DRAFT

Recommendations for Great Lakes Air Toxics Monitoring

William Barnard
Robert Harless
Robert Lewis
Dale Pahl
Robert Stevens
Tom Dzubay
Alan Hoffman
Yaacov Mamane
Jack Shreffler
Joseph Walling

Atmospheric Research & Exposure Assessment Laboratory
Research Triangle Park, N.C. 27711

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Field Monitoring Team

Milt Bowen, AREAL
Bobby Edmonds, AREAL
Alan Hoffman, AREAL
Mack Wilkins, AREAL
Ev Quesnell, AREAL
Bob Stevens, AREAL
Alf Wall, AREAL

Quality Assurance Team

Bill Barnard, AREAL
Bernie Bennett, AREAL
Bill Mitchell, AREAL
Rocky Rhodes, AREAL

Data Analysis, Interpretation, and Report Preparation Team

Bill Barnard, AREAL
Aubrey DuPuy, ECL/OPTS
Tom Dzubay, AREAL
Steve Eisenreich, U. Minn.
Marie Collins, AREAL
Don Gatts, ISWS
Bob Harless, AREAL
Alan Hoffman, AREAL
Ed Klappenbach, GLNPO
Bob Lewis, AREAL
Chuck Lewis, AREAL
Yaacov Mamane, AREAL
Danny McDaniel, ECL/OPTS
Dale Pahl, AREAL
Joachim Pleil, AREAL
Shari Pricer, AREAL
Rocky Rhodes, AREAL
Jack Shreffler, AREAL
Bob Stevens, AREAL
Clyde Sweet, ISWS
Joe Walling, AREAL

Research Management Team

Gary Foley, AREAL
Tom Hartlage, AREAL
Ed Klappenbach, GLNPO
Dale Pahl, AREAL
Jack Shreffler, AREAL
Wayne Wilford, GLNPO

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1.0 EXECUTIVE SUMMARY

During 1988-1989, the EPA's Great Lakes National Program Office (GLNPO) established a pilot atmospheric monitoring network at the University of Wisconsin, Green Bay Campus (UWGB). The objectives of this network are to collect and measure atmospheric loadings of nutrient and toxic compounds to the Great Lakes watershed and to identify the sources of these compounds.

Eventually, this pilot monitoring program will be expanded by GLNPO and its Canadian counterpart to temporally and spatially characterize nutrient and toxic loadings over the entire Great Lakes watershed. However, because the sampling and analytic techniques appropriate to this objective require testing and evaluation, the UWGB site is being operated during 1989 and 1990 as a pilot-scale air monitoring network.

In June 1989, the GLNPO asked EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) to evaluate the pilot network. To gather information for this evaluation, AREAL conducted a short-term field study at the UWGB site. Additionally, AREAL conducted performance and systems audits to evaluate the components of the GLNPO monitoring/instrument systems and the field and laboratory quality control practices. The information developed by these studies is presented in this report to:

- provide a short-term ambient air characterization at the UWGB site to help determine the appropriateness of the current pilot network data collection and source apportionment objectives;
- evaluate the pilot network quality assurance project and program plans as well as the quality assurance and quality control (QA/QC) practices used in the field and by the GLNPO analytic laboratories; and
- recommend changes in the pilot network design and operation to facilitate the achievement of GLNPO measurement and source apportionment objectives.

The following sections of this chapter summarize AREAL's findings in each of these three areas.

1.1 Short-Term Atmospheric Characterization at the UWGB Monitoring Site

During September 1989, AREAL conducted a field monitoring study located at the UWGB site and coordinated with the GLNPO instruments and sampling schedule. The AREAL and GLNPO data collection objectives and monitoring instruments are summarized in Tables 4-1 and 3-1 respectively; the sampling schedule is presented in Figure 4-2.

Analysis of the AREAL measurements indicates that, during this short-term study, ambient atmospheric concentrations of particulate matter, acid aerosol species, precipitation metals, PCBs, PCDDs, PCDFs, aldrin, dieldrin, and volatile organic compounds were either at background levels (typical of rural/suburban concentrations measured by AREAL in other parts of the country) or, in the case of aldrin and dieldrin concentrations, were below the limits of instrument quantitation. A detailed discussion of these analytical results is presented in Chapter 6 of this report.

Chemical mass balance and multiple linear regression models were used to apportion the chemical species data acquired during the field monitoring study to potential sources of the species. Identified sources included combustion and incineration stack gases, pulp and paper mill emissions, motor vehicle emissions, and metal processing industry emissions. Additional sources of the chemical species include crustal material, burning of conifers (eg, slash burning), and plywood veneer drying. More than half of the fine particle mass collected is of a regional, rather than local, origin and is composed of sulfate and related anions typical of fine particles in the eastern half of the United States. Source apportionment of volatile organic compounds collected by AREAL was precluded because of QA/QC problems identified with the sampling protocol used at the UWGB site. Additional source apportionment analysis and discussion is presented in Chapter 6 of this report.

1.2 Quality Assurance and Quality Control Review of GLNPO Monitoring Site

The quality assurance and quality control (QA/QC) review consisted of a systems audit, the coordinated field monitoring study described in Section 1.1

above, and a performance audit. The results of this review are discussed in detail in Chapter 5 of this report.

The AREAL systems audit included an evaluation of the design of the UWGB site and the pilot network as expressed in the quality assurance program and project plans as well as the components of the monitoring, measurement, and analysis systems in the field and laboratory. The audit determined that fundamental "systems design documents," the quality assurance project and program plans, had not been prepared for either the UWGB site or the pilot network. An on-site audit of the Bionetics Laboratory (one of the two analyzing UWGB samples) indicated that the laboratory was adhering to all the established QA/QC requirements. A systems audit of the other laboratory, the Illinois State Water Survey (ISWS) Laboratory, was not conducted as a part of the AREAL systems audit for GLNPO. However, the ISWS is routinely audited as a part of AREAL's acid precipitation monitoring programs. Recent audits of the ISWS Laboratory (spring and fall of 1989) indicate that this laboratory also does an excellent job of adhering to QA/QC requirements. An evaluation of sample and data handling procedures identified the need for identifying and tracking collected samples from the initial monitoring instrument through laboratory analysis to final data base. This objective could be achieved with the use of a bar-coding and computer tracking system. Finally, an on-site audit of the UWGB site utilizing criteria developed for the State and Local Air Monitoring Sites (SLAMS) indicated that both the site and individual monitoring instruments are appropriately located, with one exception. The proximity of the dirt road at the UWGB site may contribute some amount of coarse particulate matter to particulate samplers during high wind velocity or heavy traffic episodes.

Send copy to Bruce Bennett

Good Recommendation

On September 8, 1989, AREAL conducted a performance audit at the UWGB site. The audit consisted of flow measurements. With the exception of the coarse flow from one dichotomous sampler, all flows were in excellent agreement with AREAL's standards. Other performance audits included duplicate audit canisters for volatile organic compounds and spiked PUF cartridges. Results from the VOC audit canisters identified a high positive bias for 5 of the 17 compounds, and indicate that interpretation of the VOC data during the AREAL field monitoring study would be questionable.

1.3 Recommended Changes in the GLNPO Pilot Monitoring Design and Operation

After completing the field monitoring study, source apportionment analyses, and QA/QC reviews summarized above, AREAL assembled a team of environmental professionals in atmospheric monitoring, deposition, and chemistry to evaluate the findings of these reviews and to recommend changes in the network design or operation. The team confined its recommendations to those that would improve the achievement of GLNPO measurement and source apportionment objectives and the scientific credibility of the results of attendant analyses. The GLNPO objectives were determined through personal contacts with GLNPO managers as well as through analysis of the Great Lakes Water Quality Agreement (As Amended in 1987), the Five Year Program Strategy for the Great Lakes National Program Office, and the Mass Balancing of Toxic Chemicals in the Great Lakes: The Role of Atmospheric Deposition. AREAL's recommendations are summarized in five key areas:

Send Bruce Bonnett QAPP(s) Tony Has funding for QAPP Draft.

Recommendation 1. There is a fundamental need for GLNPO quality assurance project and program plans (QAPP's) for the pilot and full-scale (Great Lakes Basin-Wide) air monitoring network. These plans must identify data collection, measurement, and analysis objectives and relate them to the major goals of the GLNPO studies of the Great Lakes. Without a QAPP, it will not be possible to make an adequate assessment of the design, implementation, or ultimate success of the GLNPO atmospheric monitoring, deposition, and mass balance programs.

Recommendation 2. The premise underlying the selection of the UWGB site for the pilot monitoring program is that it would provide a representative location for the testing and evaluation of sampling and analytic techniques. However, the measurement data collected during the AREAL field study contradict this premise. Although these data are not representative of long-term conditions, measured levels of PCBs, PCDDs, PCDFs, VOCs, aldrin, and dieldrin were near or below instrument or analytical quantitation levels. This suggests that data collection objectives or monitoring site selection criteria should be evaluated before proceeding with network development. For example, the absence of detectable concentrations of aldrin and dieldrin is consistent with both current and recent agricultural practices in the United States. Perhaps these

compounds should be eliminated from the network data collection objectives and replaced with pesticides and herbicides currently used in the U. S. and Canada.

Recommendation 3. AREAL's evaluation of the GLNPO monitoring instruments indicates that their selection has precluded source apportionment analysis. However, source apportionment should be fundamental to the design of the monitoring network and to the interpretation of monitoring data and deposition estimates. The instruments and analysis that AREAL used in its evaluation demonstrate that source apportionment is practicable for aerosol and nutrient compounds and for PCB's, ~~PCDD's, and PCDF's~~. Although the VOC canister data AREAL collected at the UWGB site were considered unacceptable for source apportionment because of potential QA/QC problems, AREAL's experience with VOC source apportionment in other studies demonstrates that VOC source apportionment techniques are viable across the range of urban, urban, and wetland environments found in the Great Lakes and surround areas.

