



Project Summary

Impact of Primary Sulfate and Nitrate Emissions from Selected Major Sources: Phase I. Coal-Fired Power Plant

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The impact of local point sources emissions on the near source atmosphere has been investigated. This study was in two phases. The phase 1 study was to investigate the impact of a coal-fired power plant on the near source atmosphere. Phase 2 was to study the impact of a sulfuric acid plant and a pulp and paper mill. The results of phase 2 are presented in a separate report.

Sampling for phase 1 took place during late January and early February, 1981 at the Scholz Steam Plant of the Gulf Power Company, located in Northwest Florida. Source measurements were made for emission rates of H_2SO_4 , particulate sulfate and nitrate, SO_2 , NO_x , total particulate matter, and elemental compositions by particle size. Ambient sampling was made for all the preceding pollutants plus HNO_3 and pertinent meteorological parameter required for dispersion modeling.

The Scholz Plant was found to be the dominant source of gaseous sulfur and nitrogen oxides in the area. However, it was found to contribute only about 1.5% of the ambient particulate sulfate and nitrate. The H_2SO_4 was about 95% of the sulfate emissions and account for most of the ambient H_2SO_4 .

Four factors in the Principal Component Fraction Analyses accounted for about 80% of the variance in the input data matrix. They were: the first factors showed the plant was connected heavily with SO_2 , NO , NO_2 , As, Se, and sulfate; the second factor showed a connection among mineral elements, TSP, and sulfates; the third factor tied alkali

metals, Cl, Mn, and P together but no satisfactory source was found; and the fourth factor coupled Br, S, mineral elements and total nitrate. This factor was probably related to vehicular traffic.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Most current studies on the mechanisms of sulfate and nitrate formation and transport in the atmosphere have dealt with long-range transport. However, a significant portion of the problems associated with these compounds may arise in the vicinity of the source. The program described here was intended to provide information on the partitioning of sulfates and nitrates in ambient air between local primary sources and long-range transport/secondary sources. The report presents the results of the first phase of a two-phase source-ambient study. This first phase concerned the impact of a coal-fired power plant. Phase 2 concerned the impacts of a sulfuric acid plant and a pulp and paper mill. The results of Phase 2 are presented in a separate report.

Sulfur and nitrogen compounds are of particular concern because of their preponderance in flue gas and in decomposition products of other process streams. High levels of SO_2 , NO , NO_2 , and various



sulfates and nitrates are found in ambient air associated with industrial activity and in areas with high automotive traffic densities. Serious deterioration of the environment has been linked to these compounds. In 1964, SO₂ emissions began to be regulated in this country. The use of high-sulfur fuels was inhibited, and taller stacks were employed to improve local air quality. This improved the measured levels of SO₂; however, ambient air sulfate levels have not been substantially improved. Thus, it is important that the specific contributions of sulfate aerosols to the atmosphere be delineated, the controlling mechanisms be determined, and the local and long-range concentrations and transports be determined.

Sampling for Phase 1 took place during late January and early February 1981, at the Scholz Steam Plant of the Gulf Power Company, located in Northwestern Florida. Three approaches were taken to quantify the impact of the plant on the study area. First, dispersion modeling was used to predict average downwind concentrations. Second, principal component factor analysis (PFA) was applied to an ambient air data base comprised of the concentrations of SO₂, NO_x, total suspended particulates (TSP), sulfates, nitrates, wind direction relative to the source and sampler locations, and the concentrations of a number of elements found in the particulate matter collected by hi-vol samplers. Finally, target transformation factor analysis (TTFA) was used in data analysis to isolate and quantify the impacts of specific sources at each sampling location.

Measurement Methods

The primary variables of interest in this study were particulate and gaseous sulfates and nitrates in the ambient air that were directly or indirectly the result of emissions from the Scholz plant. Further, it was desirable to differentiate between sulfate and nitrate salts and sulfuric and nitric acids. Thus, data were needed on the ambient air and source concentrations of these species and their precursors.

