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Project Summary

Air Quality Data for Nonmetallic Inorganic Ions: Nitrate and Sulfate for 1979 from the National Air Surveillance Networks

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The National Air Surveillance Networks provide information on air quality for many urban and nonurban locations within the United States. This report summarizes the network data for two nonmetallic inorganic ions (nitrate and sulfate) determined from high volume samples collected during the year 1979. Concentration values are presented in the form of cumulative frequency distributions. Arithmetic and geometric sample statistics are also reported, as are measures of the precision and bias associated with the analytical methods employed. Comparison of the 1979 data with that from previous years in the decade shows that network nitrate concentrations on a nationwide basis increased substantially during the 1970's. The average annual rate of increase was 6.2% during the nine-year period in areas classified as urban and 9.6% in areas classified as nonurban. Average network sulfate concentrations did not exhibit a consistent trend through the 1970's, but have apparently increased since 1976 in both urban and nonurban areas. Some of the variability from year to year in the national frequency distributions may be attributed to different sets of sites being used in the summarization, depending upon the completeness criteria for valid data and changes in state and local agency participation in the networks over the years.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The U.S. Environmental Protection Agency (EPA) conducts a variety of air sampling activities to obtain information about the quality of the nation's air. Often this work is accomplished with the assistance and cooperation of state and local government agencies. One such program consists of the National Air Surveillance Networks (NASN) which have reported air quality data for more than 20 years. Although the operation of the sampling sites is decentralized, the determination and publication of trace pollutant concentrations remains the responsibility of EPA's Environmental Monitoring Systems Laboratory at Research Triangle Park (EMSL/RTP).

The air quality monitoring stations of the NASN are located throughout the country in areas originally classified as urban or nonurban. Urban-classified sites were generally located within a city, town, or adjacent suburb. Nonurban-classified sites were originally located in rural or remote areas; but, over time, many of these areas became more

heavily populated and subjected to the influences of spreading urbanization.

This report summarizes the 1979 network data for nitrate and sulfate ion concentrations as measured by colorimetric analysis of high volume particulate samples.

Procedure

Preweighed glass-fiber filters were distributed to the cooperating local agencies for sample collection. After high-volume sampling, the filters were returned to the EPA for final weighing and chemical analysis. Analyses for inorganic ions during 1979 were performed by Northrop Services, Incorporated - Environmental Sciences, under Contract No. 68-02-2566.

An 8.3 percent section of each particulate filter was cut and extracted in water for autoanalysis. The analytical procedure for each ion was as follows:

1. The aqueous extract was analyzed for nitrate ion by reduction of the nitrate to nitrite by a copper-cadmium reduction column. The nitrate was reacted with sulfanilamide in acidic solution to form a diazo compound. This compound then coupled with N-1-naphthylene diamine dihydrochloride to form a reddish-purple azo dye which was determined colorimetrically at a wavelength of 520 to 540 nm.

2. The extract was analyzed for sulfate ion by the methylthymol blue (MTB) method using a single channel Technicon Autoanalyzer II system equipped with a linearizer. The MTB method is based on the spectral difference which exists in basic solution (pH 12.5 to 13.0) between the barium complex of MTB and free MTB. At this pH, the barium complex is blue and free MTB is brownish-red (absorbs light at 460 nm). Thus, the color of solutions containing both the free MTB and the complex appears as gray. The amount of free MTB, monitored colorimetrically at wavelengths of 460 to 480 nm, was the measure of the amount of sulfate in the sample.

Independent estimates of laboratory precision and bias were determined for these data to aid in interpreting analytical results. However, several potential sources of measurement error associated with sample collection and handling procedures (flow control, artifact formation, shipping and storage losses, etc. that were not directly controlled by EMSL/RTP) were not considered in the estimates of data quality presented here.

Analytical precision estimates are based upon percent differences determined from analyses of two filter strips taken from the same filter. Thus, the measure of precision includes variation caused by cutting, extracting, and analytical processing as well as any actual differences which may exist between filter strips. Duplicate strips of every 20th sample were analyzed for the purpose of estimating precision.

