

**U.S. DEPARTMENT OF COMMERCE
National Technical Information Service**

PB-293 485

**Association Between Meteorological
Conditions and High Ozone and Sulfate Concentrations
A 1974 Episode in the Eastern United States**

(U.S.) Environmental Sciences Research Lab., Research Triangle Park, NC

Feb 79



Association Between Meteorological Conditions and High Ozone and Sulfate Concentrations

A 1974 Episode in the Eastern United States

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL HEALTH EFFECTS RESEARCH series. This series describes projects and studies relating to the tolerances of man for unhealthful substances or conditions. This work is generally assessed from a medical viewpoint, including physiological or psychological studies. In addition to toxicology and other medical specialties, study areas include biomedical instrumentation and health research techniques utilizing animals — but always with intended application to human health measures.

ASSOCIATION BETWEEN METEOROLOGICAL CONDITIONS
AND HIGH OZONE AND SULFATE CONCENTRATIONS
A 1974 Episode in the Eastern United States

by

Gerard A. DeMarrais
Meteorology and Assessment Division
Environmental Sciences Research Laboratory
Research Triangle Park, N.C. 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711

DISCLAIMER

This report has been reviewed by the Office of Research and Development, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Mr. DeMarrais is a meteorologist in the Meteorology and Assessment Division, Environmental Sciences Research Laboratory, Environmental Research Center, Research Triangle Park, N.C. 27711. He is on assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

ABSTRACT

A 1,000,000 km² area of the Eastern United States had sulfate concentrations exceeding 10 µg/m³ on July 10, 1974, and there were indications that parts of the area had high concentrations on prior days. The meteorology associated with the high concentrations and correlations of high ozone and sulfate concentrations are discussed. It appeared that slow moving and subsiding air contributed to the high concentrations of both pollutants. Long range transport, as shown by trajectory analyses, was a factor in the problems in most areas, but the worst situations with regards to sulfates were associated with emissions from nearby, upwind sources. While high ozone concentrations were observed immediately prior to high sulfate concentrations in many areas, there were high sulfate concentrations that were not associated with high ozone concentrations. In the latter situation, the high sulfate concentrations were associated with air which had earlier movement over areas with high SO₂ emission.

CONTENTS

Abstract.	iii
Figures	vi
Tables.	viii
Postscript and Acknowledgement.	ix
1. Introduction	1
2. Conclusions.	2
3. Background and Methods	4
Sulfates, reactions producing sulfates, and measuring of sulfates.	4
The ozone episode	5
The SO ₂ to sulfate conversion and long-range transport. Diurnal variations of sulfates.	7
Meteorological conditions associated with high concentra- tions of ozone and sulfates	7
Potential source areas of ozone and sulfate precursors. Meteorological resources.	9
4. Results.	11
Background.	11
Sulfate data.	11
The ozone data.	14
Temperature data.	15
Visibility.	16
Synoptic weather situation.	18
Other meteorological observations	20
Trajectories of the surface-to-1000-m layer	20
5. Summary.	25
References.	27-30

FIGURES

<u>Number</u>	<u>Page</u>
1. Annual hydrocarbon emissions by state in 1973 (1000 tons). . . .	31
2. Annual SO ₂ emissions from power plants by state in 1974 (1000 tons).	32
3. Locations of sulfate monitoring stations of state and local agencies (see Table 1 for station names)	33
4. Sulfate concentrations ($\mu\text{g}/\text{m}^3$) July 10, 1974	34
5. Station locations (see Table 4 for station names) TVA network. .	35
6. Maximum hourly ozone concentrations (ppb) July 6, 1974	36
7. Maximum hourly ozone concentration (ppb) July 7, 1974.	37
8. Maximum hourly ozone concentration (ppb) July 8, 1974.	38
9. Maximum hourly ozone concentration (ppb) July 9, 1974.	39
10. Maximum hourly ozone concentrations (ppb) July 10, 1974.	40
11. Maximum hourly ozone concentration (ppb) July 11, 1974	41
12. Maximum temperatures (°F) July 6, 1974	42
13. Maximum temperatures (°F) July 7, 1974	43
14. Maximum temperatures (°F) July 8, 1974	44
15. Maximum temperatures (°F) July 9, 1974	45
16. Maximum temperatures (°F) July 10, 1974.	46
17. Visibility (miles) July 6, 1974, 1 p.m., e.s.t.	47
18. Visibility (miles) July 7, 1974, 1 p.m., e.s.t.	48
19. Visibility (miles) July 8, 1974, 1 p.m., e.s.t.	49
20. Visibility (miles) July 9, 1974, 1 p.m., e.s.t.	50