Not our Goal

Recommendation 4. Based on AREAL's perception of the monitoring and source apportionment objectives of the GLNPO monitoring network, AREAL recommends several changes in the selection and operation of monitoring instruments to be included in the network. These changes include:

- replace currently used TSP high volume samplers with PM_{10} dichotomous samplers and TSP high volume virtual impactor samplers. This change is essential if source apportionment objectives are to be achieved. Moreover, the change will improve measurement precision by eliminating the windspeed/direction problems encountered with TSP high volume samplers;
- ? add monitoring equipment for the sampling of VOC's such as the canister sampling instruments used by AREAL. Data on VOC's are essential if source apportionment objectives are to be achieved;
- determine wind-sector average samples based on the direction of air parcel trajectory rather than surface wind (except in cases where there are specific local sources that need to be considered). These samples can be composited for organic carbon analysis by season and by direction of air parcel trajectory: XAD traps, canisters, and

high volume filters;

- o schedule at least two "intensive" studies during the next year of operation of the pilot monitoring network and during the first year of operation of the large-scale U.S.-Canadian network. These intensive studies should be of 2- to 3-week duration with consecutive 12-hour sampling periods to permit analysis of temporal variability and to permit the development of detailed receptor modeling relationships; and
- o schedule instrument sampling during routine (ie., non-intensive) network operation for 24-hour periods every other day.

* OK

Will this give anything above 24?

Agree, use for GLAD Now

<u>Recommendation 5.</u> AREAL's experience with large monitoring networks suggests the need for an automated system to identify and track samples through the instrument, analysis, and data analysis phases of the network. Such a system could be similar to the bar-code and computer tracking systems used for large monitoring networks. Although this system is not essential for the small-scale UWGB site, it should be implemented on a pilot-scale before being deployed in the full-scale network.

2.0 INTRODUCTION

The Great Lakes National Program Office (GLNPO) was created in 1978 to manage the implementation of the United States' obligations under the Great Lakes Water Quality Agreement of 1978. That Agreement between the United States and Canada calls for a comprehensive ecosystem approach to the management of Great Lakes water quality.

To provide information essential for proper water quality management, GLNPO funds and directs extensive surveillance and monitoring activities in the Great Lakes and surrounding watersheds. The surveillance activities include routine sampling of water, fish tissue, and sediment. Air monitoring networks are operated in the Great Lakes Basin by GLNPO and other federal and state agencies to measure the quantity of pollutants entering the Basin from airborne sources.

Over the past ten years, this monitoring activity has indicated that atmospheric transport and deposition may be an important, and in some cases the dominant, pathway by which nutrient and toxic substances reach the Great Lakes. Although there are many potential industrial, agricultural, and urban air pollution sources, an understanding of the transport, transformation, and deposition mechanisms for these substances must be developed before remediation strategies can be devised and implemented.

None of these substances is yet present in the lakes in concentrations known to be acutely toxic to organisms or disruptive to ecosystems in which these organisms exist. Rather, concern focuses on the possible long term effects of small quantities of numerous substances transported through the atmosphere and deposited in the Great Lakes Basin. This concern resulted in the 1987 amendment to the Great Lakes Water Quality Agreement that reflects the increasing awareness of the importance of the atmospheric pathway and expands the environmental objectives of the Agreement to include atmospheric monitoring for toxic air pollutants.

Responding to this amendment, GLNPO and its Canadian counterpart have embarked upon the development and deployment of a Basin-wide monitoring network for the measurement of atmospheric loadings of nutrient and toxic air pollutants and for the identification and apportionment of their sources. Because sampling and analytic techniques appropriate to this task require testing and evaluation, this network is being tested during FY89-90 in a pilot-scale configuration at a single site at the UWGB.

To assist in the evaluation of the pilot-scale site, GLNPO requested assistance from the Atmospheric Research and Exposure Assessment Laboratory (AREAL). AREAL participation in the pilot-scale network has included an on-site collocated monitoring study, a review of the GLNPO quality assurance project plan and data quality and collection objectives, and a QA/QC review of the GLNPO laboratory program which supports the analysis of samples from the UWGB site. These activities have been conducted to achieve two objectives:

- A determination of whether the network sampling and instrumentation design

is appropriate for GLNPO measurement and source apportionment objectives; and

- A determination of whether the network design and quality assurance project plan can achieve GLNPO air and water quality management objectives: (1) to provide data needed to develop and apply a mass balance model for toxic and other pollutants in Green Bay and, eventually, in the larger Great Lakes Basin, and (2) to provide information essential in developing remediation strategies needed to reduce emissions of pollutants which are significantly contributing to the deterioration of water quality in the Great Lakes Basin area.

The results of the AREAL evaluation of the GLNPO pilot-scale network are presented in following four sections of this report. Section three presents the GLNPO network design and quality assurance objectives. Section four discusses the AREAL collocated monitoring study conducted at the UWGB site during September 1989. Section five discusses the results of the quality assurance reviews of the GLNPO quality assurance project plan and laboratory analyses. Section six presents, compares, and analyzes the results of the AREAL/GLNPO monitoring study. Finally, the appendices provide details about the sampling, analysis, and operating procedures for the instruments AREAL employed in the September 1989 monitoring study.

3.0 GLNPO MONITORING PROGRAM

The Green Bay site is located on the UWBG campus about 1 km southeast of the shore of Green Bay. Its coordinates are latitude: 44°31'59", longitude 87°54'44". The samplers are located in an open grassy field on a 30 x 10 m plot surrounded by an 8-foot high cyclone fence. The area is open to the north, south and west with trees and a low ridge about 150 m to the east. There are paved roads with light traffic about 150 m to the east and 100 m to the west of the site. The site is served by a dirt driveway used by service vehicles only. The only obstruction at the site is a small utility shed (3x4x3 meters) in the northeast corner. The site has 110 V electrical service and platforms for sampling equipment.

3.1 GLNPO Objectives

The GLNPO established the Green Bay sampling site to assist in providing data needed to apply a mass balance model for toxic pollutants in Green Bay. The mass balance approach requires the determination of system inputs, internal transformations and storage and outputs. If all of the important terms can be measured or estimated accurately, and if inputs, less storage and transformations, equal outputs, then the system can be assumed to be adequately understood so that contaminant concentrations can be accurately modeled. Analysis of air and precipitation samples as well as meteorological measurements are required to determine source/receptor relationships. In considering these relationships, compounds that must be evaluated include pesticides, PCBs, PAHs, dioxins/furans, and metals such as Pb, Zn, and Cd.

These were not done for Green Bay

3.2 Samplers

Table 3-1 displays a summary of the types and quantities of samplers deployed at the UW-GB monitoring site to meet the GLNPO objectives. The following is intended to provide additional descriptive details.

Equipment at the site includes both precipitation samplers and three types of high-volume air samplers. The precipitation samplers are MIC Model B samplers (MIC Inc., Thronhill, Ont.) modified for all-weather operation. The modifications include an insulated enclosure underneath the sampler heated by a small space

TABLE 3-1. GLNPO SAMPLERS DEPLOYED AT THE GREEN BAY MONITORING SITE

SAMPLER	NUMBER	SAMPLING FREQUENCY	SAMPLE DURATION	SAMPLING MEDIA	ANALYSIS	SAMPLE HANDLING
MIC (precipitation)	3	1/14	14 days	XAD-II	PCB's, dieldrin	
Wet/~~Dry~~ Precip Aerochem ~~Metrics~~ (GLADSITE)	2	1/? weekly if 500ml has been collected	cont.	--	Metals, nutrients	
TSP Hi vol	1	1/6	24 hrs	8x10 ~~Quartz~~ Glass	Mass, TOC, CE	
Modified Hi vol directional	3	1/14	14 days	8x10 ~~Quartz~~ Glass XAD-II	PCB's; dieldrin	
Cascade Impactor	1	1/3 mos.	7 days	Impactors	Particle sizing	
Wind speed/dir	1	cont.	cont.	--	--	
T,R.H., SR	1	cont.	cont.	--	--	
Rain Gauge	~~1~~ 2	cont.	cont.	--	--	1 Nifer Shield 1 ~~std~~ Belfort

heater. Temperature is maintained at about 10-15°C, which provides enough heat to melt snow falling into the catch basin. Rain or melted snow passes through a 15-cm column of XAD-2 resin by gravity flow.

The air samplers used are standard high-volume samplers with automatic flow controllers (Model GS2310 Accu-Vol, General Metal Works, Village of Cleves, OH). An unmodified version of this sampler is used to collect total suspended particles and total organic and elemental carbon in airborne particles. To sample for the target chemicals, a modified version is used. The modifications consist of adapters and an aluminum tube between the filter holder and the motor designed to hold an 8.7 x 4.4 cm stainless steel resin cartridge capable of holding 40-50 g of XAD-2 resin. The motor is also replaced with a 2-stage Lamb motor (Model 115937, Amtek-Lamb, Kent, OH). The modified air samplers are also fitted with automatic filter covers (G8550, Sample Saver, General Metal Works) to prevent passive loading. Finally, another modified high-volume sampler is fitted with a 4-stage cascade impactor (Model 234, Anderson Samplers, Inc., Atlanta, GA) for determination of particle size distribution.

In addition to the air and precipitation samplers, the site also has the following meteorological monitoring equipment mounted on a 10 m tower: a solar radiation sensor (LI 200S pyramometer, LI-Cor, Lincoln, NE), temperature and humidity sensors (Campbell Scientific, Logan, UT), wind speed and direction sensors (Met-One, Grants Pass, OR), a standard Belfort rain gauge (Belfort Instrument Co., Baltimore, MD), and a Belfort rain gauge fitted with a Nifer wind shield. All meteorological sensors are automatically recorded every six seconds by a Campbell 21X data logger (Campbell Scientific, Logan, UT) that also calculates and records hourly averages.

3.3 Schedule and Operation

Sampling Schedule

The site is operated on a biweekly sampling schedule. All resin columns, air cartridges and air filters are changed every other Tuesday. At the same time, the meteorological data tape is changed. The buckets on the Belfort rain

gauges are emptied weekly, if needed. The TSP/TC sampler takes a 24-hour sample on the six-day U.S. EPA schedule and the cascade impactor sample collects a seven-day sample on an occasional basis (approximately quarterly).