Source measurements were made of the emission rates of sulfuric acid, sulfate salts, sulfur dioxide particulate nitrates, nitrogen oxide, nitrogen dioxide, total particulates matter; and of elemental composition by particle size. Measurements in the ambient air included all of the preceding plus nitric acid and all pertinent meteorological parameters required for dispersion model predictions of

downwind concentrations. The sources total particulate measurements were made by using a modification of EPA Method 17, which minimized the inclusion of sulfuric acid in the sample. Sulfuric acid determinations were made by using the method described by Cheney and Homolya. The plant's SO₂, NO_x, O₂, and H₂O monitors were used to provide the data needed for source variables.

A grid of acceptable monitoring locations was developed in the vicinity of the plant and, based on anticipated wind flow, sites were selected for monitoring at the beginning of each test day. Data were taken at four fixed stations and two mobile stations. TSP samples were collected by hi-volume samplers equipped with Sierra Model 234 cascade impactors. Similar samplers without the impactors were used to obtain samples for sulfate, nitric acid, and nitrate analysis. Conventional glass fiber filter media were used in the impactor-equipped samplers; these were analyzed gravimetrically to determine TSP concentrations. Teflon membrane filters were used in sampling for sulfate, nitric acid, and nitrates to minimize artifact formation. A sodium chloride-impregnated filter was installed downstream of the Teflon filter for the nitric acid determination. Segments of the Teflon hi-vol filters were also submitted for X-ray fluorescence (XRF) and neutron activation analyses (NAA) to determine elemental compositions of the deposited particulate matter for use in apportioning the material found on the filters among the various possible sources.

Sulfuric acid and sulfate salts were measured separately by techniques previously developed by Southern Research Institute. The concentrations of SO₂ were measured with Meloy Model SAE-185-2A SO₂ monitors. Meloy 8440E monitors were used for NO and NO₂ measurements.

Data to identify dispersion characteristics were taken from a 60-m (200-ft) meteorological tower maintained by Gulf Power Company. Upper air measurements were made by using pilot balloons and temperature sonde equipment.

Measurement Results

An overview of the source emission parameters is given in Table 1. This table summarizes all emission rate measurements for the principal components of interest; particulate matter, SO₂, H₂SO₄, and NO_x.

When sulfuric acid was excluded, between 2 and 5% of the total particulate

matter emissions were found to be soluble sulfates. The data indicated that the H₂SO₄ present in the flue gas was essentially all in the vapor phase; the sulfate was associated with H₂SO₄ at concentrations 10-15 fold greater than that associated with the fly ash. The particle size distribution of the emissions could be reasonably well represented by a log-normal distribution with a mass median diameter of about 10 μm.

A summary of the ambient air data is given in Table 2. All values in this table represent averages over the time periods during which the hi-vol samplers for sulfate and nitrate determinations were in operation.

Only a few days of data were obtained with the ambient air H₂SO₄ samplers. The sampler operations concentrated on the collection of data in the plume; therefore, the ambient air H₂SO₄ data are highly biased toward in-plume samples and are not representative of average conditions. The data indicated that the plant's contribution to the local, ambient air sulfate was about 90 to 95% H₂SO₄.

Particle size distribution measurements were attempted in two ways. First, high volume impactor heads were used on the TSP samplers; second, Lundgren impactors were used to provide samplers for the determination of the distribution of selected elements by particle size-XRF and NAA analyses of the material collected by the impactor were used for the latter purpose. Neither technique was notably successful because the ambient air particulate concentrations actually encountered were much lower than anticipated. The data show that the ambient aerosol is probably comprised of two modes, a sub-micron mode typified by sulfur and perhaps containing other "condensable" species and a second super-micron mode typified by more refractory mineral elements.

