Atmospheric Sulfur Dioxide and Sulfate

Distribution of Concentration at Urban and Nonurban Sites in United States

Aubrey P. Altshuller

Environmental Protection Agency, Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, N.C. 27711

■ The interpretation of results from the U.S. National Air Surveillance Networks indicates that large differences in sulfate concentration levels exist between eastern and western urban and nonurban sites in the United States. Sulfates contribute a larger portion of the sulfur compounds at western urban sites than at eastern urban sites. The relationship of sulfur dioxide to sulfate is nonlinear over the range of concentrations at urban sites. Statistical relationships have been computed relating urban sulfate to urban sulfur dioxide and also to the ratio of sulfur dioxide to sulfate. Background levels of water-soluble sulfate differ greatly between the eastern and western U.S. At the eastern nonurban sites, a residue sulfate level of at least 5 $\mu g/m^3$ exists. This large residue is attributed to long-distance transport of sulfur dioxide with conversion of urban sulfur dioxide to sulfate during transport. Sulfate-containing aerosols are broadly distributed throughout large regions of the eastern and midwestern U.S.

A considerable volume of measurements now has become available from 24-hr integrated network measurements of sulfur dioxide and suspended water-soluble sulfates at urban and nonurban continental and maritime sampling sites in the United States. These data make it possible to evaluate the distribution of sulfur dioxide and sulfates in the U.S., and to determine background levels for various regions of the country. The present work will emphasize the distribution of and relationships between sulfur dioxide and sulfate using the annual arithmetic averages at urban and nonurban sites. Particular attention is given to the statistical relationships between sulfur dioxide and sulfate concentration levels as a function of sulfur dioxide concentration at various types of sites.

Procedures

Sulfur dioxide and sulfate concentrations were obtained by the National Air Surveillance Networks using a 24-hr sampling period once every two weeks during the year. Results were utilized only from sites at which samples were obtained for both sulfur dioxide and sulfate analyses. Continuous monitoring sites for sulfur dioxide were not utilized because the method of analysis was different during at least part of the time period involved.

The sulfur dioxide was collected in a bubbler-train sampling into a collecting reagent containing sodium tetrachloromercurate to complex the sulfur dioxide followed by use of the method of West and Gaeke modified for the AutoAnalyzer (U.S. Environmental Protection Agency, 1972). A portion of the aqueous extract of high-volume particulate samples was analyzed for sulfate by the methyl thymol blue method modified for use on the AutoAnalyzer. The minimum detectable concentration for sulfate is estimated as 0.6 $\mu g/m^3$ (U.S. Environmental Protection Agency, 1972). Sampling methods and results are contained in the publications of Air Quality Data from National Air Surveillance Networks for 1964-65, 1966, 1967,

and in tabulations of analytical results for samples collected in 1968 (U.S. Department of Health, Education, and Welfare, 1966, 1968; U.S. Environmental Protection Agency, 1971, 1972).

Results

Urban Sites. Urban sites for which both sulfur dioxide and sulfate results were available were limited to one site for each urban area (except the Philadelphia metropolitan area). The sampling results from which concurrent sulfur dioxide and sulfate annual averages were available between 1964 and 1968 included 148 annual averages (71%) for sites east of the Mississippi and 60 annual averages (29%) for sites west of the Mississippi. The population sizes of the urban areas varied over the entire range existing in the U.S. The sites themselves were characterized as industrial, commercial, mixed industrial–commercial, mixed residential–commercial, and industrial–residential–commercial. Relatively few of the urban sites utilized were characterized as purely residential. Data on sulfur-containing fuels in terms of tons/mi^2/year for 69 standard metropolitan areas (SMSA) are available (U.S. Department of Health, Education, and Welfare, 1968). The total emissions of sulfur dioxide were obtained either from available emission inventories or estimates of consumption of sulfur-containing fuels. Most of the SMSA's with the higher densities (tons/mi^2/year) were located east of the Mississippi in the various industrial regions stretching from the East Coast into the Central Midwest.