The three MIC samplers at the site are used to take biweekly duplicate and field blank samples. The three modified high-volume samplers are operated on a wind-directed basis by the Campbell data logger. In other words, each sampler operates only when the wind direction is from a predetermined sector. For instance, at Green Bay one sampler is programmed to sample air coming off the bay while another samples air coming from the industrial areas of the city of Green Bay. Finally, single cascade impactor and standard high-volume samplers are also located at the site.

3.4 Calibration/QC Procedures

The calibration procedures and frequencies of checks vary with the type of sampler being used. For the MIC sampler the amount of precipitation collected in the bottle at the bottom of the sampler after the precipitation has passed through the XAD-2 resin cartridge is compared to the amount of rain collected by the Belfort rain gauge. This comparison is done on a biweekly interval; however, the Belfort rain gauge chart is changed on a weekly interval.

The air sampling equipment is operated and calibrated according to the manufacturer's recommendations. Flow rates of the high-volume samplers are calibrated monthly using a standard General Metal Works manometer. The samplers with resin cartridge vapor traps are set 566 ℓ/min (20 ft^3/min) and the TSP/TC high-vol is set at 1133 ℓ/min (40 ft^3/min). A small reference manometer is used as a qualitative check to verify normal operation between calibrations. The meteorological monitoring equipment was calibrated during the initial set-up, and it is rechecked quarterly. Where standard methods have been established, such as for TSP and TOC measurements, the standard procedures of the American Society for Testing and Materials (ASTM) are followed.

3.5 Collection Media

Airborne particles are collected on high purity glass fiber filters (Whatman EPM 2000, Whatman Ltd., Maidstone, UK). Airborne vapors and precipitation samples are passed over specially purified XAD-2 resin. The resin obtained from the manufacture (Rohm and Haas, Philadelphia, PA.) is extensively washed with deionized water to remove fines and impurities. The cleaned resin is then Soxlet extracted for 24 hours with each of four solvents, methanol, acetone, hexane, and methylene chloride. Another set of four-hour extractions with hexane, acetone, methanol, and a final exchange with deionized water is carried out prior to storage. For precipitation sampling about 15 g of this material is packed in a 30 cm glass column. For air sampling, the water is drained off and about 40 g of resin is packed into the high-vol cartridges. Packed columns are sealed with teflon caps, and cartridges are wrapped in aluminum foil and sealed in air tight metal cans. Shipment is by surface mail (2-5 days).

3.6 Field Blanks

Quantification standards are prepared and compared with EPA standards and with standards from other laboratories. Blanks are run on all equipment, reagents, and other materials to be used for the samplers and in the laboratory procedures. Blanks and standards are run through the entire procedure, and the system is shown to be in analytical control before samples are collected and processed. Laboratory and field blanks are run at regular intervals for quality assurance. Results from analysis of samples from the duplicate rain collectors serve as a measure of overall reproducibility of the sampling and analysis procedures.

As a check on the identification and quantification of different peaks in the GC spectra, samples are run periodically on another GC-MS at a different laboratory. Also, known amounts of standards are added to about 20% of the samples which have been quantified. These samples are then re-run and the peak identifications and quantifications checked. About 50% of the laboratory efforts are devoted to quality assurance of the project.

Field blanks are taken in conjunction with the third MIC sampler. XAD-2 resin columns are forwarded to the Green Bay site to determine if any contamination can be detected from a resin column which is placed on a sampler for a period of fourteen days but the sampler is inoperative because the electrical power has been purposely disconnected. Another resin column is sent to Green Bay and then mailed back to the analytical laboratory without exposing the column to the ambient air. The object of these field blank comparisons is to determine whether a difference in PCBs can be detected between the sample which remains in the field for fourteen days and the sample which is returned to the laboratory upon its receipt at the Green Bay site.

3.7 Sample Analysis

Samples collected at the master site are shipped to a laboratory for analysis. EPA Method 608 serves as the procedural basis for organic sample analysis, but modifications are made to the project to accommodate its more demanding requirements.

Analysis of the high-volume filters for TSP and TOC follows standard EPA methodology. The filters are weighed before and after their 24-hour exposure in a temperature controlled room. The mass of matter on the filter is determined from these weights and the monthly manometer calibrations.

4.0 AREAL MONITORING PROGRAM

4.1 Objectives

The primary purposes of the AREAL monitoring program was to obtain ambient air samples similar to those obtained by GLNPO at the UWGB site so that a comparison could be made between analytical data obtained by AREAL and GLNPO. A secondary purpose was to provide additional air characterization data on air toxic compounds, particulate matter, and trace metals to use in receptor models and to guide future sampling and network design.

4.1.1 Data Quality Objectives

The data quality objective for this comparison study was to obtain data with measurement precision and accuracy within ± 10% or better. This is usually as good as the analytical method could provide. For particle monitoring (TSP,PM-10) data quality objectives for comparing similar samplers are reasonably attainable at ± 10%. When analyses for elemental composition, dioxins, furans, and PCB's at low concentration levels are included, an additional ± 15% error would need to be added due to uncertainty associated with the analytical method. Therefore, the DQO will depend on the pollutant being compared and the variability expected from the analytical technique used for that pollutant.

4.1.2 Data Quality Indicators

There are five indicators of data quality. These are completeness, comparability, representativeness, accuracy, and precision. Several of these indicators are not relevant to this study (i.e., comparability and representativeness) on a macroscale. This is because the purpose of the study is to compare data at one site during a short-term sampling program. However, general siting protocols, such as distances between samplers and height above ground, were followed to assure representativeness on a microscale level.

Completeness can be measured in terms of samples taken vs. the number scheduled to be taken. Precision and accuracy were to be addressed through quality control checks and independent quality assurance audits which were conducted at the site by an EPA contractor. Overall precision of methods is evaluated by collocation of the identical samplers. For this study, two dichotomous samplers were operated to determine the precision of PM_{10} concentrations, and several duplicate VOC samples were collected during the study period.

4.2 Samplers

The AREAL samplers deployed at the Green Bay site are shown in Table 4-1 along with the sampling frequency, sampling media and analyses. A diagram of the

TABLE 4-1. AREAL SAMPLERS DEPLOYED AT GREEN BAY MONITORING SITE

SAMPLER	NUMBER	SAMPLING FREQUENCY	SAMPLE DURATION	SAMPLING MEDIA	ANALYSIS	SAMPLE HANDLING
PM_{10} Dichotomous	2	1/2	24 hrs.	37 mm Teflon	Mass Elemental Composition XRF	Weigh and handcarry to RTP
PM_{10} Dichot-directional	1	1/7	7 days	37 mm Teflon	Mass Elemental Composition,XRF, SEM Microscopy	Weigh and handcarry to RTP
TSP HVVI	1	1/2	24 hrs.	2x6 Quartz 8x10 Quartz	Mass, Ce/CV, IC	Weigh and handcarry to RTP
TSP Hi vol	1	1/6	24 hrs.	8x10 Quartz	Mass, Elemental	Weigh and handcarry to RTP
PS-1	2	1/6	24 hrs.	Quartz, PUF	PCB's; Aldrin/ dieldrin; Dioxin/ Furans	Airborne to Contractors
PS-1 Directional	1	1/7	7 days	Quartz, PUF	PCB's; Aldrin/ dieldrin	Airborne to Contractors
VOC	1	1/3	24 hrs.	6 l. Canister	GC/MS	Airborne to RTP weekly
Annular Denuder	1	4 Samples	24 hrs.	47 mm Quartz 47 mm Teflon	Gases and Aerosols	Handcarry to RTP
Wind Speed Wind Direction	1	cont.	cont.	--	--	--

sampler placement at the site is shown in Figure 4-1. All samplers were placed on a plywood platform and secured with screws. The height above ground averaged about three meters. (The terrain sloped slightly.) A total of eleven samplers was deployed. Additionally, a meteorological system was erected to provide wind-directional controlled operation to two of the samplers.

The two directional samplers -- PM-10 dichotomous and a PS-1(PUF plug sampler) -- were operated so that comparisons of pesticides/PCB's and dioxin/furans could be made with GLNPO's sampling/analysis system. The TSP hi-vol was also set up to directly compare with GLNPO's hi-vol sampler. The other samplers enabled AREAL to provide air characterizations not currently performed by GLNPO such as elemental composition, PM-10 size fractions, acid aerosols, carbon analysis, and PAH's.

4.3 Sampling Schedule and Operation

4.3.1 Schedule

In general, 24-hour samples were collected except for the wind direction controlled dichotomous and PS-1 samplers which were operated for seven days but when the wind was from the southwest (180 to 270 degrees). See Table 4-1. Samples were started at 0730 ± 30 minutes and run for 24 hours. A copy of the actual sampling schedule used is shown in Figure 4-2 .

4.3.2 Sampling Procedures

Filter samples were prepared, uniquely labeled at the lab and placed in cassettes for transport to the field. The PS-1 samples (PUF and quartz filter) were labeled and transported to the site in containers as provided by the contractor. A site observation log sheet was filled out for each sampling day and then entered into the field computer data system (See Figure 4-3).

