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Project Summary

A Regional Fine Particle Field Study: Data Base and Initial Results

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The Fine Particle Network (FPN), a group of rural sites located in the northern two-thirds of the eastern United States, has been used to determine fine particle concentrations during selected periods between August 1988 and February 1989 and then continuously from July 1989 through May 1990. Samples from the network, collected 24 h each day, were analyzed for the most abundant elements by wave length dispersive x-ray fluorescence (WDXRF). About 30 sites were in operation during each sampling period. These included 17 sites that were operating during the entire program schedule and others that were available only during parts of the schedule.

The FPN data base can be used to enhance the understanding of the seasonal variation of fine particle concentrations in the eastern United States. The data base, combined with meteorological data, will be useful for evaluation of regional aerosol models and the development of methodologies to estimate regional contribution to urban particulate concentrations. The 14 sampling sessions produced 12,859 samples for the 44 stations that were analyzed by WDXRF. Seasonal averages of fine particulate mass and elemental sulfur concentrations were determined for each of the seven seasons in which samples were collected. Concentrations of both were highest in the summer. The average concentrations for all sites and all collection dates were 15.5 and 1.9 $\mu g/m^3$ for the fine particulate mass and elemental sulfur, respectively.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

A sampling program has been sponsored by the Environmental Protection Agency to sample ambient air fine particles daily at 44 rural sites in the northern two-thirds of the eastern United States during periods of 1988, 1989, and 1990. This Fine Particle Network (FPN) consisted of a subset of sampling locations selected from the Acid Model Operational and Diagnostic Evaluation Study (Acid MODES) surface sampling program. The Acid MODES monitoring program was designed to evaluate regional acid deposition models. Since the FPN operation was subordinate to the larger Acid MODES program, changes in the latter during December 1989 necessitated shifts in the FPN sites. Samples were delivered to EPA by the contractor responsible for collection and mass measurements, ENSR, Inc. Analyses for elemental composition by x-ray fluorescence were made by ManTech Environmental Sciences.

The objective of the fine particle field study was to obtain a data base for fine particle (less than 2.5 μm aerodynamic diameter) concentrations that would represent extensive synoptic measurements of fine particle mass. This fine particle

data base, along with other chemical species and meteorological measurements made in the Acid MODES program, is useful to

(1) develop methods for estimating and understanding regional contributions to urban fine particulate concentrations,
(2) evaluate regional particulate models, and
(3) enhance the understanding of the spatial, and temporal variations of fine particulate concentrations within each season in the eastern United States.

Estimates from previous experimental field studies indicate that regional background particulate concentrations are major contributors to urban particulate concentrations. Because this contribution is large, it is desirable in urban particulate field studies to have upwind sampling sites to estimate the regional background input. This often is difficult because the background sites may not be free of local source contributions. One alternative approach is to use concentrations from measurements made at other times during comparable meteorological conditions. However, backgrounds may vary, even for the same wind directions if the particles that arrive at the urban boundary have traveled along different trajectories.

This report describes the FPN sampling network, the sampling procedures, and the x-ray fluorescence analytical method for elemental content determination.

Network Description

The EPA-sponsored program, collectively named the Acid Model Operational/ Diagnostic Evaluation Study (Acid MODES), was a part of a large coordinated field program to evaluate acid deposition models. The fine particle measurement study sites were a selected subset of the Acid MODES stations. Selection of sites for the Acid MODES stations was based on location in a high acid deposition area, the northeastern United States, and attempts to place the sites at existing National Dry Deposition Network (NDDN) locations when those sites met certain siting criteria. These criteria included locations away from population areas, away from large sources emitting sulfur and nitrogen oxides, and away from the Great Lakes and the Atlantic Ocean. Attempts were made to select sites that were accessible in all weather conditions, secure from vandalism, and free from potential local contamination sources such as nearby plowed fields, roadways, and storage facilities.

The Acid MODES network included three groups of stations: the model evaluation (ME-35) network, a gradient resolution (GRAD) group, and sub-grid variability (VAR) set of stations. The original 35 sites of the ME-35 network were supplemented with additional stations to provide uniformly distributed site spacing for regional scale model evaluation. The 12 GRAD sites were located in Pennsylvania and New York in a relatively small area where steep concentration gradients were expected. The VAR network was five stations in western Kentucky that were spaced in a small cluster to measure variation within a model grid.