Analytical bias estimates were obtained through an audit program in which "spiked" filter strips were introduced into the ambient air sample group for routine analysis. These quality assurance samples contained known quantities of each ion and thus provided a measure of analytical recovery and its complement, bias. Every 2 weeks a set of 10 audit samples was provided to the analytical laboratory for inclusion in the routine sample processing.

Results

Estimates of the analytical precision and bias associated with the 1979 results are listed in concentration range in Table 1.

Table 1. Analytical Precision and Bias

Ion	Concentration Range ($\mu g/m^3$)	Bias (%)	Precision (%)
Nitrate	<3	+4.1	±7
	3-6	-2.5	±3
	>6	+0.4	±4
Sulfate	<6	-6.7	±6
	6-20	-2.0	±4
	>20	-2.9	±1

Air quality data are presented in Tables 2 and 3 in the form of annual cumulative frequency distributions by ion summarized for urban and nonurban locations, respectively. In the first line of Table 2, the number 3900 is the number of valid 24-hr samples analyzed for nitrate in 1971. The next entry is the minimum value detected that year, and "LD" means below the minimum detectable level of the instrument. The next seven entries are the 10 through 99 percentile values. For example, the 90 percentile value of 5.02 indicates that 90 percent of the 3900 values, i.e.,0.90 x 3900 = 3510, were equal to or less than 5.02 $\mu g/m^3$. The next entry is the

Table 2. Urban National Cumulative Frequency Distributions

			Percent of time concentration ($\mu g/m^3$) is equal to or less than								Arithmetic statistics		Geometric statistics	
Ion	Year	Number of Samples	Min.	10	30	50	70	90	95	99	Max.	Mean	Std. Dev.	Mean	Std. Dev.
NO_3^-	1971	3900	LD	0.69	1.55	2.29	3.22	5.02	6.48	11.85	26.17	2.77	2.30	2.13	2.06
	1972	5519	LD	0.66	1.58	2.47	3.55	5.90	7.88	13.50	24.99	3.05	2.61	2.32	2.10
	1973	4775	LD	0.81	1.71	2.58	3.65	6.24	8.31	14.61	37.36	3.25	2.87	2.44	2.13
	1974	4562	LD	0.83	1.74	2.54	3.63	6.46	8.62	17.50	54.89	3.36	3.40	2.36	2.32
	1975	4113	0.20	0.96	2.00	2.91	4.12	7.18	9.90	17.07	33.71	3.73	3.31	2.79	2.15
	1976	3817	0.08	1.07	1.99	2.80	3.83	6.48	9.53	20.65	43.16	3.71	3.83	2.58	2.34
	1977	4531	0.07	1.07	2.09	2.99	4.15	6.76	10.40	20.63	97.67	3.89	3.97	2.87	2.18
	1978	3610	LD	1.08	2.21	3.24	4.56	7.78	11.18	22.91	56.96	4.22	4.10	3.07	2.26
$SO_4^=$	1971	3916	LD	3.4	5.7	8.0	10.9	18.0	22.0	33.5	69.2	9.6	6.8	7.84	1.89
	1972	5519	LD	3.9	6.7	9.4	12.7	20.3	25.4	37.9	75.9	11.1	7.7	9.15	1.87
	1973	4774	LD	3.9	6.3	8.1	10.9	17.5	22.7	35.4	162.0	9.9	7.0	8.06	1.89
	1974	4564	LD	3.9	6.3	8.3	11.3	17.9	22.8	34.8	69.1	10.0	6.7	8.34	1.83
	1975	4110	0.2	3.5	6.1	8.3	11.5	18.1	23.8	35.8	72.6	10.0	7.0	8.22	1.88
	1976	3871	0.2	3.1	5.4	7.4	9.9	16.5	20.0	29.2	66.7	8.8	5.8	7.33	1.83
	1977	4531	0.7	3.1	5.7	7.6	10.3	17.1	20.9	29.9	76.4	9.1	6.1	7.44	1.72
	1978	3610	LD	3.1	5.7	7.8	10.6	16.6	20.4	34.5	228.4	9.4	7.5	7.55	1.95