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FIGURE 4-2
AREAL SAMPLING SCHEDULE

SUN	MON	TUES	WED	THURS	FRI	SAT
DRIVE TO GREEN BAY			SITE SET UP FLOW CKS & CAL.		1 1 TSP 2 DCT 1 HVVI 1 CAN 2 PS1	2 FLOW CHECKS
3 2 DCT 1 HVVI	4 1 CAN	5 2 DCT 1 HVVI 1 DCT-D 1 PS1-D	6 FLOW CHECKS	7 1 TSP 2 DCT 1 HVVI 1 CAN 2 PS1	8 AUDIT	9 2 DCT 1 HVVI
10 1 CAN I CAN COL FLOW CHECKS	11 2 DCT 1 HVVI	12 1 DCT-D 1 PS1-D	13 1 TSP 2 DCT 1 HVVI 1 CAN 2 PS1	14 2 DCT 1 HVVI (XTRA RUN)	15 2 DCT 1 HVVI	16 1 CAN FLOW CHECKS
17 2 DCT 1 HVVI	18 FLOW CHECKS	19 1 TSP 2 DCT 1 HVVI 1 CAN 2 PS1 1 DCT-D 1 PS1-D	20 2 DCT 1 HVVI (XTRA RUN)	21 2 DCT 1 HVVI	22 1 CAN I CAN COL FLOW CHECKS	23 2 DCT 1 HVVI
24	25 1 TSP 2 DCT 1 HVVI 1 CAN 2 PS1	26 FLOW CHECKS	27 2 DCT 1 HVVI 1 CAN	28 SITE TEAR DOWN	29 DRIVE TO RTP	30

FIGURE 4-3
AREAL SITE OBSERVATION LOG SHEET

1 OPERATOR

2 DATE ARRIVAL TIME

3 SAMPLERS OPERATING OK? YES NO

4 GENERAL METEOROLOGY FOR SAMPLING

4a Sky cond. 1.clear 2 part cloudy 3.cloudy
4. foggy

4b Wind Dir. 1. N 2. NE 3. E 4. SE

5. S 6. SW 7. W 8. NW

4c Wind speed 1. 0-5 2. 5-20 3. >20

4d Precip. 1. none 2. drizzle 3. rain

4. flurries 5. snow 6. sleet

7. other

5 Unusual events:

6 Visual traffic count(veh/min)

a. Dichotomous Sampler/Hi-Vol Sampler

Operation was in accordance with the EPA-approved procedures described in Appendices A,B,& E. The instruments were calibrated at AREAL, RTP and transported to the field. Flow checks were performed at the beginning, at least once per week, and at the end of the study and had to be within 10 % of the set point value. The set points were determined based on the September average conditions for Green Bay using thirty-year average weather records published by NOAA. One blank filter was run for each sampling day for each sampling media type. Each teflon filter was transported to the field and stored in labeled petri dishes. The quartz filters were folded in half and stored in manila folders and placed in labeled envelopes for storage. Following sample collection, filter samples were transported back to the lab's environmental chamber, conditioned to the same temperature and relative humidity when tared (20 degrees C and 40 % relative humidity) for a minimum of 24 hours and then weighed. Before equilibrium each filter was weighed to determine a rough weight and this information was entered into the computer. The rough concentrations helped to determine if the samplers were operating properly. Field information was entered on Figure 4-4 and stored in the field computer daily.

b. VOC Canisters

One half of the canisters used for VOC sampling were cleaned at RTP and brought to the field with the rest of the sampling equipment used in the study. The other half were cleaned and shipped via air express about ten days after sampling began. This helped to minimize the amount of time between cleaning and use of the canisters. After sampling the canisters were shipped back to AREAL, RTP on a weekly basis. Appendix D contains more detailed sampling procedures that were followed during the study.

After completion of the VOC sampling, a routine QC check indicated that the sampling probe had been obstructed during the entire sample schedule. Consequently, the sampled air was pulled in through the manifold auxiliary vacuum pump instead of through the sampling probe (See Figure 4-5). It is not possible to say whether there was any significant impact on the ambient concentrations

FIGURE 4-4
AREAL FIELD DATA SHEET

GREAT LAKES STUDY—GREEN BAY, WISC.

OPERATOR _____
DATE _____
START TIME _____
STOP TIME _____

DICHOTOMOUS SAMPLERS

SAMPLER ID	COARSE NO.	FINE NO.	CRS ROT/MAN.		TOT. ROT/MAN		ELAPSED TIME (min)
			INIT.	FINAL	INIT.	FINAL	

PS-1 SAMPLERS

SAMPLER ID	FILTER NUMBER	PUFF CART. NUMBER	INDICATOR READINGS			ELAPSED TIME (min)
			START	END	AVG	

FIGURE 4–4 CONT.
AREAL FIELD DATA SHEET

GREAT LAKES STUDY—GREEN BAY, WISC.

OPERATOR_____
DATE_____
START TIME _____
STOP TIME _____

VOC SAMPLER

SAMPLER ID	SAMPLE NUMBER	VACUUM START	PRESSURE END(PSI)	SAMPLER FLOW(l/min) INITIAL	END	AVG	ELAPSED TIME

HI-VOL SAMPLER

SAMPLER ID	SAMPLE NUMBER	SET POINT	SAMPLER FLOW INITIAL	END	AVG	ELAPSED TIME

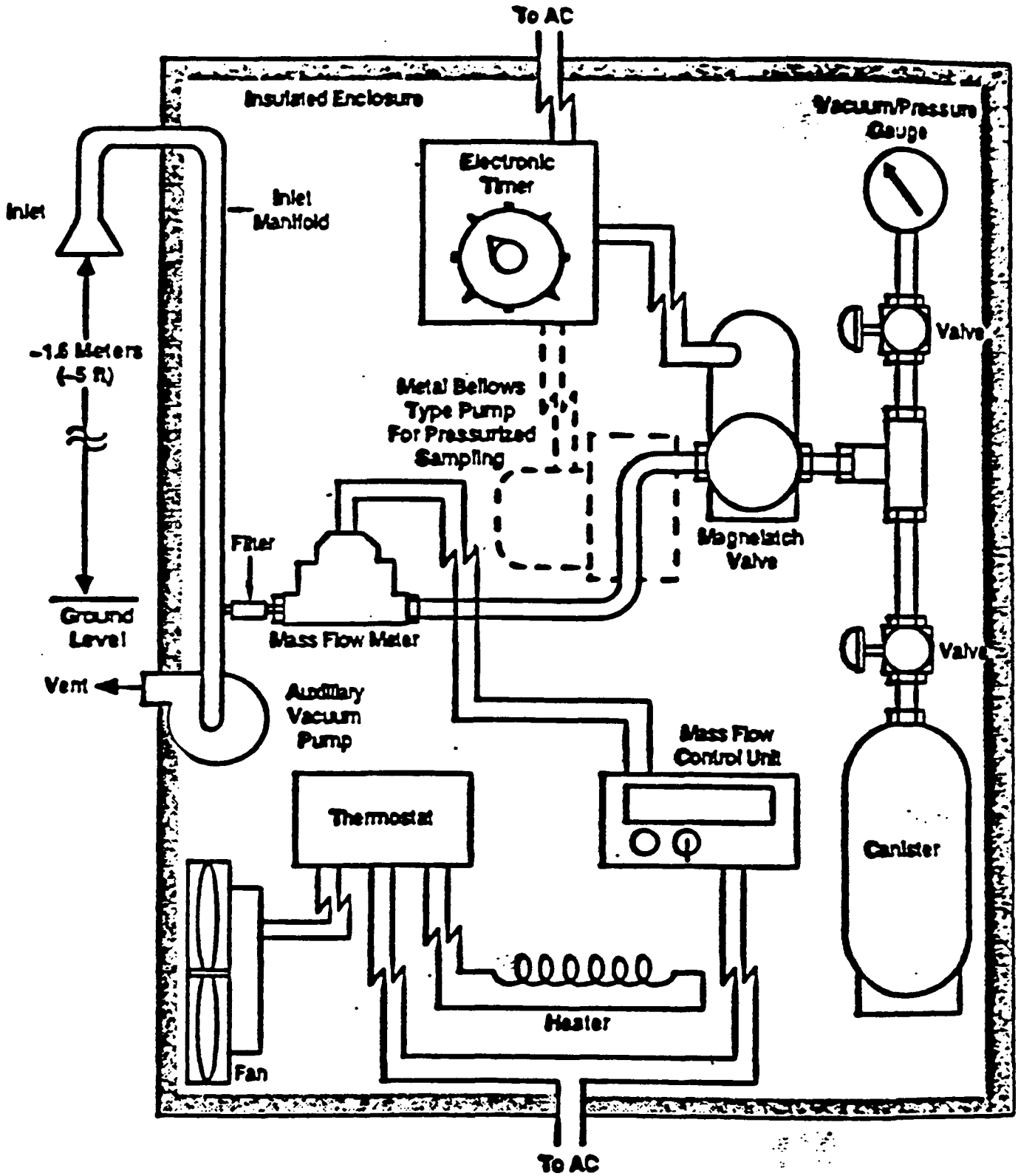


FIGURE SAMPLER CONFIGURATION FOR SUBATMOSPHERIC PRESSURE OR PRESSURIZED CANISTER SAMPLING

FIGURE 4-6
AREAL FIELD BLANK DATA SHEET--GREEN BAY

AMBIENT BLANKS

SAMPLE TYPE	SAMPLE NUMBER
DICHOT--37mm	
BMI(8x10)	
BMI(2x6)	
PS-1--QUARTZ	
PS-1--CART.	
TSP(8x10)	
OTHER	

INSTRUCTIONS: Bring to site; open container; leave open for two minutes; close container; leave at site; return to lab at end of sampling period.

as a result of this obstruction. It is possible that if the manifold fan assembly were clean, or if the 41 compounds of interest were not present in significant levels in the vacuum pump, the results would be totally unaffected by this event. The effect of this obstruction will be discussed more completely in Section 6.

c. PS-1 (PUF SAMPLER)

Operation was in accordance with EPA-approved methods described in Appendix C. The instruments were calibrated at the Green Bay site. One point flow checks were done at the beginning, at least once per week and at the end. The samples were handled as specified in Appendix C to minimize dermal contact. Samples were refrigerated on dry ice after sampling and shipped to the analysis lab in the same refrigerated condition. All field data were recorded on Figure 4-4 and entered into the field computer that day.

d. Annular Denuder

For selected periods annular denuder samples were collected to obtain data on the SO_2, HNO_3, ammonia, sulfate and nitrate concentrations. An annular denuder system (ADS) consists of a cyclone inlet to remove particles larger than 2.5 μm, annular denuders chemically coated with Na_2CO_3 to collect SO_2, HNO_3, and citric acid to collect NH_3; the denuders are followed by a filter pack to collect the fine particle sulfate and nitrate aerosol. The aqueous extracts of the denuders and filter pack are analyzed for NO_3^-, $SO_4^=$, NO_2^- concentrations. Subsequent data processing of annular denuder data provide the quantitative measurements expressed $\mu g/m^3$ for HNO_3, HNO_2, SO_2, $SO_4^=$, and NO_3^- present in each ADS sample.

e. Meteorological Sampling

The Climatronics Wind Direction Controller System was used to control power to a dichotomous sampler and a PS-1 sampler as a function of the wind direction. The system was used to turn on the samplers when the wind came from the range of 180 to 270 degrees. The wind direction was sensed by a wind vane coupled to

a precision low torque potentiometer. The wiper voltage of the potentiometer is a measure of the wind direction and is used to control a relay which in turn controls the samplers. A time delay of approximately 10 seconds was used to turn the relay on and off in order to prevent chattering of the relay contacts.