The broad range of measurements made at all Acid MODES stations included precipitation chemistry (pH, conductivity, and the pollutant species sulfate, nitrate, chloride, ammonium, sodium, potassium, calcium and magnesium) aerosol particle chemistry (sulfate, nitrate, and ammonium), and gases (sulfur dioxide, nitric acid, nitrogen dioxide, and ammonia).

The Fine Particle Network did not include all Acid MODES stations. Sites that were included at one time or another during the FPN program are listed in Table 1. Duplicate samplers to determine collection repeatability were placed at close proximity at three stations: State College, PA (306), Oxford, OH (322) and Plainville, IL (359). The duplicate sites were designated by 100 units higher than their companion site (i.e., sites 406, 422, and 459).

At the start of the FPN sampling program the original 32 sites were selected from the 68 Acid MODES stations. Because of budget and program changes, 29 Acid MODES stations were shut down in December 1989. Of these, 16 were FPN sites including one of the co-located stations (Plainville, IL). However, fine particulate samplers were transferred and installed at other Acid MODES stations that were not previously included in the FPN study. Therefore, during the last four months of operation, the total complement of FPN sites was brought back to 28. One of the new sites (Oxford, OH, site no. 322) had co-located samplers. Besides affecting the sampling continuity, the change of sites altered the geographic distribution of the network.

Sampling Procedures and Schedule

The fine particle measurement samplers were assembled for the FPN sites by ENSR Consulting and Engineering, Inc. The sampling system consisted of a train of the following sequence of components positioned in a protective cabinet: a small cyclone for removing coarse particles, a 47-mm filter holder for a fluorocarbon-type membrane filter, a critical flow orifice to maintain an 8.8-l/min flow, and the pumping system with flow-metering devices. During the course of the sampling program the type of fluorocarbon filters being used was changed. The high incidence of filter breakage with the fragile Teflo filters and its higher cost led to its replacement with Zefluor in the last 11 sampling sessions.

The Fine Particle Network sampling was started at the original 32 sites on August 15, 1988 and concluded at a different combination of sites on May 31, 1990, but sampling was not continuous during the entire period. The first three sessions were six week periods starting in mid-August 1988, mid-October 1988 and mid-January 1989. After examination of the data produced in the total Acid MODES program the network managers proposed some changes so that sampling was not resumed until July 1989. After that time operation was continuous until May 31, 1990 with the exception of one week before January 1, 1990. The interruption unfortunately eliminated the collection of samples in the spring of 1989 and limited sampling in the spring of 1990 to two months.

The sampling schedule was further complicated by the closing of some of the original sites and starting new sites, as described in the network description section. Only 17 sites operated from the start to the end of the program. Specific dates that each site operated are indicated in Table 1.

Analytical Procedures

After the samples were delivered to EPA, those with invalid quality control codes were removed and the remainder were analyzed by wavelength dispersive x-ray fluorescence (WDXRF) spectrometry. The WDXRF spectrometer, a Siemens MRS-3 system with one scanning monochromator and 13 fixed monochromators, gives analytical capability for elements from sodium through bismuth. The fixed monochromators were tuned to one element and dedicated to that element; all other elements were analyzed sequentially by the scanning monochromator. A chromium target x-ray tube operated at 54 kv and 44 ma was used to excite the samples. The characteristic radiation from each element was defracted by a crystal and its intensity measured by a detector for each monochromator. The type of crystal and detector employed was optimally selected for the characteristic wavelength of each element. Spectrometer operation and data