Source Impact on Study Area

The Factor Analysis was performed on the correlation matrix of the complete set of elemental analysis data from the hi-vol filters augmented by the concentrations observed for nitrates, nitric acid, sulfates, SO₂, NO, NO₂, TSP, and a variable related to the wind direction relative to the source and sampler locations. Elements that showed low values of communality in this analysis were excluded from the data set used in further analyses. This analysis showed that four factors were sufficient to explain 79% of the variance in the input data matrix. The first factor showed heavy

factor loadings for SO₂, NO, NO₂, As, Se, and sulfate and clearly represented the plant. The second factor showed no significant connection with the gaseous pollutants, but had high factor loadings for the mineral elements, TSP, and sulfates. This was taken to represent a soil component. A third component was found to be tied to the alkali metals, chlorine, manganese, and phosphorus. No satisfactory source for this factor was identified; it may have been related to the scrubber, as it showed some connection to the wind direction variable, or it may have resulted from contaminants from the impregnated filters used in conjunction with the Teflon filters. The fourth factor showed strong ties with bromine, sulfur, the mineral elements associated with soil, and a significant loading for total nitrates. This factor was probably related to vehicular traffic.

Conclusions

The Scholz Steam Plant, around which this study was performed, was found to be the dominant source of gaseous sulfur and nitrogen oxides in the area. However, it was found to contribute only about 15% of the ambient particulate sulfate and nitrate burdens. The major contributor to the ambient particulate nitrates appeared to be automotive in origin, while the sulfates appeared to be primarily associated with windblown soil, possible automotive sources, and indeterminate sources lying at large distances from the test area.

The plant's oxides of nitrogen emissions were almost entirely in the form of NO in the stack; approximately 40% had oxidized to NO₂ within 2 to 5 km of the plant. The ratio of sulfate to SO₂ associated with the plant's emissions was found to be about twice as large in the ambient air as in the stack. This could have resulted from continuous oxidation of SO₂ at a rate of about 0.25%/h, but the data also supports a much more rapid oxidation rate immediately upon discharge from the stack that was followed by a much slower rate. Approximately 95% of the sulfate emissions from the plant were in the form of sulfuric acid. The available data do not indicate that any significant neutralization took place before the plume reached the sampling sites.

As expected, the dispersion models did not predict plume concentrations of reactive components well. However, the poor performance of the ISC model in prediction of concentrations near the source probably resulted from over-predictions of plume height by the Brigg's

Table 1. Plant Emission Summary

	Unit 1	Unit 2	Scrubber
Gas flow, m ³ /s	104	108	20.2
Gas temperature, °C	148	147	-*
Unit load, MW	48.9	49.9	-
Particulate matter, mg/DNM ₃	26.5	44.4	2.7
H ₂ SO ₄ ppm	2.94	6.21	NA
SO ₂ ppm	2030	1900	~200
NO _x ppm	472	440	~450

*Values not determined?
NA = Not applicable.

Table 2. Ambient Air Data Summary

	Upwind	Crosswind	Downwind
<i>Sampling parameters</i>			
Average distance from plant, km	1.72	2.63	2.53
Average distance from major road, km	2.09	4.04	6.24
Average sampling duration, min	480	473	348
<i>Measured concentrations</i>			
Particulate matter, µg/m ³	29.8	30.8	43.2
Sulfates, µg/m ³	1.71	2.35	3.82
Nitrate salts, µg/m ³	0.48	0.20	0.27
Nitric acid, µg/m ³	1.13	0.88	0.75
Bromine, ng/m ³	1.54	5.80	6.63
SO ₂ ppb	0.63	1.04	50.9
NO _x ppb	2.38	2.86	20.6
NO, ppb	0.22	1.15	11.9
<i>Concentrations attributed to plant by target transformation factor analysis</i>			
Particulate matter, µg/m ³	0	2.16	7.60
Sulfates, µg/m ³	0	0.19	1.03
Nitrates, µg/m ³	-*	0.030	0.154
Bromine, ng/m ³	-	0.56	2.88
SO ₂ ppb	-	11.2	54.9

*Not determined?

equation, as much better results were obtained by using the Holland plume rise algorithm. The Holland algorithm results in substantially lower values for plume rise.

Target transformation factor analysis provided an excellent means of quantifying the impact of the source, but good, measure source signatures are needed for optimal application of the technique. Source vectors found in the literature were not particularly useful in this study.

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The complete report, entitled "Impact of Primary Sulfate and Nitrate Emissions from Selected Major Sources: Phase 1. Coal-Fired Power Plant," (Order No. PB 86-103 678/AS; Cost: \$16.95, subject to change) will be available only from:

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