The wind speed and direction were recorded continuously by a Campbell Data Logger. Due to problems with the either the logger, or power interruptions, most of the meteorological data was lost. Data from the National Weather Service office located at the airport was obtained to use in the analysis of the results. The airport was located approximately 10 miles west southwest and should be representative of the conditions that were encountered at the UWGB campus site.

4.3.3 Q.C. Operations

The standard operating procedures shown in the Appendices were followed in operating the samplers with the exception of the special instructions contained in this document. All samplers were flow checked when they were set up and flows set for design operation i.e. 16.7 ℓ/min. for dichots, 8 CFM for the PS-1 samplers and 40 CFM for the HVVI and Hi-Vol using the September average conditions for Green Bay (14.9 C and 743.6 mm Hg.)

a. Dichotomous Samplers

The dichots were set at 16.7 ℓ/min total and 1.67 ℓ/min coarse flow using the calibrated rotameter settings. Once set these conditions were not changed unless there was more than a ten percent deviation. A flow check was performed once per week The samplers were operated in accordance with Appendix A.

b. High Volume Virtual Impactor (HVVI)

The HVVI was calibrated at RTP and the flows were set at 40 CFM total and 2 CFM coarse. Once set, the flows were not changed unless the rotameter readings varied more than 10 % from the original set points. A flow check was done at least once per week. The samplers were operated and checked using procedures in Appendix B.

c. PS-1(PUF SAMPLER)

The PS-1 samplers were calibrated on site in Green Bay. The samplers' flows were set and checked using the standard top hat orifice. The samplers were operated according to Appendix C which is a reprint of Method TO 13.

d. VOC/Canister samplers

The operation of this sampler is covered in Appendix D. Several co-located samples were collected randomly during the study to allow for estimates of precision.

e. TSP Hi-Vol

The TSP Hi-vol was operated using the EPA-procured quartz fiber filters to minimize extrinsic sulfate formation in accordance with the procedures shown in Appendix E. The sampler was calibrated at RTP and recalibrated in Green Bay and the flow set for September average conditions.

f. Additional Aerochem

In July-September, GLNPO had an additional Aerochem Metrics rainwater collector placed at the Green Bay site. The primary objective of this augmentation was to allow GLNPO test the effect of the addition of nitric acid to samples for the purpose of preserving metals. Data have shown that leaving samples unacidified results in large losses of the heavier metals to the walls of the sample bottles. Under the usual procedures, rainwater is collected in a ~~the~~ Aerochem bucket until a ½-liter sample is available. The sample is ~~put in a~~ sealed in the Metrics bag polyethylene ~~bottle~~ bag and shipped to the Illinois Water Survey where it is spiked with 1 ml of Ultrex 2 nitric acid solution. The spiking is intended to reduce the pH to less than 2. During the period of July-September 1989, eight spiked samples were split, with half going to the Central Regional Laboratory (CRL) and half going to AREAL, RTP. Both Laboratories conducted ICP analyses for metals, allowing an intercomparison

of analytic results. Unspiked samples from the second Aerochem were analyzed only by the CRL, and results are reported in this document.

4.3.4 Sample Handling and Shipment

This section covers procedures used for handling samples before and after sampling and their subsequent shipment to contractors and EPA for analysis. Generally, samples were prepared the afternoon before the sampling day. Filters were placed in cassettes, all field data sheets were filled out, labels were placed on each sample or sample container to indicate date of sample, time of day, and sampler number. Non-PVC gloves were worn during handling of any samples. Dry ice for storage/shipment of the PCB/pesticides and dioxin samples was obtained by no later than 1100 of the day the samples were removed i.e. the samples were exposed to ambient conditions for no more than three hours. Care was taken not to expose the samples to heat or sunlight after they were removed from the samplers.

The PCB/dioxin samples were stored on dry ice and shipped to the appropriate lab in insulated boxes with dry ice. Airborne next day delivery was the method for shipment. The VOC canisters were shipped via Airborne to RTP twice weekly. The remainder of the samples were stored in labeled envelopes inside the weighing van's humidity/temperature controlled chamber. Upon return to RTP, they were provided to the appropriate EPA personnel for analysis.

4.4 Calibration Procedures

This section describes the frequency and procedures that were employed in the calibration of the sampling and analytical devices that were used in this project.

4.4.1 Frequency

Five point flow rate calibrations of each PM sampler were performed before the equipment was shipped to the field. Additional calibrations were scheduled to be done any time a one point flow check was greater than 10% different from

the set point or if a performance audit differed by more than 10%. This situation occurred one time during the study and the sampler was recalibrated.

4.4.2 Procedures

a. TSP Hi-Vol sampler calibration

The five-point flow calibration of the Hi-Vol samplers was performed in accordance with the procedures described in Section 8 of Appendix B with the following exceptions: sampler calibration equations were determined for each sampler using September average temperature and pressure rather than seasonal.

b. Dichotomous Sampler Calibration

A flow calibration analogous to the five point calibration of the Hi-Vol sampler was performed before the equipment was shipped to the field in accordance with procedures described in Section 5 of Appendix A with the following exceptions: for the coarse and total rotameters Q ambient was determined using the September average temperature and pressure.

c. PS-1 Hi-Vol Calibration

A five-point calibration curve was developed using a standard top hat orifice following the procedures described in Section 8 of Appendix B.

4.4.3 Calibration Checks

Routine flow rate checks of each sampler were performed at the start of the study and at least weekly during the study. An independent performance audit was performed by an EPA contractor to check the flow rate of all samplers.

4.4.4 Balance Calibration

Both balances (Model H16 Sartorius and the Cahn microbalance) used in the study were checked at the start of the project with NIST certified standard

weights. Calibration checks were performed routinely during gravimetric analysis as described below.

At the start and finish of every weighing session, a type-S standard weight (5.0 g) was weighed on the Model 16 analytical balance to check the calibration. The internal calibration weight was used as the calibration check standard for the Cahn microbalance. In addition to these calibration checks, reference filters were weighed during each weighing session to provide a measure of the variability in mass determinations. These measurements were recorded on the filter weight data sheets by the operator along with the temperature, pressure and relative humidity.

Additionally, the zero of each balance was checked by the operator at the start of each weighing session and after every fifth weighing (i.e. after every fifth filter). The zero values must fall within ± 1.0 mg of true zero for the Model H16 balance to be acceptable and within ± 4.0 ug of true zero for the Cahn microbalance to be acceptable. Sample filters were reweighed if the zero drifts exceeded these criteria. The zero values were recorded on the filter weight data sheets with a check mark to indicate their acceptability.

4.4.5 Weigh Room

A portable weigh facility was transported to Green Bay and located outside of the UWGB Laboratory Sciences Building. The weigh facility was temperature and humidity controlled to maintain conditions at 20 degrees C and 40 percent relative humidity. A recording hygrothermograph was used to record conditions in the weigh facility on a continuous basis. Reference filters were weighed at the beginning and end of every weighing session to provide a means of comparing conditions from day to day.

4.5 Collection Media

The filter collection media were selected based on AREAL's past experience with sampling of this type and the need for specific types of analyses to be performed. Care was taken to assure low and uniform trace material background

levels in the filters to minimize variability in sample analysis. The collection media selected were as follows:

Hi-Vol: Whatman Quartz fiber meeting EPA procurement specs
Dichot: Gelman Teflo meeting EPA performance specs
PS-1: Quartz filter and PUF cartridges
VOC: 6-liter SUMMA polished canisters

4.6 Field Blanks

Blank samples were required for each sampling period with at least one blank of each filter media or sample type used. The blanks were carried into the field with the normal run filters/samples and left with the samplers(in their cassettes) if weatherproof space was available. At the completion of the sampling, they were brought back to the weighing van and then equilibrated or stored with the normal run filters/samples.

Information on blanks was placed on the form shown in Figure 4-6 and entered into the field computer system daily. For the dichots, one 37 mm blank was required for each sampling day. For the TSP Hi-Vol and the HVVI, one 8 x 10 filter and one 2 x 6 filter were required for each sampling day. For the PS-1 samplers, one blank PUF and one quartz filter were required for each sampling day and for each analysis lab.

4.7 Sample Analysis

The procedures for analysis of the filters for mass determinations is shown in Appendices A and E. The analyses performed are summarized in Table 4-1 and are described in more details in the following sections.

4.7.1 Ambient Particle Mass

The filter samples which were to have mass determinations made, were first tared at 40% relative humidity and 20 degrees Celsius. After sampling, the filters were equilibrated to the same conditions as when they were tared and then

reweighed. The results were then entered into the field computer and air quality concentrations at EPA standard conditions (25 degrees C and 760mm Hg) were reported.

4.7.2 XRF Analysis of PM Filter Samples

The elemental composition of the dichotomous (37 mm) filter samples was measured nondestructively using energy dispersive x-ray fluorescence (EDXRF) procedures. The x-ray device used for these analyses was fabricated by Lawrence Berkeley Laboratory and uses a pulsed x-ray tube to excite a secondary target which in turn excites the sample with nearly mono-ergetic x-rays. To obtain high sensitivity for a wide range of elements, each sample is excited by four different secondary targets. For the K x-rays of elements with atomic numbers in the range of a 13-20, 16-25, 25-38, and 38-56 the secondary targets are titanium, cobalt, molybdenum and samarium respectively. The Mo target also excites the L x-rays of lead (Pb) and other heavy elements. The EDXRF system's calibration is checked daily using thin film standards, and the calibration is validated daily by using standard reference materials prepared by NIST.