Table 3. Nonurban National Cumulative Frequency Distributions

Ion	Year	Number of Samples	Min.	Percent of time concentration ($\mu g/m^3$) is equal to or less than								Arithmetic statistics		Geometric statistics	
				10	30	50	70	90	95	99	Max.	Mean	Std. Dev.	Mean	Std. Dev.
NO_3^-	1971	671	LD	0.06	0.31	0.71	1.20	2.19	2.67	3.81	6.04	0.95	0.92	0.68	2.26
	1972	928	LD	LD	0.15	0.50	1.01	2.08	2.59	4.19	6.59	0.79	0.92	0.52	2.52
	1973	831	LD	0.04	0.28	0.71	1.26	2.35	2.83	4.47	6.67	0.99	1.02	0.69	2.34
	1974	706	LD	0.12	0.37	0.83	1.37	2.52	3.16	5.13	6.65	1.10	1.07	0.79	2.25
	1975	630	0.20	0.20	0.20	0.73	1.41	2.74	3.28	4.85	11.85	1.13	1.16	0.78	2.35
	1976	467	LD	0.10	0.36	0.82	1.51	2.82	3.54	4.73	6.15	1.18	1.16	0.84	2.27
	1977	681	LD	0.17	0.55	1.05	1.81	3.07	3.84	5.22	11.57	1.39	1.26	0.85	3.21
	1978	458	LD	0.30	0.59	1.07	2.03	3.77	4.74	8.09	11.77	1.69	1.72	1.06	2.78
$SO_4^=$	1971	686	0.4	1.5	3.0	4.7	7.2	11.8	15.5	23.6	35.4	6.0	4.9	4.7	2.03
	1972	929	LD	1.4	2.9	5.2	7.8	13.7	17.4	24.8	42.7	6.6	5.4	5.1	2.05
	1973	831	LD	1.3	2.7	4.4	6.3	12.0	17.0	29.8	53.2	6.0	5.9	4.2	2.29
	1974	706	0.1	1.4	2.6	4.8	7.2	12.2	16.6	27.0	90.0	6.2	6.2	4.4	2.30
	1975	630	0.2	0.7	2.1	4.0	6.4	11.6	15.2	28.7	48.3	5.5	5.7	3.8	2.36
	1976	493	0.2	0.9	1.8	4.0	6.5	11.3	13.9	21.3	36.3	5.3	4.9	3.8	2.22
	1977	681	LD	1.2	2.5	4.7	7.4	12.8	17.1	24.6	43.3	6.1	5.4	4.0	2.72
	1978	458	LD	1.2	3.0	4.9	7.2	13.4	17.0	21.0	38.5	6.2	5.3	4.2	2.71

maximum annual value. Arithmetic means and standard deviations, and geometric means and geometric standard deviations are presented in the last four columns in the table. Comparison among years for a given pollutant provides a relative indication of national trends. Some of the variability from year to year, however, may be attributed to different sets of sites being used in the summarization, depending upon the completeness criteria for valid data and changes in state and local participation in the network over the years.

The annual arithmetic mean concentrations for nitrate and sulfate ions are shown in Figures 1 and 2, respectively.

Conclusions

It is clear from Figure 1 that network nitrate concentrations on a nationwide basis increased substantially during the 1970's. In areas classified as urban, the average annual rate of increase was 6.2% while nitrate ion in nonurban areas increased at an average annual rate of 9.6% during the nine-year period. Daniel's Test for Trend showed significance at the 99% probability level for the positive trends apparent in both urban and nonurban nitrate ion concentrations.

Average network sulfate concentrations, shown in Figure 2, do not exhibit a consistent trend through the entire period, but do appear to have increased since 1976 in both urban and nonurban areas.