The arithmetic annual average sulfur dioxide concentration values ranged from as low as 6 $\mu g/m^3$ to as high as 448 $\mu g/m^3$ with an overall five-year average of 53 $\mu g/m^3$ (1964–68). For the eastern sites, the overall five-year average was 66 $\mu g/m^3$, with 44% of the values ranging up to 40 $\mu g/m^3$, 31% of the values between 41 and 80 $\mu g/m^3$ and 25% of the values above 80 $\mu g/m^3$. For the western sites, the overall five-year average was 22 $\mu g/m^3$, with 85% of the values ranging up to 40 $\mu g/m^3$, 5% of the values between 41 and 80 $\mu g/m^3$, and 10% of the values above 80 $\mu g/m^3$. These distributions for eastern and western sites correspond generally to the sulfur dioxide emission densities by SMSA in the eastern and western U.S.

The arithmetic annual average sulfate concentration values ranged from 2.4 to 48.7 $\mu g/m^3$, with an overall five-year average of 11.4 $\mu g/m^3$ (1964–68). For eastern urban sites, the overall five-year average was 13.5 $\mu g/m^3$, with 26% of the values ranging up to 10 $\mu g/m^3$, 67% of the values between 10.1 and 20 $\mu g/m^3$ and 7% of the values above 20 $\mu g/m^3$. For western urban sites, the overall five-year average was 6.4 $\mu g/m^3$, with 88% of the values ranging up to 10 $\mu g/m^3$, 12% of the values between 10.1 and 20 $\mu g/m^3$, and no annual average above 20 $\mu g/m^3$.

The overall average ratio of sulfur dioxide to sulfate (in $\mu g/m^3$) was 4.7:1 for the five-year period. The average ratio of sulfur dioxide to sulfate at eastern sites was 4.9:1 and at western sites was 3.4:1 for the five-year period. The lower ratio of sulfur dioxide to sulfate at western sites results from the sulfur dioxide concentration level averaging only 33% of the level for eastern sites while the sulfate

concentration level averages 47% of the level for eastern sites.

To examine the relationships between sulfur dioxide and sulfate concentration levels in more detail, 20 sampling sites in 20 cities were identified for which either five or four complete years of analyses were available. Only one to three years of data were available at the other sites utilized during the five-year period. Fourteen of these sites (70%) were east of the Mississippi and six of the sites (30%) were west of the Mississippi. These sites were located within the following cities: New Haven and Hartford, Conn.; New York, N.Y.; Newark, N.J.: Wilmington, Del.; Pittsburgh, Pa.; Charleston, W.Va.; Youngstown and Cleveland, Ohio; East Chicago, Ill.; Indianapolis, Ind.; Nashville and Chattanooga, Tenn.; Milwaukee, Wis.; St. Louis and Kansas City, Mo.; Des Moines, Iowa; Salt Lake City, Utah; Portland, Oreg.; and Seattle, Wash.

A possible variable of significance is population size. The population classes and number of sites by class were as follows: class 1 (3,000,000 and more), 1 site; class 2 (1,000,000-3,000,000), 0 sites; class 3 (700,000-1,000,000), 3 sites; class 4 (400,000-700,000), 5 sites; class 5 (100,000-400,000), 8 sites; class 6 (50,000-100,000), 3 sites. These populations are for the cities themselves not the corresponding SMSA. The averaged sulfur dioxide and sulfate concentrations in $\mu g/m^3$ at sites in these population sizes was as follows: class 1, 383, 28.2; class 3, 72, 13.7; class 4, 65, 11.6; class 5, 41, 10.6; class 6, 69, 21.2. Although there is a decrease in averaged sulfur dioxide and sulfate from class 1 to class 5, the averaged sulfur dioxide and/or sulfate concentrations for class 6 sites exceeded those for classes 3, 4, and 5. The three class 6 sites are in heavily industrialized SMSA's with two of the three sites adjacent to neighboring SMSA's with high sulfur densities also. The third site was atypical compared to all other sites in that the sulfur dioxide concentrations were low, but the sulfate concentrations were very high.