4.7.3 PCB/Pesticide Analysis

The samples were analyzed for aldrin, dieldrin, and PCBs by Southwest Research Institute (SWRI). The filter and PUF plug were Soxhlet extracted together with the exception of those filters that were received in broken petri dishes. These filters were analyzed separately.

The PCBs in the field samples generally covered a broad spectrum of PCB standard peaks. The data were reported as total PCBs in relation to 23 prominent peaks from a mixture of aroclors 1016 and 1260. Quantitation was obtained by summing areas of these peaks found in the sample and corresponding peak areas in the 1016/1260 standard.

4.7.4 Dioxin/Furan Analysis

Filter and PUF plug samples were sent to the EPA Laboratory at Stennis Space Center, Mississippi for sample analysis preparation. Respective PUF and filters were combined, spiked with $_{13}C_{12}$ labeled dioxin and furan internal standards and subjected to a 16-hour soxhlet extraction using benzene. The extracts were sent to AREAL for analysis by High Resolution Gas Chromatography (HRGC) - High Resolution Mass Spectrometry (HRGC-HRMS) for polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). A number of analyses were performed prior to sampling to ensure that the PUF plugs were free of contamination. The analytical procedures and quality assurance plan used in this study are presented in Appendix G.

4.7.5 Volatile Organic Compound (VOC) Analysis

The VOC canisters were analyzed (for the list of 41 compounds shown in Appendix F) using an automated cryogenic sampling and gas chromatographic system. The system consists of a Hewlett-Packard 5880A Level 4 gas chromatograph equipped with a high resolution capillary column; an electron capture detector (ECD); a flame ionization detector (FID); and a modified Nutech 320-01 cryogenic preconcentrator unit. It takes about one hour for the analysis of each canister which covers system initialization, sample collection, analysis and report narration.

Typo? The VOCs are collected from each of the 6 l. canisters by pulling the sample through a reduced temperature trap. Various compounds are concentrated on the trap but the major air components nitrogen and oxygen pass through. The VOCs are then thermally desorbed onto the high resolution column where they are separated by gas chromatography in conjunction with oven temperature programming and detected simultaneously by ECD and FID.

Before analysis, the system is calibrated using NIST traceable standards in pressurized cylinders that contained mixtures of the target VOC compounds at concentrations of about 10 ppm as working standards. The working standards are diluted with humid zero air to about 10 ppb. Prior to being sent to the

field for use, the canisters were cleaned and certified. One out of every four canisters was certified as being clean by filling with humid air and analyzing on the system. If one canister in a batch was found to be contaminated all of the canisters in that batch were recleaned. Audit canisters provided by the Quality Assurance Division of AREAL were analyzed to check the analytical system. In addition, a small number of samples was analyzed using a mass selective detector (MSD MAS SPEC) for analysis.

4.7.6 Sulfate/Nitrate Analysis By Ion Chromatography(IC)

Samples collected with the annular denuder and aliquots from the high volume virtual impactors (HVVI) were analyzed for nitrite, sulfite, nitrate, and sulfate content by ion chromatography (IC) procedures. Aliquots cut from the fine and coarse HVVI filters were extracted in 0.003 M sodium carbonate solution and analyzed by the Dionex 2000i ion exchange chromatograph. The fine particle samples typically represented 65 m^3 of sampled air, while the coarse particle sample represented approximately 320 m^3 of sampled air. These air volumes take into account the percent of the total area of each filter that was actually used in the analysis.

4.7.7 Elemental/Volatilizable Carbon (C_e/C_v)

Elemental and volatilizable carbon present in the fine and coarse samples collected on the HVVI were determined by a combustion procedure. An aliquot of the quartz filter is inserted into a combustion assembly and heated to 650 degrees C in a helium atmosphere. Organic material that volatilizes from the filter is oxidized to carbon dioxide and then converted to methane. The methane is then measured with a flame ionization detector (FID). The remaining non-volatile elemental carbon is then measured by raising the temperature of the sample to 800 degrees C and adding oxygen to the helium stream. This oxidizes the elemental carbon to carbon dioxide and the carbon dioxide is converted to methane and subsequently measured with the FID.

4.7.8 Precipitation Metals Analysis

Six precipitation samples collected in an Aerochem bucket at Green Bay were received and analyzed by AREAL for metals using ICP. These samples had been split, with the other half going to the CRL for similar analysis.

A brief summary of the technique and results from these analyses and QA activities follows. It should be noted that:

1. A range of pH's was observed in the samples when they were received at AREAL. The meaning of this is not clear; but, it was not expected.

2. A new ICP instrument with which AREAL has little experience was employed. Special conditions are needed to determine Li, K and Na, and the conditions could not be optimized. Results make the difficulties apparent and skepticism is appropriate for those elements.

Analysis was done at AREAL on a Jobin-Yvon Model 70 Plus ICPAES. Grouped 1989 standards made by Inorganic Ventures, Inc. were diluted 1:100 in two steps in a matrix of 0.25% v/v HNO_3 and 0.20% v/v HCL to yield a concentration range of 400 to 16,000 mg/l. Ultrex concentrated HCl and HNO_3 were used to adjust the acid content and prepare the reagent blank. The pH values of the six rain samples were measured prior to adjustments with concentrated Ultrex HCl to give an acid matrix of 0.20% HCl which matched the standards. It was assumed that the rain samples had been properly acid stabilized to 0.25% HNO_3 prior to receipt, so no HNO_3 was added.

4.7.9 Annular Denuder

For selected periods during the study (as described previously), samples were collected with the annular denuder assembly. The aqueous extracts from the various denuder tubes and filters were analyzed for nitrate, sulfate, and nitrite

concentrations. Subsequent processing of the data provided quantitative measurements for nitric acid, nitrous acid, SO_2, sulfate, and nitrate present in each sample.

4.8 Field Data Handling System

The data handling system consisted of a PC (Compaq 286) with a 40 mb hard disk and one high density floppy drive. Due to the small number of samples collected during the study, samples were not bar-coded for subsequent identification. The software to store, process, and perform the necessary calculations on the data was developed for EPA by NSI, Inc for the Integrated Air Cancer Program (IACP) and uses a compiled version of dBase III+. The system requires a definition of the sampling site, the samplers with their appropriate calibration curves, calibration and flow check standards. Descriptive data are entered on each sample taken along with tare and final weights of any filters where mass concentrations are to be calculated. The system is capable of generating a whole series of standard reports ranging from printouts of the raw data inputs to summary of daily activities and chain of custody for shipping samples.

5.0 QUALITY ASSURANCE AND QUALITY CONTROL REVIEW

5.1 Introduction

The QA and QC review of the GLNPO pilot site at UWGB consisted of a systems audit, a collocated sampling study, and a performance audit. A systems audit consists of a qualitative evaluation of all components of the measurement/surveillance system. It evaluates both field and laboratory quality control practices and reviews the documentation surrounding each facet of the program. However, it must be noted that the lack of a Quality Assurance Project Plan (QAPP) from GLNOP did not permit a comprehensive systems audit. AREAL conducted a systems audit of the UWGB data retrieval system to determine how the monitoring and QA/QC data are incorporated into the data base. AREAL also conducted a site and laboratory systems audit to assess the contractor's capabilities and to determine if the siting criteria were suitable for this

project. These audits enabled AREAL to; (1) determine the adequacy of the QAPP, (2) determine if the project is adhering to the QAPP, (3) determine if the data quality objectives are being met, and (4) determine the completeness of the data base.

Accuracy, precision, and representativeness were evaluated through the AREAL collocated sampling project at the University of Wisconsin in Green Bay. A discussion of the colocated sampling site was presented in Section 4 of this report. Accuracy was determined for specific segments of this project through AREAL's performance audits on its own monitoring effort at the UWGB site and on the Illinois State Water Survey's samplers. Sampler precision and representativeness were determined through the results of comparisons between similar samplers at the two UWGB sites.

Laboratory audits of the AREAL canister samplers verified the accuracy of the VOC portion of the program. Duplicate spiked canisters provided both accuracy and precision figures for laboratory analyses. Other laboratory analyses were audited by providing the respective laboratories with spiked samples of the necessary pollutants. AREAL has the capability to provide audit samples for PUF, XAD, XRF, canister and other types of analyses, including metals. Such samples will provide values for laboratory accuracy, precision, and MDLs. These values combined with field performance audits, usually in the form of sampler flow audits, give an overall quantitative review of the accuracy of the measurement system.

5.2 Great Lakes National Program Office

5.2.1 Quality Assurance Project Plan: Analysis and Findings

All GLNPO documents pertaining to the operations of the UWGB site were requested by AREAL. These included; 1) the Quality Assurance Project Plan (QAPP) for the GLAD Network, (2) the station operator's manual for the network, (3) the Quality Assurance Plan for the Bionetics Corporation, (4) the QAPP for the organic sample analyses for the GLAD Monitoring Stations, (5) the QAPP for the operation of a master atmospheric deposition site at Green Bay, (6) numerous

SOPs used by Bionetics in performing the analyses under EPA's contract, and (7) a number of documents which refer to a "Green Bay Mass Balance Project".

This is not clear

The only crucial project document which was not provided by GLNPO was QAPP for the overall air pollution monitoring project. Recent conversations with GLNPO staff indicate such a document has not been written.

It is recommended that the QAPP for the Operation of a Master Site and the one for Organic Sampling Analyses be combined in a more general QAPP for the entire network. This QAPP would describe all aspects of sampling, analyses, data retrieval, and how the monitoring data will achieve the GLNPO's "Mass Balance" objectives. It is essential that the key parameters for the "Mass Balance Study" be identified and that the accuracy and precision of the measurements of these parameters be specified. Responsibilities for each section within the overall scope of the project need to be addressed. Such documentation is necessary for external auditors and other members of the scientific community to judge the merits of the overall program.

