&EPA Project Summary

Impact of Primary Sulfate and Nitrate Emissions from Selected Major Sources: Phase II: Sulfuric Acid Plant and Pulp and Paper Mill

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

Sampling for phase II took place during August of 1981 at the sulfuric acid plant operated by American Cyanamid and the pulp and paper mill operated by the Union Camp Corporation. Both plants are located in Savannah, Georgia. Source measurements were made for emission rates of H_2SO_4, particulate sulfate, SO_2, NO_x, and total particulate matter; and elemental composition by particle size was determined. Ambient measurements were made for all the preceding pollutants plus HNO_3, particulate nitrate, and pertinent meteorological parameters required for dispersion modeling.

The average concentration of TSP in the ambient was about 120 $\mu g/m^3$, while the average sulfate and nitrate concentrations were, respectively, 6 $\mu g/m^3$ and 2 $\mu g/m^3$. Factor analysis based on elemental analyses of ambient air particulate samples, the plants' particulate emissions, and local soil samples indicated that wind-blown soil was the dominate source of the ambient particulate matter. Factor analysis, dispersion modeling, and comparative upwind-downwind concentrations indicated that primary sulfate and nitrate emissions from the target sources were responsible for only a small fraction of the observed ambient concentrations of these materials. The major source of the observed sulfates and nitrates appeared to be secondary aerosols, perhaps dominated by long-range transport.

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 addressed the problems of long-range transport. However, a significant portion of the problems associated with these compounds may arise in the near-source vicinity. The program described here was intended to provide information on the partitioning of sulfates and nitrates in ambient air between primary (local) and secondary (long-range-transport) sources. This report presents the results of the second phase of a two-phase source-ambient study. Phase I results of the program are reported elsewhere. Phase II concerned the impacts on the ambient air

of a sulfuric acid plant and a pulp and paper mill. Sampling for Phase II took place during August 1981 in the environs of Savannah, Georgia.

Sulfur and nitrogen compounds are of particular concern because they are preponderant 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 areas with high automotive traffic densities. Serious deterioration of the environment has been linked to these compounds. In 1964, regulation of SO_2 emissions began in this country. The use of high-sulfur fuels was inhibited, and taller stacks were employed to improve local air quality. This reduced the measured levels of SO_2; however, ambient sulfate levels have not been substantially improved. Thus, it is important that the specific contributions of these aerosols to the local- and long range concentrations transport be determined.

Three approaches were taken to quantify the impact of the plants 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 data base comprising the concentrations of SO_2, NO_x, TSP, SO_4^{-2}, and NO_3^-; 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 analyzing the data to isolate and quantify the impacts of specific sources at each sampling location.

Test Site

The study was carried out in and around the city of Savannah, Georgia. The targeted sources were a pulp and paper mill operated by the Union Camp Corporation and a sulfuric acid plant operated by American Cyanamid, Inc., located on an east-west line along the Savannah River. American Cyanamid's facility is located at the eastern extreme of the industrial development, and Union Camp is located inland; the two facilities are equidistant from the Savannah central business district. The industrialized area extends another 8 km (5 mi) westward from Union Camp. The industrial and urban developments are confined wholly to the south side of the Savannah River.

Two additional sulfuric acid plants were in operation in this industrialized area; one of these has a rated capacity of about 10 percent of that of Cyanamid and the other a capacity of about half that of Cyanamid. In addition to Union Camp, several pulp mills operate in the area, only one of which uses the Kraft process; this plant, with about one quarter the capacity of Union Camp is located at the western end of the industrial development.

The Savannah plant, of the Union Camp Corporation is the world's largest pulp and paper plant with a pulp capacity of 2850 tons per day, of which 2550 tons per day are produced by the Kraft process. The major emission sources within the complex are three each recovery boilers, lime kilns, and power boilers.

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 results of emissions from the acid and pulp and paper plants. Further, it was desirable to differentiate between sulfate and nitrate salts and sulfuric and nitric acid. Thus data were needed on the ambient and source concentrations of these variables and their precursors.

