Reports

Bacteriogenic Sulfur in Air Pollution

Abstract. *On a yearly basis, the major source of atmospheric sulfur compounds in and near Salt Lake City, Utah, is industrial. Isotopic studies suggest that the next most important source is bacteriogenic sulfur released by anaerobes from muds. On a seasonal basis, the bacteriogenic source of sulfur compounds may rival the industrial source in importance.*

Biogenic sulfur is often overlooked or underestimated in connection with pollution studies, but isotopic studies of atmospheric sulfur oxides in and near Salt Lake City suggest that bacteriogenic contributions may rival or exceed industrial contributions on a seasonal basis. Under a 3-year NIH research grant (*1*), investigators at the Laboratory of Isotope Geology of the University of Utah conducted a study of the use of natural variations in isotopic abundance as identifying "fingerprints" for atmospheric fluids (*2*). Table 1 shows some of the isotopic values for sulfur compounds, from both natural and industrial sources, in and near Salt Lake City.

The dominance of the sulfur from the copper smelters is apparent from the fact that the isotopic values of sulfur in the atmosphere and in precipitation reflect the smelter values rather closely. However, there is a small but consistent shift toward heavier isotope values that indicates mixing with compounds of heavier isotopic character. There is also a seasonal shift to heavier isotopes for about 4 to 6 weeks in the late summer. The possible sources of heavier sulfur can be seen in Table 1. They are: (i) petroleum refineries, (ii) advected sulfates, (iii) automobile exhausts, and (iv) bacteriogenic sulfur from lake- and river-bottom muds and marshes near Great Salt Lake. Quantitative analysis of control samples indicates that the amount of advected sulfur is inadequate to significantly affect the isotope values. Since no industrial activity is known to exhibit a seasonal variation in this area, the bacteriogenic source was a prime suspect (*3*).

During July 1971, the copper workers struck, and the smelter was inactive. The concentration data for sulfur oxides for this period (*4*) indicated that the region toward the west of the study area, near the smelters, promptly showed a marked drop from about 25 to about 1 part per billion (ppb) (by volume), whereas the east, or metropolitan, side of the study area showed very little change, or perhaps a slight increase from the average of about 12 ppb. The strike occurred at a time when the seasonal peak in isotope value would have been expected.

In this report sulfur isotope measurements are expressed as $\delta^{34}S$ values, defined by

$$\delta^{34}S = 10^3\ (^{34}S/^{32}S)_x/(^{34}S/^{32}S)_s - 10^3$$

which expresses the parts-per-thousand deviation of the isotope ratio of the sample, x, from that of the standard, s (Canyon Diablo troilite). The precision of a single measurement is about 0.2 per mil.

Isotope studies during the strike period showed that the sulfur isotopic values on the west side averaged around 5.3 per mil, while that on the east side averaged around 6.39 per mil. At the end of the strike, the averages approached 1.5 per mil on the west side of the study area and 3.1 per mil on the east side. Apparently, the sulfur contributions from the smelter rapidly began to dominate at the end of the strike.

During the strike both the east side and the west side showed isotopic values well within the range of bacteriogenic sulfur, but the west-side values were nearer the mean. The results suggest that the west-side values are due predominantly to bacteriogenic sulfur, whereas the east-side values reflect a mixture of bacteriogenic sulfur with isotopically heavier sulfur from a source on the east side, which is no doubt a mixture of refinery effluents and automotive exhausts. The isotopic data suggest that, during the strike, about 90 percent of the east-side sulfur was bacteriogenic and about 10 percent was from petroleum.

A simple geochemical balance calculation indicates that the suggested magnitude of the bacteriogenic contribution is not unreasonable. Data on local water chemistry (*5*) show that about 20,000 metric tons of sulfur are brought into the Great Salt Lake Basin annually by surface waters. Within the basin, before reaching the lake, the waters pick up an additional 40,000 tons of sulfur, probably from old lake

Table 1. Sulfur isotope values for sources of atmospheric compounds, in the area of Salt Lake City. The values for water samples refer to dissolved sulfates. Precipitation and air samples are divided into three groups: normal values, values during the strike of the copper workers, and control values, collected well away from local sources of an anthropogenic nature. Local petroleum refineries operate mainly on Uinta-basin crude oils.

Source	Sulfur isotope values (per mil)		
	Range	Mean	Standard deviation
Automobile exhaust	12.1 to 17.0	15.1	
Uinta crude oils		16.6	
Great Salt Lake	10.3 to 17.0	15.3	0.5
Streams	4.3 to 11.1	9.6	0.8
Bacteriogenic	0.5 to 8.7	5.3	1.7
Precipitation			
Normal	−1.5 to 5.3	2.2	1.0
Strike	4.7 to 6.5	6.0	
Control	8.0 to 10.2	9.0	0.3
Air samples			
Normal	−1.0 to 3.1	1.3	0.3
Strike	5.0 to 7.5	6.0	0.4
Control	8.0 to 10.0	9.0	0.2
Smelter plume	−3.8 to 3.4	1.0	0.3
Copper ores	−4.3 to 2.4	0.0	0.6

sediments and wind-borne material. The influent sulfur has an isotopic value of about 10 per mil. Sulfate in the lake shows values of about 15 per mil, and bacteriogenic sulfur averages near 5 per mil. On the basis of only the new input of 20,000 tons of sulfur, a balance calculation suggests that bacteriogenic sulfur amounts to about 10,000 tons per year. Some of this H_2S undoubtedly reacts with metallic ions to form sulfides, but Great Salt Lake shows little sulfide in the sediments, so that much of the H_2S produced there may be oxidized (*6*).