Not Necessarily

5.2.2 Components of a Quality Assurance Program Plan

A quality assurance project plan describes; (1) the study's purpose, (2) the involved personnel's responsibilities, (3) the measurement and analytical procedures that will be part of the field study, and (4) presents an outline of the standard operating and analytical procedures that will be followed in the laboratory. The plan also identifies all quality assurance activities and guidelines that will be included in the study. Among the various aspects of QA that must be addressed by the QAPP are explicit requirements to:

(1) identify and establish specific data quality goals to be achieved during the project;

(2) describe the procedures that will be used to measure or assess the quality of the environmental measurements obtained during the project; and

(3) describe the nature of the report or reports that will be prepared to document the quality of the measurements.

Presently, guidelines define four measures of data quality, namely; precision, accuracy, completeness, and method detection limit (MDL).

Precision

Precision is a measure of agreement among individual measurements of the same property, under prescribed similar conditions. Precision is determined by measuring the agreement among a number of individual measurements (replicates) of the same sample or concentration. For this program, precision of the total measurement system will be measured through the collocation of similar instruments. Other, more limited or specific measures of precision should be included in the internal QC program, such as replicate analyses of control samples.

Accuracy

Accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. It is determined by analyzing a reference material of known pollutant concentration or by reanalyzing a sample to which a material of known concentration has been added.

Completeness

Completeness is a measure of the valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been (i.e., were planned to be) collected. Completeness is not intended to be a measure of representativeness -- i.e., how closely the measured results reflect the actual concentration or distribution of the pollutant in the media sampled. A project could produce 100% data completeness (all samples planned were actually collected and found to be valid), but the results may not be representative of the pollutant concentration actually present. For example, the method might be biased, or the sampling times or locations might not provide

a representative indication of the actual distribution of the pollutant in that area.

Method Detection Limit

The method detection limit (MDL) is the minimum concentration that can be detected with reasonable certainty. MDL is determined by measuring the variability of replicate measurements at or near zero sample concentration. Frequently this may be accomplished by measuring a zero concentration reference material.

5.2.2 System Audits and Results

The systems audit conducted for the UWGB site included (1) a review of the SOPs for the Bionetics laboratory practices, (2) a review of the Bionetics laboratory facilities, (3) a review of the Atmospheric Deposition and Precipitation Sampling Network Station Operator's Manual, and (4) a review of two of the operating sites.

A systems audit of the Illinois State Water Survey (ISWS) Laboratory was not conducted. However, this laboratory does participate in AREAL's semi-annual acid rain analysis audit. The ISWS laboratory was audited by the acid rain program in the spring and fall of 1989 (See Appendix H for the results). The Geological Survey routinely audits the Water Survey Laboratory as part of their responsibilities associated with the NADP/NTN.

The laboratory SOP's and QAPP were used as a basis for conducting a systems audit of the Bionetics Laboratory (See Appendix I). The auditor from AREAL concluded that Bionetics was doing an excellent job of following both the QAPP and the SOPs. Their record keeping was meeting all the requirements established in the QAPP. QA/QC data was being kept in log books that had been kept since the beginning of the project. Control charts were being maintained on the analyses that were reviewed. The auditor found a few areas that could be improved. Employee training, working hours, acknowledgments in EPA documents, safety training, and filling the position of Q.C. coordinator are topics which

need to be addressed by either the contractor or EPA. Further detail is available in the audit report. The copy of the network station operator's manual AREAL received to review was out of date (1985) and much of the material is presently not being used in the network. AREAL was asked to review the older version and supply comments. The older version needed updating and revising to include such things as standard headings for page number, revision number, and section number.

AREAL conducted an abbreviated systems audit of the site at the University of Wisconsin in Green Bay. The site was visited briefly and pictures were taken. Pictures indicate the site to be located in an excellent area with good air flow from all directions. Site logs were not obtained but have been requested for review. A report will be written once these logs have been obtained and reviewed. The close proximity of the dirt road at the University site may contribute some amount of coarse particulate matter to the dichotomous and high volume samplers at times of high wind velocity and heavy traffic.

No systems audit has been performed on the total data system operated by the GLNPO, including the archival of data at the Great Lakes National Program Office in Chicago. It is recommended that a data audit be performed, however, a complete QAPP is a necessary precursor to such an audit.

5.2.3 Performance Audit Results

On September 8, 1989, a flow audit was performed on 2 high volume samplers operated for the GLAD network by the Illinois State Water Survey. Results showed excellent agreement with AREAL's flow standards. External audits are necessary to ensure the accuracy of any monitoring system. Future performance audits will include all the meteorological equipment, precipitation samplers, aerosol sampler flows, and other parameters that AREAL is capable of auditing.

5.3 Atmospheric Research and Exposure Assessment Laboratory

5.3.1 Quality Assurance Project Plan

AREAL developed a monitoring plan for the project at the University of Wisconsin site at Green Bay. Because of the limited scope and duration of AREAL's monitoring of the UWGB site, a QAPP was not developed. Most of the items that are required in a QAPP are addressed in the monitoring plan.

5.3.2 Systems Audit Results

Because this was a short duration study, a complete systems audit was not done for the AREAL monitoring project at Green Bay. However, documentation in the form of logbooks, Q.C. records, and the monitoring plan were reviewed. Recommendations from this audit were incorporated into a revised work plan and included in the AREAL monitoring study. Summary sample completeness data appear in Table 5-1.

5.3.3 Performance Audit Results

On September 8, 1989, a performance audit was conducted on the AREAL monitoring project at the UWGB site. The audit consisted of measuring the flows of the 3 hi-volume samplers, two dichotomous samplers, two PUF samplers, and one hi-volume PM-10 virtual impactor sampler. With the exception of the coarse flow from one dichotomous sampler, all flows were in excellent agreement with AREAL's flow standards.

Other performance audits include duplicate audit canisters for the volatile organic compounds, and spiked PUF cartridges. Results from the VOC audit canisters show 5 of the 17 compounds having a high positive bias (45%<HPB<90%) with the remaining compounds being within ±20%. Results from the PUF analyses show that the overall results are acceptables with most values having a high degree of accuracy (i.e. being within ±15%).

TABLE 5-1. COMPLETENESS OF SAMPLING FOR AREAL MONITORING AT GREEN BAY (Sept 1989)

	No. of Scheduled	No. of	No. of

Sampler Type	No.	Sample Periods	Samples	of Samples Taken	Valid Samples	% Total[a]	% Total[b]
Dichotomous	2	16	64	64	48	100	67
HVVI	1	16	32	32	32	100	100
TSP	1	5	5	5	5	100	100
PS-1	2	5	10	10	10	100	100
Dichot-Dir	1	3	3	3	3	100	100
PS-1-Dir	1	3	3	3	3	100	100
VOC	1	10	10	10	0	100	0*
TOTAL	9	58	127	127	101	100	80

[a]Ratio of samples taken to number scheduled (expressed as percent)

[b]Ratio of number of valid samples to number taken (expressed as percent)

* See Section 6.1.7 for discussion.

It was noticed that exact methodologies were not duplicated between the GLNPO and AREAL monitoring sites. The AREAL project utilized the VOC canisters, and PUF samplers for the organic compound collection, in place of the XAD cartridge methodology employed by GLNPO. The only method of comparison between the two programs was the high volume sampler employed by each. As it turned out even the samples from these two hi vols did not have good agreement with each other. Without comparable monitoring and analysis schemes, the representtiveness and comparability of the data at the two sites is very questionable.

6.0 ANALYSIS OF MONITORING RESULTS

The following sections present the results from the analysis of samples collected by AREAL and comparisons of AREAL data with that obtained by GLNPO. Additional interpretive information is presented by way of microscopic analyses and source apportionment modelling to provide some explanation for the measured concentrations.

6.1 Colocated Measurements

The following sections present the AREAL data and that from GLNPO which were collected simultaneously at the Green Bay monitoring site.

6.1.1 TSP Hi vol

Table 6-1 shows the results of side by side TSP High volume measurements. The data are plotted in Figure 6-1. Five data pairs were taken with poor overall agreement (r^2=0.46) if all five data points were plotted. If the one outlier is removed (9/20/89), the agreement improves substantially (r^2=0.93) as shown in Figure 6-2.

TABLE 6-1. GREEN BAY PARTICULATE MATTER DATA COMPARISON AREAL/GLNPO

DATE	TSP AREAL	TSP GLNPO	AREAL/ GLNPO	% DIFF	DCT/AREAL TOTAL	DCT/AREAL FINE	DCT/AREAL COARSE	HVVI/AREAL TOTAL	HVVI/AREAL FINE	HVVI/AREAL COARSE
01-Sep-89	26.4	27.1	0.97	-2.6	12.5	5.5	7.0	10.9	6.9	4.0
07-Sep-89	38.1	44.0	0.87	-15.4	23.3	17.6	5.7	24.3	18.8	5.5
13-Sep-89	8.8	14.7	0.60	-66.4	6.3	3.6	2.7	5.5	5.0	0.5
19-Sep-89	53.6	33.0	1.63	38.5	36.8	28.3	8.5	38.9	32.3	6.6
25-Sep-89	28.2	37.3	0.76	-32.1	11.9	3.9	8.0	18.2	4.3	13.9
AVERAGE	31.0	31.2	0.96	-15.6	18.2	11.8	6.4	19.6	13.5	6.1

The GLNPO data are consistently higher than the AREAL data with the exception of the one outlier on 9/20/89. However, the data from other AREAL samplers for that date are consistent with each other. For example, the PM_{10} dichotomous sampler which collects those particles below 10 μm as compared to the 25 μm for the TSP hi vol has a lower concentration than the TSP hi vol and the HVVI (which also did not have a PM_{10} inlet.