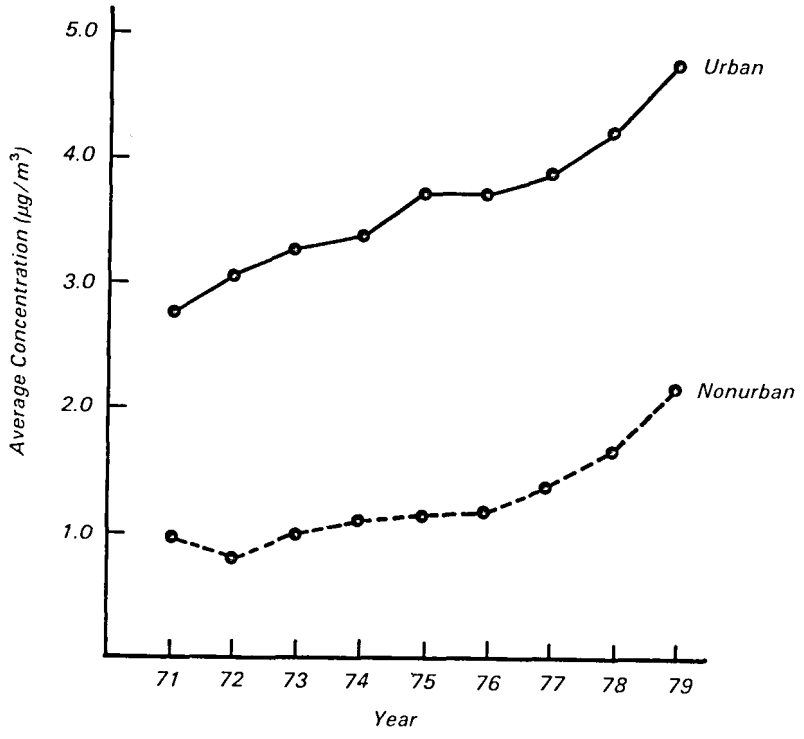

Figure 1. Annual arithmetic average concentrations for NASN nitrate ion.

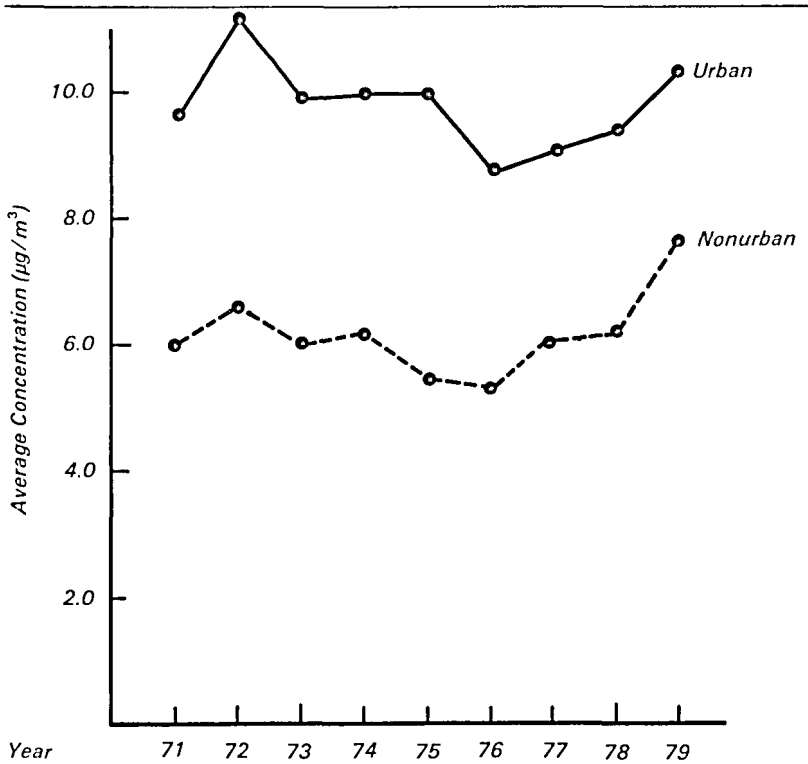

Figure 2. *Annual arithmetic average concentrations for NASN sulfate ion.*

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The complete report, entitled "Air Quality Data for Nonmetallic Inorganic Ions: Nitrate and Sulfate for 1979 from the National Air Surveillance Networks," (Order No. PB 83-172 502; Cost: $10.00, subject to change) will be available only from:

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