On an annual basis, 10,000 tons of sulfur amounts to about 10 percent of that released by the smelters, but the bacteriogenic production is seasonal, and thus, during periods of peak activity, the bacteriogenic sulfur may even be the dominant source in the area. It is quite clear that an improved understanding of the role of sulfate-reducing bacteria is essential to the rational management of sulfur in some environments, as suggested by earlier studies (*3*).

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References and Notes

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Satellite Radiation Measurements and Clear Air Turbulence Probability

Abstract. *Radiance gradients determined from data gathered by the infrared spectrometers aboard the Nimbus III and Nimbus IV satellites were related to the probabilities of clear air turbulence, as inferred from regular pilot reports. Such radiance gradients represent rather large-scale vertical wind shear. Clear air turbulence is least likely in regions where the radiance gradient is small. The results of this exploratory study show that satellite data can be used to design flight paths so that the probability of encountering clear air turbulence is extremely small.*

The satellite infrared spectrometer (SIRS), carried on board the Nimbus III and Nimbus IV spacecraft, is designed to measure the vertical temperature structure of the atmosphere. The eight observing channels of the SIRS measure the amount of infrared radiation emitted vertically upward by the atmosphere in seven narrow intervals of the carbon dioxide band and in one interval in the 11.1-μm atmospheric window (*1*). The radiance received in channel 4 is a measure of weighted average temperatures, with maximum weight near 9 km (*2*), which is near the altitudes at which commercial aircraft operate while in flight.

About 45,000 pilot reports issued over the continental United States were supplied by American Airlines for the months of September 1969 and January, March, and June 1970. These were sorted to isolate the reports which coincided (within 3 hours and 1 degree of latitude and longitude) with the passage of the Nimbus III satellite. A total of 602 such coincidences were obtained.

Of interest was, not so much the value of the radiance per se, but the horizontal gradient of the radiance measured by the satellite in the vicinity of the pilot report. It can be shown that, in the absence of clouds in the field of view, the horizontal gradient of the radiance measured by channel 4 of the SIRS represents a rather large-scale vertical wind shear in the atmosphere (*3*). Thus, a high value of the horizontal radiance gradient implies a large vertical wind shear near 9 km, and clear air turbulence (CAT) is most likely in areas of large vertical wind shear (*4*). The horizontal radiance gradient in the vicinity of the pilot report is denoted by the quantity ΔR_4, which is the difference between the maximum and minimum values of the radiance measured in channel 4 within 2 degrees of the latitude of the pilot report along the satellite track. Each of the 602 pilot report–satellite coincidences was classified according to the value of ΔR_4 and the degree of turbulence reported. The data in the top half of Table 1 show that the probability of turbulence varies from about 4 percent in regions of small radiance gradient (that is, $\Delta R_4 \leqq 1.5$ erg sec^{-1} cm^{-2} sr^{-1} cm) to nearly 20 percent in regions of large gradient ($\Delta R_4 > 3$ erg sec^{-1} cm^{-2} sr^{-1} cm). It is worth noting that of the three pilot reports of moderate turbulence in the sample, two were associated with the largest value of ΔR_4 encountered. Of the 11 reports of turbulence with small ΔR_4 values, four occurred in a region where there was a large horizontal temperature gradient perpendicular to the track of the satellite, so that it could not be detected from the satellite data.

We stated that the radiance received by channel 4 of the SIRS comes from levels in the atmosphere centered near 9 km. However, some radiation is being received in channel 4 from levels well above and below 9 km. What are the effects of this extra radiation on the values of ΔR_4, and can they be removed? Since channel 5, which receives radiation from levels centered near 13 km, has small ΔR values (typically about one-quarter of the corresponding ΔR_4 values), the contribution of higher-level radiation to ΔR_4 is small. However, the radiation received from lower levels of the atmosphere does have an effect on ΔR_4. For example, if there is a large north-south temperature gradient near 6 km, we would expect the value of ΔR_4 to be fairly large, since channel 4 receives some radiation from that level. But we would not expect the aircraft to report turbulence, since they generally fly 3 km or so higher. However, since channel 3 receives radiation from levels centered near 6 km, we would expect a large value of ΔR_3. Of the 41 pilot reports associated with large ΔR_3 values and fairly large ΔR_4 values, only one was a report of turbulence. Thus, radiance data from channel 3 can be used to improve the conditional probabilities of turbulence.

It might be expected that we could achieve similar results by using more conventional data, for example, the isotherm spacing on upper-air charts. To test this hypothesis, the positions of the pilot reports were marked on 300-mb charts. (These charts contain