The type of site, the density of usage of high sulfur fuels, and the presence of adjacent industrialized areas upwind must be taken into consideration. The importance of these other factors is shown by the sulfur dioxide and sulfate concentrations at different sites in the same population class. For class 4, the sulfur dioxide and sulfate individual annual average concentrations ranged from 6-204 $\mu g/m^3$ and from 5.5-18.3 $\mu g/m^3$, respectively. For class 5, the sulfur dioxide and sulfate individual annual average concentrations ranged from 11-136 $\mu g/m^3$ and from 3.6-18.7 $\mu g/m^3$. Therefore, there is a wide range of concentrations within a population class and much overlap between population classes because of these other factors.

The statistical relationships between annual average concentration for sulfur dioxide and sulfate and between sulfur dioxide and the ratio of sulfur dioxide to sulfate were computed for 18 of the sites. One of the two sites not included had atypically high sulfate concentration levels compared to all other sites. The other site was in a class 1 population area with very high sulfur dioxide and sulfate concentration levels. The annual averages at this site were so much higher than those at the other sites as to make difficult their inclusion into the statistical treatment. The results included contained sulfur dioxide annual averages ranging from 6-204 $\mu g/m^3$ and sulfate annual averages from 3.6-20.3 $\mu g/m^3$.

Statistical relationships were computed for a large number of combinations of intervals. The most appropriate statistical results obtained were as follows: 6-80 range in $\mu g/m^3$, C (SO_4^{-2}) = 0.144($\pm$0.013,1σ) C (SO_2) + 4.92($\pm$0.57,1σ) with a correlation coefficient of 0.82 and for the 100-204 range in $\mu g/m^3$ C (SO_4^{-2}) = 0.0016($\pm$0.013,1σ) C (SO_2) + 16.9($\pm$1.7) (Figure 1). The slope in the latter interval was not statistically distinguishable from zero so the sulfate concentration was independent of the sulfur dioxide concentration level. An intermediate region between these two ranges occurred between 80 and 100 $\mu g/m^3$ of sulfur dioxide. The statistical relationship between sulfur dioxide concentration in the 6-204 $\mu g/m^3$ range and the ratio of sulfur dioxide to sulfate concentration in $\mu g/m^3$ was as follows: ratio (SO_2/SO_4^{-2}) = 0.0475($\pm$0.0021,1σ) C (SO_2) + 1.69($\pm$0.15,1σ) with a correlation coefficient of 0.93 (Figure 2).

Nonurban Sites. Sulfur dioxide concentrations at nonurban sites are available starting from 1968. Annual averages were available for four eastern and one western nonurban sites; the values ranged from 6-15 $\mu g/m^3$ and averaged 10 $\mu g/m^3$. The lowest one third of the values at four of five of these sites ranged from 2-5 $\mu g/m^3$.

Arithmetic annual average sulfate concentrations were available at 12 eastern sites for the years 1965-68 and at two additional eastern sites for three of these four years and at 12 western sites for the years 1965-68 and at three additional western sites for three of these four years. For eastern nonurban sites, the sulfate annual average concentrations ranged from 5.3-14.1 $\mu g/m^3$ and averaged overall 8.1 $\mu g/m^3$. At these eastern sites, 83% of the annual averages ranged up to 10 $\mu g/m^3$ and 17% of the annual averages were between 10.1 and 15 $\mu g/m^3$. For western nonurban sites the sulfate annual average concentrations ranged from 0.5-5.3 $\mu g/m^3$ and averaged overall 2.6 $\mu g/m^3$. At 10% of these western sites annual averages were in the 0.5-1.0 $\mu g/m^3$. Therefore, the ranges of sulfate concentra-
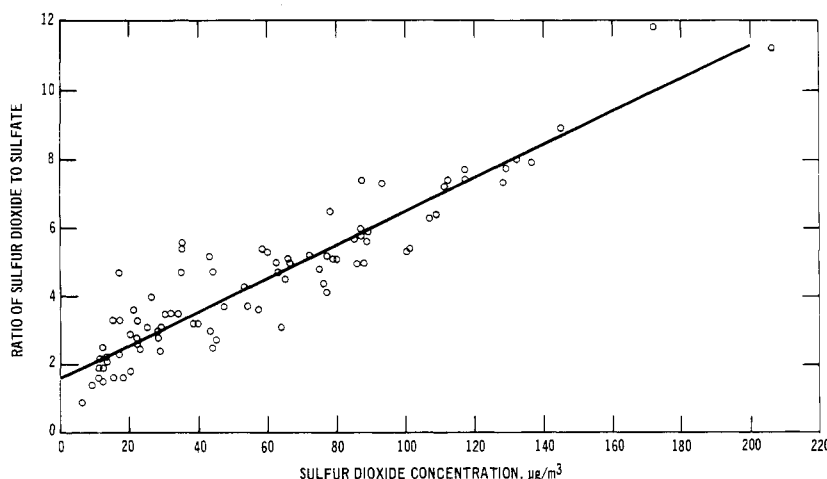