FIGURES (Continued)

<u>Number</u>	<u>Page</u>
21. Visibility (miles) July 10, 1974, 1 p.m., e.s.t.	51
22. Daily weather maps, July 6, 1974	52
23. Rainfall during sulfate sampling period of July 10, 1974	53
24. 48-h trajectories (12-h segments) of layers of air between the surface and 1000 m for selected cities, July 6, 1974 (arrival time 1 p.m., e.s.t.)	54
25. 47-h trajectories (12-h segments) of layers of air between the surface and 1000 m for selected cities, July 7, 1974 (arrival time 1 p.m., e.s.t.)	55
26. 48-h trajectories (12-h segments) of layers of air between the surface and 1000 m for selected cities, July 8, 1974 (arrival time 1 p.m., e.s.t.)	56
27. 48-h trajectories (12-h segments) of layers of air between the surface and 1000 m for selected cities, July 9, 1974 (arrival time 1 p.m., e.s.t.)	57
28. 48-h trajectories (12-h segments) of layers of air between the surface and 1000 m for selected cities, July 10, 1974 (arrival time 1 p.m. e.s.t.)	58

TABLES

<u>Number</u>	<u>Page</u>
1. Names of Stations in Sulfate Monitoring Network (see Figure 3) for station locations)	59
2. Sulfate Concentrations ($\mu\text{g}/\text{m}^3$) at CHESS Stations in the New York City Area, July 6-11, 1974	60
3. Sulfate Concentrations ($\mu\text{g}/\text{m}^3$) at Electric Power Industry Sites in Northern United States, July 6-11, 1974	61
4. Station Names, TVA Network (see Figure 5 for station locations).	62
5. Sulfate Concentrations ($\mu\text{g}/\text{m}^3$) TVA Network, July 3-11, 1974.	63-64

POSTSCRIPT

After the final draft of this report was completed, a technical article examining the same sulfate episode was published. This article, Spatial and Temporal Distributions of Airborne Sulfate in Parts of the United States in Atmospheric Environment, V.12, 735-752, (1978), by G. Hidy et al., briefly discusses with isopleth maps the high sulfate concentrations of July 8-11, 1974.

This EPA report differs from the technical article in that major emphasis is given to the coexistence of high ozone and high sulfate concentrations. In addition, more consideration is given to details. These details show that isoplething masks out discrepancies and on occasion does not show a significant feature; for example, the isopleth map for July 10 indicates a concentration of approximately $10 \mu\text{g}/\text{m}^3$ in the vicinity of West Virginia whereas two stations in the area showed concentrations four and five times as great.

ACKNOWLEDGEMENT

The patience of Mrs. Hazel Hevenor in retyping the many drafts of this report was appreciated.

SECTION 1

INTRODUCTION

Sulfate concentrations are frequently above average when ozone concentrations are relatively high¹. In a southern California investigation², it was shown that an 8-d sulfate episode coincided with an ozone episode. To further test the cofrequency hypothesis, a period was sought during which high ozone concentrations occurred in that 16-state area* that has consistently shown higher sulfate concentrations than the rest of the nation³. Such an ozone event occurred over the area during July 6-10, 1974, and a preliminary correlation of the ozone concentrations and meteorological conditions was previously noted⁴. In this report the available sulfate data (they are not as abundant as ozone data), ozone concentrations, and meteorological conditions for the period are discussed.