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

A grid of acceptable monitoring locations was developed in the vicinities of the plants, and based on anticipated wind flow, sites were selected for monitoring at the beginning of each test day. Because of the relatively large separation between the acid plant and the pulp and paper plant, sampling was concentrated in the vicinity of each in turn for about one half of the tests. Data were taken at three mobile stations, one of which was deployed at an upwind location while the remaining two were located downwind of the target source(s). Wind flow was monitored throughout each test day, and the mobile stations were moved when winds shifted in order to maximize the amount of data obtained in the plumes. The monitoring sites were selected as much as possible in open areas, where the prevailing wind flow was not significantly disturbed by local topography or vegetation. Sites near other local sources of pollutants were avoided.

Data to identify dispersion characteristics were taken from a portable 10-m meteorological tower provided by TRC. Upper air measurements were made using pilot balloons and temperature sonde equipment.

Measurement Results

Source

An overview of the source emission parameters is given in Table 1. This table summarizes for each unit at the two facilities all emission rate measurements for the principal components of interest particulates, SO_2, H_2SO_4, and NO_x.

Samples were taken for determining the composition of the plant's emissions in six particle-size fractions with Southern Research Institute series cyclone systems and with a special purpose impactor designed and constructed by SoRI under a previous EPA contract. Specimens from each size fraction from each of these samplers were analyzed by X-ray fluorescence (XRF) and those from the cyclones were analyzed by neutron activation analysis (NAA) as well. These analyses provided the desired "emission signature" for the plants.

Ambient

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

Two methods of measuring ambient SO_2 concentrations were employed, continuous monitors and peroxide bubblers. The primary integrated samples were to be taken coincident with each sulfuric acid sample. Problems were encountered with each method that in the end resulted in significant loss of data.

High ambient NO_x concentrations showed essentially no correspondence with occasions when the sources of interest were located upwind of the sampling stations. This result was not unexpected, as none of the sources except perhaps the power boilers at the pulp mill were significant NO_x emitters.

The results of all ambient sulfate and sulfuric acid sampling are given in Table 2. The values reported on each line of the table are for samples that were taken over approximately the same time intervals; however, they seldom represent truly coincident samples. In a few cases samples obtained with one method over-

Table 1. Source Emissions Summary

Source	Gas Flow (actual m³/s)	H₂O (%)	Temp. deg. C	Stack HGT. meters	Stack DIA meters	Part. CONC. mg/dnm³	Part. SO₄ mg/dnm³	H₂SO₄ CONC mg/dnm³ (C & H)	Total SO₄ = SO₄ mg/am₃	ppm	NOₓ ppm
Am. Cyanamid											
Acid Plant	28.2	0	90.6	45.7	1.83	5.26	5.00	24.49	23.00	417	15
West Calciner	34.9	21	68.3	56.4	2.13	206.00	200.00	223.07	136.00	787	32
East Calciner	32.8	24	71.1	56.4	2.13	48.06	48.00	48.11	31.00	336	25
Union Camp											
12 Rec. Boiler	115	29	151.7	71.3	1.83	22.88	13.50	0.46	6.90	78	38
13 Rec. Boiler	105	34	154.4	71.3	1.83	18.77	7.03	< 0.22	3.20	64	32
14 Rec. Boiler	219	34	148.9	93.4	2.74	36.61	28.40	0.88	13.30	2.5	42
12 Smelt Tank	10.9	36	73.9	70.3	1.52	252.00	22.00	< 0.22	12.00	16	1.8
13 Smelt Tank	11.5	36	73.9	70.3	1.52	252.00	29.00	< 0.22	16.00	14	0.25
14 Smelt Tank	25.6	36	73.9	93.4	2.44	188.00	28.00	< 0.22	15.00	10	——
4 Lime Kiln	24.1	41	76.7	41.6	1.98	352.00	60.80	——	30.00	26	45
5 Lime Kiln	25.8	51	81.1	41.6	1.98	263.00	(40)	——	16.00	NA	46
6 Lime Kiln	32.6	36	73.9	41.6	1.98	18.08	10.10	——	5.40	13	NA
11-12 Po. Blr.	360	16	218.3	93.9	5.49	222.00	6.00	< 0.22	3.20	4.7	95
10 Power Blr.	108	12	190.6	56.9	3.35	——	——	——	——	——	148