Figure 1. Relationships between annual average sulfur dioxide and sulfur dioxide and sulfate concentrations for 18 U.S. cities
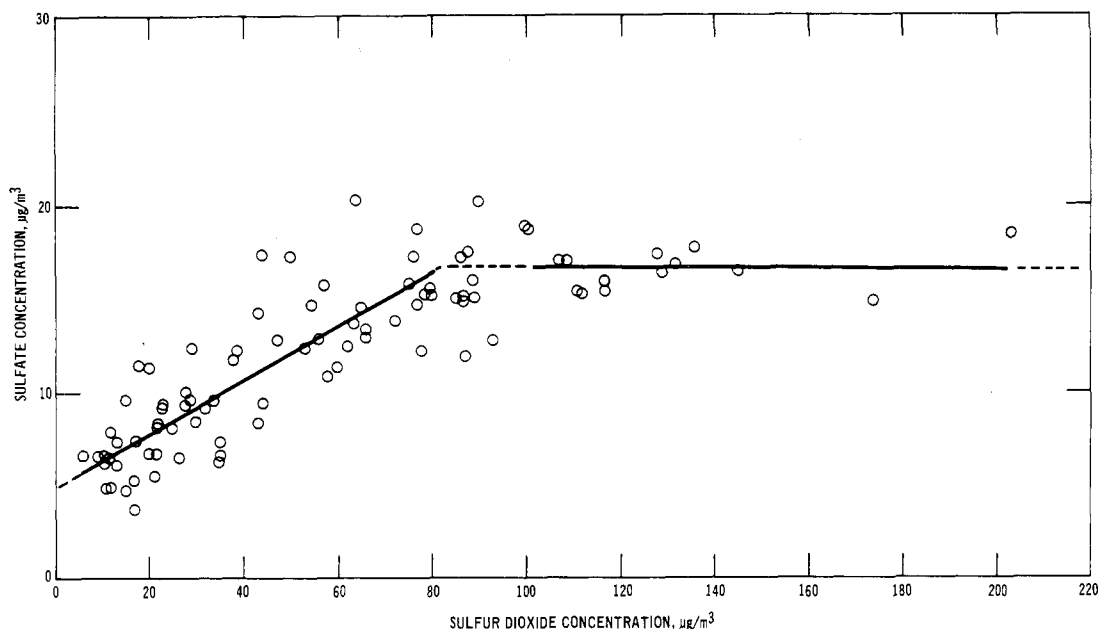
Figure 2. Relationship between annual average sulfur dioxide concentrations and ratio of sulfur dioxide to sulfate for 18 U.S. cities

tions at eastern and western nonurban sites appear to represent separate, distinct populations of sulfate levels.