* This 16-state area is east of the Mississippi River, and is roughly bounded by Illinois and Massachusetts to the north and Tennessee and North Carolina to the south.

SECTION 2

CONCLUSIONS

On the basis of the analysis of the daily ozone, sulfate, and meteorological data, the following conclusions are drawn:

1. A large-scale ozone episode occurred over the Northeastern United States from July 6 to 10, 1974, and midway through the episode sulfate concentrations became high and eventually spread over a 1,000,000 km² area of the Eastern United States.
2. The ozone episode was initially associated with only the air behind a cold front that pushed southeastward over the area on July 6. The air mass eventually became the warmest of the year (most locations in the ozone episode area had the highest temperatures of the year during this 5-d period) and was characterized by slow movement at the surface and aloft (stagnation) and subsidence. The high sulfate concentrations each day were not restricted to the high temperature areas but were associated with the slow moving and subsiding air.
3. The areas of high ozone concentrations on each day did not correspond to the areas with restricted visibility or precipitation. The areas of high sulfate concentrations on each day corresponded somewhat to the areas with restricted visibility during several days when the sulfate data were limited and on the one day (July 10) with abundant sulfate data. The area with high sulfate concentrations on July 10 corresponded to the area with rainfall. After the passage of a front toward the end of the period, the ozone concentrations were reduced, and the restrictions to visibility eliminated, but the sulfate concentrations remained high.
4. The trajectory analysis frequently showed that air with a high ozone or sulfate concentration at a receptor had had a high concentration

at an earlier time in an upwind location; long-range transport, although limited by stagnation, did occur. However, at times air arrived from areas that did not show a high ozone or sulfate concentration, but at these times the air usually came from an area that was a large emitter of precursors.

SECTION 3

BACKGROUND AND METHODS

SULFATES, REACTIONS PRODUCING SULFATES, AND MEASURING OF SULFATES

Most sulfur in the atmosphere, land surface, and water exists as the hexavalent oxidized sulfate ion ($\text{SO}_4^{=}$) in such diverse forms as sulfuric acid; ammonium bisulfates; calcium sulfate (the major component of gypsum); magnesium sulfate (epsom salts); sodium and potassium sulfates (in seawater); and other metal salts, such as copper, nickel, iron, lead, and zinc sulfates¹.

On a global scale, natural sources contribute about two-thirds of the sulfur compounds in the atmosphere by weight, and human activities the remainder. In the continental United States, probably 90% of the atmospheric sulfur is the result of anthropogenic emissions in the form of sulfur dioxide (SO_2)¹. Most of the SO_2 is oxidized to the sulfate form within a few days, and, while this oxidation is taking place, the pollutants in the air can be transported long distances; the sulfate receptors may be hundreds of km from the sources of primary emissions⁵.

The important mechanisms by which SO_2 is converted to sulfuric acid and sulfate salts^{3,6} are: 1) direct photooxidation; 2) indirect photooxidation; 3) air oxidation in liquid droplets; 4) catalyzed oxidation in liquid droplets; and 5) catalyzed oxidation on dry surfaces.

A substantial fraction of the man-made sulfate problem is believed to be associated with SO_2 emitted by large power plants¹. The 16-state area with the higher sulfate concentrations correlates spatially with high SO_2 emission density, high rainfall acidity patterns, and a high density of power plant locations³.

The majority of sulfate data evaluated in this report were supplied by the National Aerometric Data Bank (NADB) and the CHESS (Community Health and Environmental Surveillance System) program of the U.S. Environmental Protection

Agency (EPA). The sulfate data in the NADB came from State and local air pollution control agencies and were generally collected every 12th day in accord with a preset schedule (in July 1974 nearly all stations had data for the 10th and 22nd); some stations sampled on additional days at random times. The stations in the CHESS program were operated every day. Sulfate data from stations in a network operated by the electric power industry⁷ and 49 stations in a Tennessee Valley Authority (TVA) network are also considered in the analyses. Each sulfate measurement is made from a small strip of filter on which suspended particulate had been collected in a high volume air sampler. Each sampling period is 24-h, and the filters are changed at midnight (local standard time). The filter strip is extracted with water, and a portion of the aqueous extract is analyzed for sulfate by the methyl thymol blue method.