Table 2. Summary of Ambient Sampling Results, Savannah, August 1981

Date	Wind Direction Within 30°* (% of Time) CYAN	U.C.	Wind Speed m/s	SULFATE CONC. (µg/m³) Lund. Total	Acid Sys. Total	HI-VOL	Lund. Filt.	PART. CONC. (µg/m³) Acid Part	Sys. H₂SO₄	HI-VOL µg/m³	Lund. µg/m³	SO₂ ppb	NO ppb	NOₓ ppb	NITRATE (µg/m³) HNO₃ µg/m³	PART. µg/m³
11	0	0	4-5		NA	0.86		NA	NA	63	NA	NA	21.60	74.80	0.45	0.56
11	100	0			4.03		0.82			80	138		NA	NA	1 73	0.69
11	100	0				4.81	0 82	1.41	3.40		138	428				
11	100	0			NA	0.90		NA	NA	62	NA	NA	NA	NA	2.68	1 95
12	12	25	2-7		NA	2 33	4.56	NA	NA	35	251	NA	NA	NA	1.44	0.60
12	25	30		8.84	NA	2 43	3.06	NA	NA	0	305	352	NA	NA	2.50	0.47
15	25		3-4				4.10				214					
15-16	29	62	2-4			8.25	NA			78	68		NA	NA	1.52	0.38
15-16	29	47		9.96		8.47	3.14			NA	52		NA	6.33	1.41	0.44
16	0	67	2-6			6.15				38			NA	NA	1.47	0 10
16	0	0		7.2	6.67		4.84	2.50	4.17		239	275				
16	43	57		18.90	3 79		6.82	1.81	1.98		148	344				
16	40	50		16 40	2.16		6.82	0.59	1 57		98	337				
16-17	33	25	2-6		NA	5.73		NA	NA	38		NA	NA	NA	1.45	0.26
17	25	0	4-6	8.35	1.40	NA	2.00	0 77	0.63	NA	219	36	NA	NA	NA	NA
17	12	25	1-6		2.60	6.30	2.61	0 87	1.73	85	97	125	NA	NA	1.74	0 50
17	12	25					3.12					131				
17-18	0	0	3-8		NA	6.62	NA	NA	NA	28	NA	NA	NA	NA	NA	NA
17-18	0	0			NA	8.13	NA	NA	NA	24	NA	NA	NA	NA	2.92	NA
18	0	0	8-9		NA	5.41		NA	NA	39	NA	NA	NA	NA	0.78	0 78
18	0	0		7.66	3.44	4.48	2.82	1 54	1.98	37	172	74	NA	NA	0.81	0 27
20	0	0	3-5	7.58	1.18	5.50	2.28	0.45	0.73	59	95	1	NA	NA	1.36	0.06
20	100	0		12.07	5 78	4.98	4.20	1.30	4.48	32	74	0	NA	NA	0 58	0.00
20	100	0			6.28	5.12	1 97	1.25	5.03	27	>39	9	NA	NA	0 64	0.10
20	100	0	3-4		5.71	6 55	1.97	2 50	3.21	27	>39	31	12.20	18.30	2.22	0.00

lapped two samples taken with another; in these cases the entry for the longer-duration sample is duplicated for each of the shorter samples. Comparisons of average H₂SO₄ concentrations with total sulfate concentrations from the hi-vol samples show that typically about 50% of the ambient sulfate was sulfuric acid.

The peak sulfate and nitrate concentrations were measured on days when pervasive, region-wide hazes occurred. These were days when the winds were north and west. Because the upwind concentrations were as great as the downwind, even though virtually no local sources were upwind in those directions, moderate- and long-range-transport sources must be considered a real possibility.

Sections of the Teflon membrane hi-vol filters and the Lundgren impactor substrates and filters were analyzed by XRF and NAA techniques to provide information on the elemental composition of the ambient particulate matter. Thirty-eight elements were detected on some or all of the Teflon filters by the combination of XRF and NAA techniques. Some of these were found only on a few of the filters and then only near the detection limits. However, 36 of the 38 were detected at high enough concentrations on most or all of the filters to be useful in particulate source identification.