Discussion

Based on the statistical relationships between sulfur dioxide and sulfate, reduction of sulfur dioxide in a statistically average site by 90% from 200–20 $\mu g/m^3$ would result in only a 53% reduction of sulfate from 16.6–7.8 $\mu g/m^3$. The intercept value suggests a minimum sulfate level at urban sites of about 5 $\mu g/m^3$. The site in Charleston, W.Va., not included had annual average sulfur dioxide concentrations ranging from 17–31 $\mu g/m^3$ averaging 26 $\mu g/m^3$ and sulfate concentrations ranging from 16.2–48.7 $\mu g/m^3$ averaging 30.4 $\mu g/m^3$ while the sulfur dioxide to sulfate ratio ranged from 0.6–1.2 to averaging 0.9–1. These consistently high particulate sulfate concentrations and low ratios suggest very strong local primary emission sources of sulfate contributing most of the ambient air concentration of sulfate near this sampling site.

The site in New York City also not included had annual average sulfur dioxide concentrations ranging from 346–448 $\mu g/m^3$ averaging 383 $\mu g/m^3$ and sulfate concentrations ranged from 18.7–33.1 $\mu g/m^3$ averaging 28.2 $\mu g/m^3$, while the sulfur dioxide to sulfate ratio ranged from 11.3–18.5 to averaging 1–14.1. These values would fall well above the line defining the 100–200+ $\mu g/m^3$ range (Figure 1). Again, it seems likely that the primary emissions of particulate sulfate from power plants and other emissions sources near this site on Manhattan could be responsible for the high values. Examination of annual averages for sites with more limited results indicates that almost all of the values fall within the range of values shown in Figures 1 and 2. The 100–200+ $\mu g/m^3$ range statistical relationship was established from a total of 15 annual averages from five urban sites in three eastern and two midwestern cities. The few additional values in this higher concentration range from sampling sites not included in obtaining the statistical relationship would not change this relationship if included.

The annual average sulfate concentrations ranged from 5–10 $\mu g/m^3$ at six inland rural sites in farmlands, forests, and mountains in the eastern and midwestern United

States downwind of strong sulfur dioxide emissions from urban areas. Sites at or near the ocean, bays, and large lakes in the eastern U.S. were in the same range. The sulfate values decreased below 5 $\mu g/m^3$ at all of the sites west of the Mississippi River. Sulfate concentrations at sites in farmlands and forests west of the Mississippi ranged from 1.5–5 $\mu g/m^3$. Usually at most, one urban area emitting substantial sulfur dioxide concentrations existed within 100 miles of these sources west of the Mississippi. Eastern and midwestern nonurban sites could be in the downwind flow from several urban areas with high sulfur dioxide emissions. Therefore, the high sulfate emissions at eastern and midwestern nonurban sites are attributable to the chemical conversion of sulfur dioxide to sulfate during transport of sulfur dioxide downwind from urban areas. A sulfate concentration of at least 5 $\mu g/m^3$ appears to be associated with transport and transformation of sulfur dioxide.

Sulfur dioxide and sulfate results are available for a site in Central Philadelphia and at four suburban sites (Burlington County and Glassboro, N.J., and Warminster and West Chester, Pa.). The sulfur dioxide concentrations at the four suburban sites averaged one third of the sulfur dioxide level at the Central Philadelphia site for the 1964–68 period. The sulfate concentrations at the four suburban sites averaged one half of the sulfate levels in Central Philadelphia. The sulfur dioxide to sulfate ratio in Central Philadelphia was as much as twice the ratios at the suburban sites. These results also suggest that a contribution of transported sulfate could be responsible for a significant fraction of the total sulfate measured at eastern sites downwind of one or another of the other numerous nearby urban areas having high sulfur dioxide emissions. Such a common background level of sulfate from transported sulfur would explain the intercept at 5 $\mu g/m^3$ of sulfate for the lower range of urban values of sulfur dioxide.

Elevated sulfate concentrations appear to be widely distributed throughout entire regions in the eastern and midwestern portions of the U.S. If this interpretation is correct, it suggests that a uniformly large reduction in sulfur dioxide is necessary in both sections to secure substantial

decreases in sulfate concentration levels at many urban sites and at all nonurban sites.

