemble eastern values outside the core of high pollution density, so that the linear relation has implications for droplet chemistry in the East.

In summary, the annual analysis not only stands on its own, but geographical, multiple regression, and monthly studies support its conclusion: concentrations of sulfate in precipitation are consistent with a linear relation to smelter sulfur dioxide emissions.

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2. M. Oppenheimer, *Atmos. Environ.* **19**, 1439 (1985).
3. *Modeling Regional Haze in the Southwest: A Preliminary Assessment of Source Contributions* (Systems Applications, San Rafael, CA, 1985).
4. L. R. Dupuis and F. W. Lipfert, "Acid deposition, smelter emissions, and the linearity issue in the western United States" (Draft report, Brookhaven National Laboratory, Upton, NY, 1985). "Multivariate analysis of acid deposition, smelter emissions, and the linearity issue in the western United States" (Draft report, Brookhaven National Laboratory, Upton, NY, 1985). These studies were based on observations from 16 National Acid Deposition Program (NADP) stations in the intermountain region (including eight omitted from our study because of incomplete coverage) suggesting that the source-receptor relation is representative of the region as a whole.
5. C. B. Epstein and M. Oppenheimer, *Nature (London)*, in press.
6. *NADP Data Reports Precipitation Chemistry* (Natural Resource Ecology Laboratory, Colorado State Univ., Ft. Collins, CO, 1985). Manitou, Colorado, is the third station available in 1980, and this point was inadvertently omitted from our original report.
7. The five Colorado NADP stations provide a data set whose geographic composition was constant over the period considered (June 1980 through December 1984). By excluding the non-Colorado stations included in our original report, we can reduce the degree of geographic variability and limit our consideration to stations reporting chemical data from a larger percentage of total weeks possible.
   Sodium and chloride monthly VWM concentrations from the combined Colorado stations from mid-1980 through 1984 have a significant relation to inverse precipitation volume at the same stations (F tests, $P<0.10$, Na^+; $P<0.05$, Cl^-) but not to monthly SO_2 emissions. No other ions (except H^+) are related to inverse precipitation volume. Thus, Na^+ and Cl^- concentrations may be influenced by dilution or soil moisture, with the 1980 to 1981 change in annual combined VWM being a result of pooling stations available for different periods and the 1981 to 1983 changes being related to precipitation changes in the region over the period.
8. The correlations of SO_4^{2-} and Mg^{2+} with emissions cannot result from a coincidental covariation of emissions and the scavenging of soil material containing $MgSO_4$ because Mg^{2+} concentrations in precipitation average one-sixth of SO_4^{2-} on an equivalents basis.
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11. Analysis of data from a bulk precipitation chemistry network in Colorado in 1982–1983 showed through altitude and geographic concentration gradients that sulfate and calcium are not physically tied to the same source [W. M. Lewis, Jr., M. C. Grant, J. F. Saunders III, *Water Resources Res.* **20**, 1691 (1984)]. In addition, it has been shown (C. J. Popp, D. K. Brandvold, A. Long, in preparation) that sulfur isotope ratios in New Mexico precipitation do not match those in local soils. Hidy also asserts, incorrectly, that hydrogen ion is not related to sulfate. In fact, his reference 5 shows that hydrogen ion concentration is determined by sulfate together with nitrate and calcium.
12. R. R. Sokal and F. J. Rohlf, *Biometry* (Freeman, New York, 1981), p. 484.

Evolution of Color Vision

The stimulating Perspective of David Botstein (11 Apr., p. 142) contains two inaccuracies. Dichromats are not "the most common form of color blindness"; in almost all populations deuteranomalous males are most common (*1*). In addition, the statement that "New World monkeys have only a single pigment encoded on the X chromosome" is incomplete; the X chromosome of any individual male *Saimiri sciureus*—the squirrel monkey—carries one gene encoding a color vision pigment, but several alleles encoding different pigments exist and females of course can be heterozygotes (*2*).

This situation suggests, at least to me (*3*), ideas concerning the evolution of color vision in primates which add to those proposed by Botstein. While human trichromatism is indeed likely to have evolved by duplication and diversification of a single X-borne color vision locus, the *Saimiri* polymorphism probably originated by *mutation*—rather than duplication—at a single locus. Finally as any Perspective—even that of a molecular biologist—must have a historical component, one might mention J. Scott (*4*), whose clear description of a man and his uncle as dichromats (protanopes) anticipated by 20 years that of Dalton. One would also suggest that among the "great names" of those concerned with color vision might be added Goethe (*5*), who in addition to publishing observations in the *Fahrbenlehre*, conducted the first family studies of color vision deficiency (*6*).

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