Source Impact

Three approaches were taken to quantify the impact of the target sources on the study area. First, dispersion model predictions were made for downwind concentrations of sulfate, SO₂, and NOₓ at the locations of the ambient sampling stations using averaging times comparable to the sampling periods used in the sampling. Second, principal component factor analysis (PFA) was applied to the correlation matrix of an ambient data base comprising data for SO₂, NOₓ, TSP, SO₄, NO₃, wind direction relative to the source and sampler locations, and 36 elements for which reasonably good concentration values were available from the Teflon membrane hi-vol filters. This analysis provided much insight into the probable number and nature of sources that had a detectable impact on the ambient stations, but did not quantify the impact on individual stations. Finally, Target Transformation Factor Analysis (TTFA) was used in analyzing the data in an attempt to isolate and quantify the impacts of specific sources having known signatures at each specific sampling location.

A four-factor PFA solution resulted in the following. The first factor showed heavy factor loadings for elements common to soil, and fairly clearly represents windblown soil. The second factor showed high loadings on Ar, Se, Ce, and Zn. This factor was traced to samples from a single location and appeared to result from wind-transported emissions from a galvanizing plant which was ENE of that location. The third factor had significant loadings on only sulfates and nitrates and probably represents a secondary aerosol, possibly brought into the area by long-range transport. Most of the explained variance for these two variables (sulfates and nitrates) arises from this factor. The fourth factor is associated with a TiO₂/acid plant complex but does not arise directly from the sources tested. The area around the TiO₂/acid plant complex was liberally coated with TiO₂ dust, and this factor may represent resuspension of some of this material, together with fugitive emissions from the complex. The four factors are sufficient to explain 83% of the variance in the input data matrix. Inclusion of a greater number of factors resulted in additional factors whose loadings were less than their standard errors.

The TTFA input data matrix consisted of various combinations of 20 to 47 elements, gases and radicals for each of 39 filters. The data on the elemental concentrations were augmented with values for TSP from the other parallel hi-vol run; sulfate, nitrate, and nitric acid concentrations determined from the same hi-vol

Table 2. (Continued)

| Date | Wind Direction Within 30°* (% of Time) | | Wind Speed m/s | SULFATE CONC (µg/m³) | | | | | | PART. CONC. (µg/m³) | | SO₂ ppb | NO ppb | NOₓ ppb | NITRATE (µg/m³) | |
	CYAN	U.C.		Lund. Total	Acid Sys. Total	HI-VOL	Lund Filt	Acid Part	Sys. H₂SO₄	HI-VOL µg/m³	Lund. µg/m³				HNO₃ µg/m³	PART. µg/m³
22	0	0	2-4	4.92	2 50	6.88	2 08	1 30	1.20	24	39	99	NA	NA	0.79	0.17
22	0	67		7.55	4 70	1.59	3.00	0.75	3.95	202	161	32	7 39	15.38	NA	0 65
22	14	72			2 44	2 03	2.72	0.67	1 77	36	78	55	21 90	20.11	0.46	0.28
23	0	0	3-6	4.60	4.13	1.38	1 98	2.85	1 28	18	13	9	NA	NA	0.75	0.08
23	0	0		5 63	2.58	1 41	1.97	0.94	1.64	25	36	81	3 50	9 00	0.89	0 07
23	0	0		3.95	3 14	1.75	1.77	0.57	2 57	20	24	25	5.47	11 98	0.68	0.08
24	0	0	3-4	6.87	1 64	3 93	3.28	0.80	0.84	20	41	9	NA	NA	1 08	0 00
24	0	100			NA	3.33	2.74	NA	NA	190	204	44	NA	NA	0.67	0.78
24	0	50			2.80	4.61	2.74	1.20	1.60	399	204	8	NA	NA	0 32	0.65
24	0	100		7.57	4.96	4.34	3 39	1.98	2.98	55	105	22	6 00	13.10	NA	0.42
24	0	100		7.57	3.33	3.53	3.39	1 23	2.10	26	105	13	7.98	19 30	1.27	0.18
25	0	0	1-4		8 40	17.43	6.72	4.10	4.38	49	NA	92	NA	NA	6 02	0 36
25	0	100		17 79	5.30	18 87	6.39	2 15	3.15	272	NA	66	7.90	NA	2.84	1.17
25	0	100		9.94	4.91	12 94	4.91	2 40	4.21	49	NA	29	11.00	11.00	2.49	0.21
26	100	0	3-7	8.73	4.97	14.65	3 40	2 37	2.60	189	85	35	NA	NA	3 25	0 20
26	100	100		35.00	3.84	11 10	NA	1.41	2.43	55	87	40	7.10	11.00	1 24	2.00
26	100	60		12.38	5 60	4.13	4.16	2.49	3 11	88	66	55	0.68	7.40	1.69	1.50
26-27	0	0	2-4	8.73	2.32	6 65	3.40	0.93	1.39	NA	85	24	NA	NA	1 38	0.42
26-27	0	0		35.00	2 93	6.92	NA	1 28	1.65	55	87	35	24.60	34.30	0 47	0.71
26-27	8	31		12.38	2.83	8.02	4.16	1.20	1.63	88	66	35	5 00	16.90	1.61	0.64
27	25	100	2-4	16 27	3.43	6 85	4.29	2.03	1.40	32	48	28	7.10	11.00	1.06	0.62