Table 1. Locations and Operation Dates for Fine Particulate Network Stations

Site Number	Location	Latitude	Longitude	Operating Dates[a] Start	Stop
301	Pittsboro, NC	35.67	79.23	09/12/88	12/08/89
302	Wartburg, TN	36.08	84.54	02/12/90	05/31/90
303	West Point,NY	41.35	74.05	08/15/88	12/08/89
305	Whiteface Mountain, NY	44.38	73.85	10/13/88	05/31/90
306	*State College, PA	40.78	77.93	08/15/88	05/31/90
307	Parsons,WV	39.10	79.66	01/22/90	05/31/90
308	Prince Edward SF, VA	37.17	78.31	10/13/88	05/31/90
310	Danby, NY	42.35	76.49	08/15/88	12/08/89
312	Kane Forest, PA	41.60	78.77	08/15/88	05/31/90
314	Deer Creek Park, OH	39.42	83.22	08/23/88	05/31/90
315	Pickney, MI	42.42	83.90	01/21/90	05/31/90
316	Beltsville, MD	39.03	76.82	11/07/88	12/03/89
318	Tanner's Ridge, VA	38.52	78.48	08/26/88	09/18/88
319	Cedar Creek SP, WV	38.88	80.85	09/01/88	05/31/90
320	Mountain Lake, VA	37.37	80.52	09/12/88	05/27/90
321	Lilley Cornett Woods, KY	37.09	82.99	09/07/88	05/31/90
322	*Oxford, OH	39.53	84.72	01/22/90	05/31/90
323	Brokensword, OH	40.92	83.00	08/15/88	05/31/90
324	Unionville, MI	43.63	83.38	08/22/88	05/31/90
326	Roaring Creek, NC	36.11	82.05	01/22/90	05/31/90
327	Edgar Evins SP, TN	36.04	85.73	09/01/88	12/08/89
328	Arendtsville, PA	39.92	77.31	09/02/88	12/08/89
329	Perryville, KY	37.68	84.97	09/02/88	05/31/90
333	Salamonie Lake, IN	40.80	85.60	08/15/88	12/08/89
334	Perkinstown, WI	45.20	90.60	08/16/88	12/08/89
335	Ashland, ME	46.62	68.41	11/06/89	12/08/89
337	Coweeta (Otto), NC	35.05	83.43	08/31/88	05/31/90
340	Vincennes, IN	38.78	87.49	08/15/88	05/31/90
344	Washington Crossing, NJ	40.32	74.87	11/14/88	12/08/89
346	University Park, IL	41.45	87.72	08/22/88	12/08/89
357	Piseco, NY	43.45	74.52	01/25/90	05/31/90
359	*Plainview, IL	39.08	89.95	08/15/88	12/08/89
362	Hawthorne, PA	41.03	79.27	08/15/88	05/31/90
367	Renovo, PA	41.37	77.53	08/30/88	05/31/90
368	Williamsport, PA	41.17	76.92	09/12/88	12/10/89
369	Wirt, NY	42.15	78.11	01/15/90	05/31/90
370	Little Marsh, PA	41.90	77.44	08/15/88	05/31/90
373	Brackney, PA	41.94	75.92	01/15/90	05/31/90
374	North Orwell, PA	41.90	76.28	03/02/90	05/31/90
381	Eddyville, KY	37.07	88.03	01/08/90	05/31/90
383	New Concord, KY	36.53	88.09	01/11/90	05/31/90
406	*State College, PA	40.78	77.93	08/15/88	05/31/90
422	*Oxford, OH	39.53	84.72	02/14/90	05/31/90
459	*Plainview, IL	39.08	89.95	08/15/88	12/08/89

* Co-located sites

[a] All sites were shut down during these periods:

2 weeks	09/26/88 - 10/09/88	18 weeks	02/27/89 - 07/02/89
8 weeks	11/21/88 - 01/15/89	1 week	12/25/89 - 12/31/89

processing were done by dedicated laboratory computers.

For the first three sampling sessions, 33 elements were determined for all samples. A survey of these results led to a decision to reduce the analyses to these 11 elements for the last sampling sessions: Mg, Al, Si, P, S, Cl, K, Ca, Fe, Zn and Cd.

Results and Discussion

During the period from mid-August 1988 through May 1990, fine particle sampling was conducted at 45 sites. The network was not operating continuously during the entire period, but samples were collected for a total of 65 weeks. Only 17 of the sites were operating at all times during the network operation. After the removal of invalid samples, 12,589 filters (including blanks) from 14 sampling sessions were analyzed for elemental content by WDXRF spectrometry. Duplicate analyses were made by reanalyzing at a later date 13% of the filters from the first three sessions and 5% of the samples in the remaining sessions. Repeatability was excellent, greater than 90% for the six most abundant elements. Chlorine analyses were consistently lower in the second determination, apparently because of loss by volatilization, either direct or as the result of chemical reaction.

The average fine particulate mass value for all sites and all collection dates was 15.5 $\mu g/m^3$. The XRF analysis gave an average sulfur concentration of 1.9 $\mu g/m^3$, or a mean sulfur content of 12.1% for all 10,927 samples. If the gravimetric factors for SO_4^{2-} (3.00), NH_4HSO_4 (3.59), or $(NH_4)_2SO_4$ (4.13) are applied, the following equivalent percentages would be obtained: 36% SO_4^{2-}, 43% NH_4HSO_4, or 47% $(NH_4)_2SO_4$.

The seasonal averages for all sites of the fine particulate mass and sulfur concentrations are summarized in Tables 2 and 3 for each of the seven quarters in which sampling was made. The concentrations of fine particulate mass and particulate sulfur were highest during the two summers and lowest during the winter and fall seasons.