At the present time no National Ambient Air Quality Standard (NAAQS) exists for sulfates. In an EPA position paper³ on the regulation of atmospheric sulfates the highest concentration tentatively associated with adverse health effects was reported to be $10 \mu\text{g}/\text{m}^3$ (24-h average) and in this report concentrations greater than $10 \mu\text{g}/\text{m}^3$ are labeled high.

THE OZONE EPISODE

The investigation of the ozone episode⁴ examined data from approximately 100 stations in the Eastern United States extending from Ohio and Massachusetts in the north to Tennessee and North Carolina in the south. In the report⁴ data for 50 representative stations in 11 states are presented (no ozone data were available for West Virginia and South Carolina). Ozone monitoring stations are usually operated by State and local agencies, with the State agency being responsible for providing the Federal Government with a near-complete and accurate record. More than two dozen agencies collected the analyzed data. One station in Richmond, Virginia, used an ultraviolet Dasibi instrument, but all others employed a chemiluminescence instrument.

The current NAAQS (hourly value) for ozone*, not to be exceeded more than once a year, is $160 \mu\text{g}/\text{m}^3$ or 80 ppb⁸; in this report, when the NAAQS is violated, a concentration is called high. The ozone data presented came from the NADB.

*It has been proposed that the NAAQS be revised upward to $200 \mu\text{g}/\text{m}^3$.

THE SO_2 TO SULFATE CONVERSION AND LONG-RANGE TRANSPORT

The conversion of SO_2 to sulfate in the air and the possibility of long-range transport of the sulfate have been reported extensively⁹⁻¹⁶; there are many observations and findings but the agreement is not universal. One group of investigators⁹ found no clear evidence of long-range transport, another investigator¹⁰ reported obvious transport out to 1000 km, and others¹¹ found transport readily occurred but was limited to several hundred km. An incomplete knowledge of the meteorology, chemistry, and timing of processes in the conversion of man-made SO_2 to sulfates and of the eventual return to the surface by uptake and precipitation is the cause of the disagreement about the long-range transport of sulfates. Various investigators have hypothesized about features of the processes. Georgii¹², basing his hypothesis on observations over Central Europe, noted three important features. First, the vertical SO_2 concentration decreases rapidly with altitude, reaching half the ground concentration at 800 to 1200 m above the surface. Second, seasonal variations of the SO_2 concentration are limited to the 2000 m immediately above the surface. Third, inversions prevent, and convection accelerates the transport of SO_2 into higher layers; above the inversion and haze layers, the SO_2 concentration decreased markedly, whereas the sulfate concentration is not much influenced by the thermal structure of the atmosphere. The difference between the gas phase and liquid phase conversion of SO_2 to sulfate was noted by Kellogg et al.¹³. They reported the gas phase conversion showed a half-life for SO_2 of 12 d while, when SO_2 was dissolved in fog or cloud droplets, particularly where metal salts were present to serve as catalysts, the SO_2 rapidly (within hours) oxidized. Weber¹⁴ estimated that 50% of the SO_2 emitted by power plants and the space heating chimneys in the Frankfurt area was oxidized in the first 20 min to 1 hr of travel time during the winter (in relatively moist air). Atkins et al.¹⁵ in discussing sulfate concentrations over Britain, stated that the concentrations were indicative of the history of the air mass several days earlier and showed air in which oxidation of SO_2 occurred at distances up to 1000 km upwind over Central Europe. The authors¹⁵ further stated that the sulfate was removed from the atmosphere almost solely by rainfall.