*Percentage of the sampling period in which the hourly average wind direction was within 30 degrees of the line from the plant to the sampling location.

runs which provided the data on the elements; covered by the hi-vol samples. There were too many missing values in the NO_x data for their inclusion to be meaningful.

Source vectors used in attempting to regenerate the data were the measured emission strengths of the various units in the plants and combinations thereof; the compositions of soil samples from the area; and vectors obtained from the literature and the phase I test for automotive sources, power plants, sea-salt, etc. The predictive capabilities of TTFA were used to refine the vectors obtained from the literature for this specific application. No satisfactory regeneration could be obtained from any combination of these source vectors as long as sulfur (or sulfate) and nitrates were included in the data set. Uniqueness tests for these variables confirmed the conclusions reached from PFA: they do indeed exhibit unique behavior and cannot be directly related to any source which might be potentially identified by its signature in the remaining elements.

Potential source factors were also obtained by using the predictive capabilities of TTFA to independently generate a set of possible source vectors. Six possible source vectors were generated in this fashion. One of these very closely matches a composite of the soil samples, another shows high concentrations of Ti and P, and a third is very high in sulfur and nitrates and has a high association with vanadium. The Ti-P vector is, as previously mentioned, associated with the area in which the acid plant is located; but it is not directly related to the sources sampled there, nor does it have much sulfur associated with it. The sulfate-nitrate vector has no resemblance to either the acid plant sources or the pulp mill and cannot be accounted for by any range transport for its origin.

Source emission data and meteorological data for each test day were used with two versions of a dispersion model to predict average concentrations for each test day at all downwind sampling sites. Predictions were made only for the plant's contributions to SO_4^{-2} and in the case of the pulpmill, NO_x. One of the models used the Briggs plume rise algorithms whereas the other used the older Holland equations. Observations of plume behavior at the plants in question lead the authors to believe that the Holland equations are more realistic in the current application. The plume rise predicted by the Briggs equations seemed too large in all cases. The effect of the overprediction of plume rise is an underestimation of near-source impact thus the result of using the Holland plume rise algorithm is to make conservative (high) predictions of downwind concentrations as compared to those from the Briggs model. Even using the conservative model, the plants' contributions to the measured downwind sulfate concentrations were predicted to be no more than five to twenty-five percent of the totals in the case of Cyanamid, and one to ten percent in the case of Union Camp. Only ten percent of Cyanamid's predicted impact would be from the acid plant since ninety percent of the Cyanamid sulfate emissions were from the calciners. Predicted NO_x and SO_2 concentrations were also much lower than the measured downwind impact in terms of these gases.

Conclusions

Neither the sulfuric acid plant or the pulp and paper mill was found to be a significant contributor to the local ambient burdens of sulfates and nitrates. The bulk of the sulfates and nitrates appeared to result from secondary aerosols and/or long range transport, especially during periods of high sulfate concentration.

United States
Environmental Protection
Agency

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