The saturation effect for sulfate concentrations at urban sites in the higher sulfur dioxide concentration range can be explained if much of the sulfate comes from chemical reactions not from primary emissions of sulfate. The formation of sulfate in liquid droplets slows down markedly at low pH values (Junge, 1963). Ammonia and other alkaline substances can keep the pH high enough for continued reaction. However, when the sulfur dioxide concentrations are high the alkaline substances available will be insufficient to maintain the pH at a level at which the oxidation reaction continues to the degree that a saturation effect is observed. Similarly, conversion of sulfur dioxide on surfaces containing catalytically active substances would continue until all active sites were occupied with saturation—again likely to occur at high levels of sulfur dioxide.

Recent community health studies (CHESS) have demonstrated a substantial relationship between some types of morbidity and sulfate levels in the 8–12 $\mu g/m^3$ levels of sulfate. Most of the urban sulfate containing aerosol also has been well established as being in the particle size range between 0.1–1 μm which adversely affects visibility (Ludwig and Robinson, 1965; Wagman et al., 1967). The complex relationships between urban sulfur dioxide to urban and nonurban sulfate make urgent a better understanding of the atmospheric chemistry of these sulfur compounds. Without such experimental results, it will be impossible to model atmospheric sulfate concentrations or develop an air pollution control strategy for atmospheric sulfates. In view of the significant health and welfare effects caused by atmospheric sulfates, the future development of air pollution control strategies for control of sulfate would appear to be essential.

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Studies in Sweden on Feasibility of Some Methods for Restoration of Mercury-Contaminated Bodies of Water

Arne Jernelöv[1] and Hans Lann

Swedish Water and Air Pollution Research Laboratory, Stockholm, Sweden

■ Laboratory experiments and small-scale field tests have been performed to investigate some theoretically possible methods to restore mercury-contaminated lakes and rivers. Properties of the different methods with respect to practical use are discussed.

The statistics for total and methyl mercury in a lake or estuary show the relative distribution between different phases in the ecosystem to be within the following orders of magnitude (Jernelöv, 1972b):

	Total mercury, %	Methyl mercury, %
Sediment	90–99	1–10
Water	1–10	< 1
Biota	< 1	90–99

These figures clearly indicate that methyl-bound mercury normally represents a small fraction of the total amount of mercury present in the ecosystem. However, mercury content in fish is the prime concern of man and, in this respect, methyl mercury is of extreme importance (Westöö, 1966). Discharge of mercury into water has mainly involved the following compounds: divalent inorganic mercury (Hg^{2+}), elementary mercury (Hg^0), and phenyl mercury as acetate ($C_6H_5Hg^+$). Due to the physical and chemical properties of the compounds and to the condi-tions present, mercury discharged to bodies of water is very likely to end up in the sediment (Jernelöv, 1968).

From there, it can be recovered by suspending the material to which it is attached by forming soluble complex ions such as $HgCl_4{}^{2-}$ or HgS^{2-} or by biological methylation (Jensen and Jernelöv, 1967, 1968, 1969). To date two different biochemical pathways for mercury methylation have been described (Wood et al., 1968; Landner, 1971). If alkylating compounds, such as alkyllead, are present, a chemical alkylation also becomes possible (Beijer et al., 1970). The methylated mercury will then evaporate into the atmosphere in the form of dimethyl mercury (Jensen and Jernelöv, 1968, 1969) or accumulate in organisms. The process of methylation is the key reaction leading to mercury contamination of fish. The proportion of total mercury present in natural aquatic ecosystems converted annually to methyl mercury has been estimated to be ≤ 0.1% (Jernelöv et al., 1971). Thus, mercury deposits in bottom sediments may continue to release methylated mercury for a very long time unless they are removed or inactivated. The fact that the mercury level in fish, after contamination of a water system might remain high for a considerable length of time, makes it desirable to find methods for water restoration. As already pointed out, the key process leading to methyl mercury contamination of fish is biological methylation. It is therefore natural to concentrate on those methods that will lead to a reduced methylation rate.

Suggested Restoration Methods for Mercury-

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[1] To whom correspondence should be addressed.