The increase of fine particulate sulfur concentrations in the summer is consistent with results of previous studies and has been attributed to increased use of electrical power for air conditioning demands and to more intense solar radiation, which converts SO_2 to sulfate aerosols. The increase in the percentage of sulfur is demonstrated in Table 4, where the percent of sulfur in the total fine particulate is summarized for the seasons at the co-located sites 306 and 406 and for the average concentrations from all 44 sites.

Conclusions and Recommendations

A data base of fine particulate mass and 11 chemical element concentrations has been produced by daily sampling of ambient air aerosol at 44 sites selected from the Acid MODES network at intermittent periods from July 1988 to May 1990. The data base was generated from 10,952 samples that were collected during 65 weeks and seven different quarters (seasons). Analysis for elemental composition was accomplished by wavelength disper-

Table 2. Fine Particulate Mass Seasonal Averages for All Sites

SEASON	NO. OF SAMPLES	MEAN ($\mu g/m^3$)	STD. DEV. ($\mu g/m^3$)
Summer 1988	401	20.04	11.47
Fall 1988	661	12.46	5.51
Winter 1989	985	14.89	7.05
Summer 1989	2127	24.87	15.52
Fall 1989	1803	16.57	9.59
Winter 1990	1920	13.79	6.69
Spring 1990	1478	14.95	7.14

Table 3. Sulfur Seasonal Averages for All Sites

SEASON	NO. OF SAMPLES	MEAN ($\mu g/m^3$)	STD. DEV. ($\mu g/m^3$)
Summer 1988	461	2.16	1.60
Fall 1988	929	1.15	0.70
Winter 1989	1149	1.30	0.74
Summer 1989	2311	3.12	2.75
Fall 1989	2180	1.52	1.32
Winter 1990	2175	1.37	0.77
Spring 1990	1646	2.03	1.25

Table 4. Seasonal Variation of Sulfur Concentration Averages at the Pennsylvania Co-located Sites ($\mu g/m^3$)

SEASON	SITE 306		SITE 406	
	Mean	Std. Dev.	Mean	Std. Dev.
Summer 1988	2.29	1.05	2.20	1.32
Fall 1988	1.20	0.64	1.31	0.67
Winter 1989	1.50	0.54	1.48	0.62
Summer 1989	3.21	2.55	3.15	2.44
Fall 1989	1.79	1.31	1.82	1.40
Winter 1990	1.53	0.75	1.61	0.81
Spring 1990	2.08	1.42	2.12	1.49

sive x-ray fluorescence spectrometry (WDXRF) on the total of 12,589 filters (including field blanks) for the following 11 elements, which were the most consistently present: Mg, Al, Si, P, S, Cl, K, Ca, Fe, Zn, and Cd. The continuity and completeness of the FPN study was affected by budget and operational problems in the parent Acid MODES network, which caused interruptions in the sampling schedule, the closing of some of the original sites, and the moving of sites later in the program.

The original form of the data base that was generated by the collection, gravimetric, and analytical procedures consisted of 384 files with about 17.5 MB of computer data. This large data base includes for each of the 12,589 samples the weight, volume sampled, filter collection area, quality control codes, and other collection data. Each sample also contains the analytical data for each of the 11 elements, including concentrations, detection limits, and random error estimates.

A special software package was developed by ManTech Environmental to compress the large original data base to a more transportable size and to develop an interface for the user to conveniently retrieve selected information. Programs were written in Pascal language to produce a file that could be read directly into a personal computer for further data analysis.

The FPN data base produced by this field study is a valuable contribution to the understanding of the climatology of nonurban fine particulate aerosols and their contribution to urban particulate loadings. Cursory examination of the data indicate high variability of the daily concentration. Future efforts should assess the relationship between meteorological conditions and site concentrations to better understand the variations. A recommended approach is to classify samples by meteorological data. This might be done by attempting to correlate concentration levels with meteorological parameters such as surface wind direction, synoptic weather classifications (warm, cold, occluded, or stationary fronts) and by back-trajectory calculations. Initially, the concentration observations that are within distinct common wind directions may be compared. However, incoming air from the same direction can arrive through different trajectories. Attempts should be made to correlate observations with trajectory-defined sources to promote an understanding of how the observed variations are related to fluctuation in meteorology.

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The complete report, entitled "A Regional Fine Particle Field Study: Data Base and Initial Results," (Order No. PB92-106939/AS; Cost: $19.00, subject to change) will be available only from:
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