The GLNPO hi vol, on the other hand, had a lower concentration than the dichotomous sampler. This is physically impossible due to the different inlet geometries discussed above. This indicates that the GLNPO data are probably in

FIGURE 6-1 GREEN BAY TSP DATA COMPARISON

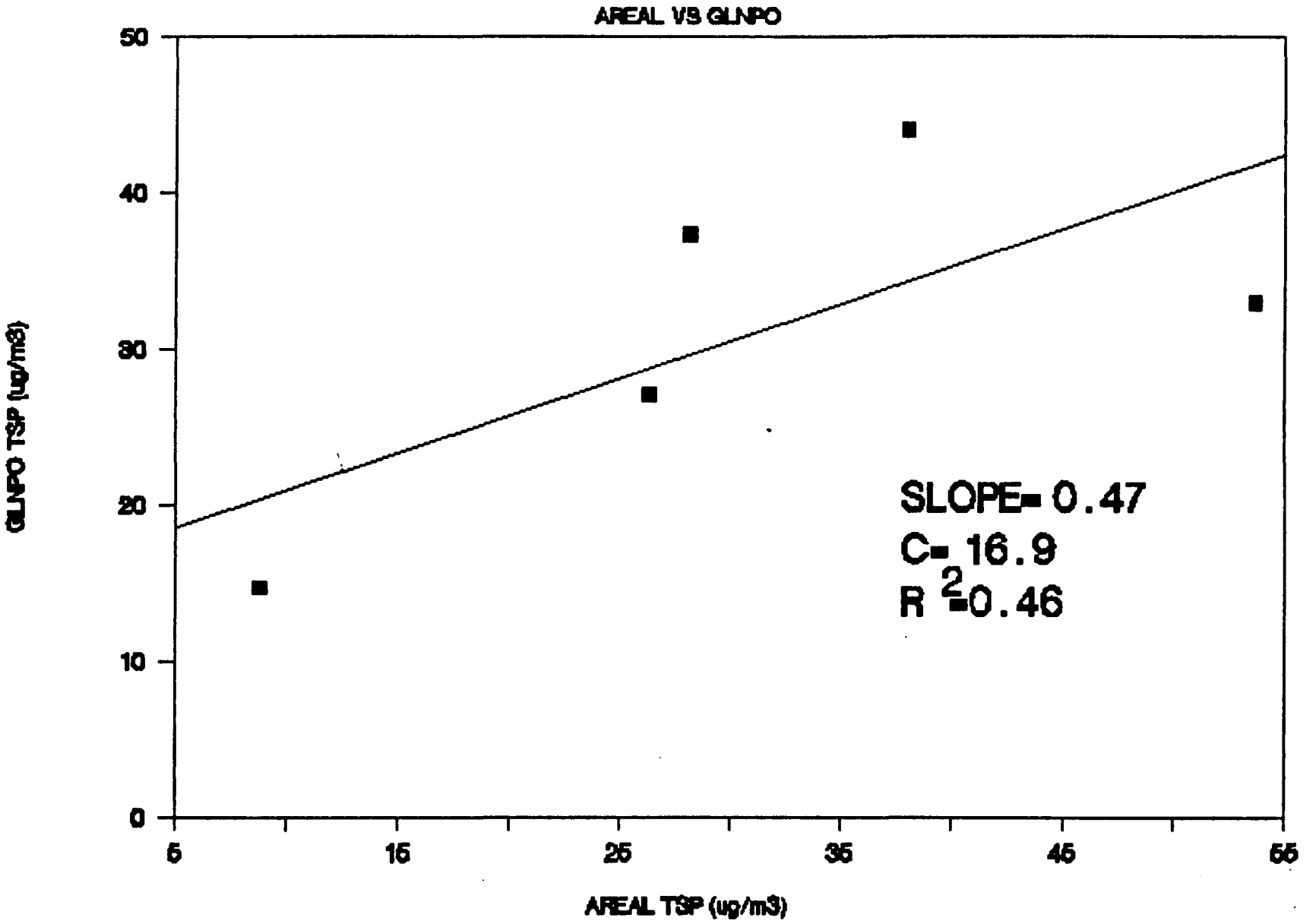
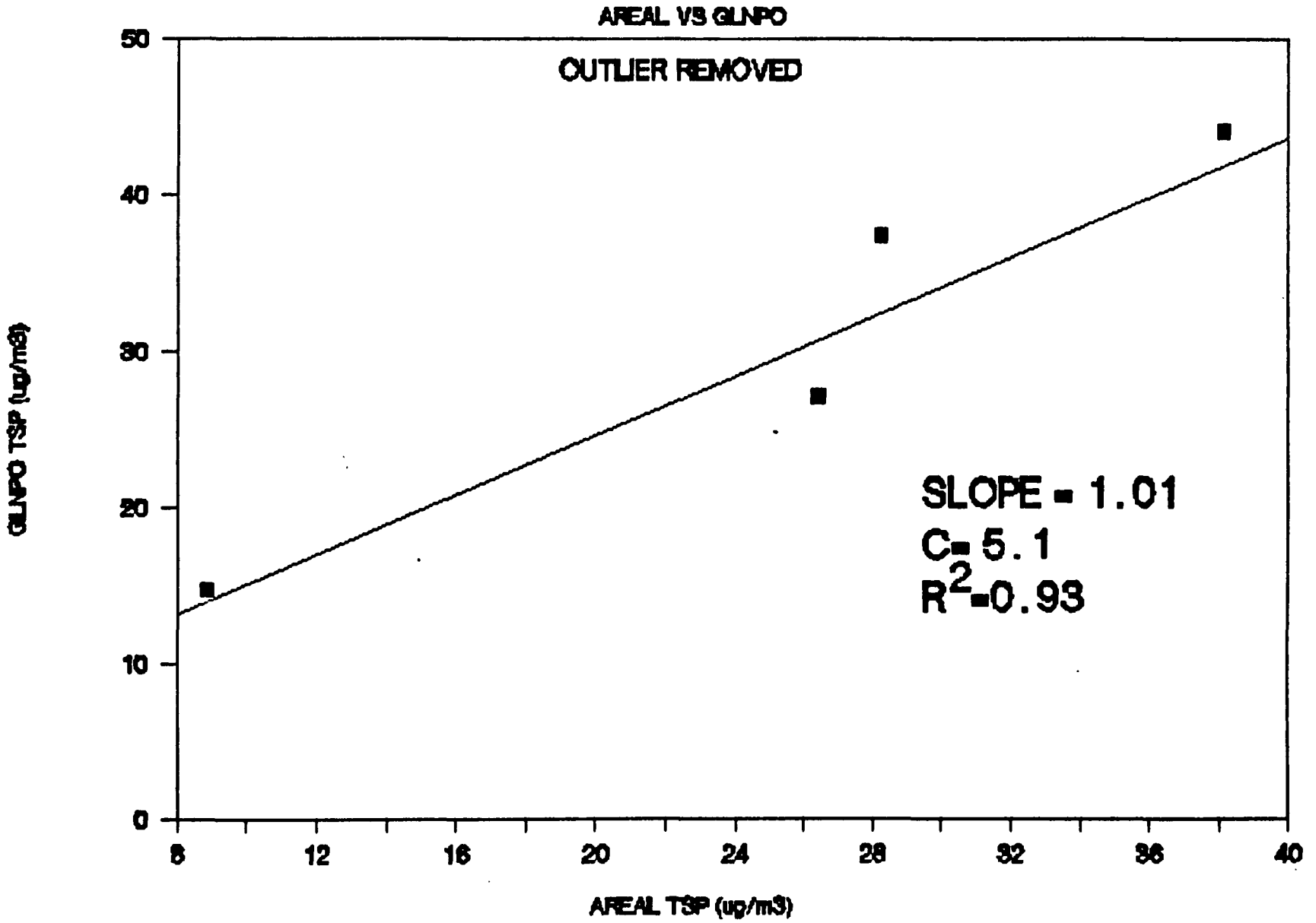


FIGURE 6-2 GREEN BAY TSP DATA COMPARISON



error. The error may have been caused by improper flow measurements, weighing error, or loss of sample in transport.

In general, there is the wind speed and direction dependence of the TSP hi vol samplers due to their nonsymmetric inlets. This dependence contributes to the poor-to-fair comparisons typically found with TSP measurements. However, PM_{10} samplers, such as the dichotomous sampler and the SSI or HVVI, do not exhibit these problems with wind dependence because they have omnidirectional inlets and well defined d50 cutpoints for collecting ambient aerosol.

The levels of PM_{10} found at the Green Bay site during September were well below EPA's health-based national ambient air quality standard (NAAQS) of 150 $\mu g/m^3$ for a 24-hour period and averaged about 50% below the 50 $\mu g/m^3$ annual average standard. Values measured at the UWGB site are typical for cities of this size. The somewhat nonurban character of the site probably contributed to the moderate concentrations measured there.

6.1.2 Total Carbon Measurements

Table 6-2 shows the total carbon measurements from the TSP hi vol samples of GLNPO compared to the fine and coarse fraction carbon measurements from the AREAL HVVI sampler. Similar to the TSP, the agreement is generally poor. Coefficient of correlation is around 0.2 (See Figure 6-3). Although the average percent difference between AREAL and GLNPO is only 24.1%, the range of difference values is from +53% to -11%.

6.1.3 Directional Samplers

Table 6-3 displays the results derived from the wind direction controlled PM samplers. The AREAL PM sampler was a conventional Sierra-Andersen PM10 dichotomous sampler. In addition, a PUF sampler was operated to collect samples for PCB and pesticide analysis without any mass measurements being made. The mass concentrations from AREAL's dichotomous sampler and CLLLLLMPO's TSP hi-vol did not compare well. This is most likely due to the large differences in the sampling times. A review of the average hourly meteorological data show that the time that the wind was from the SW quadrant compares more favorably to

Type

AREAL's measurement system. For some reason, the last sample taken by GLNPO was for a two week period and so ti can not be directly compared to AREAL's one week samples.

6.1.4 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

A comprehensive analytical report that describes many aspects of the sampling and analysis (PS-1 sampler efficiency, method efficiency, field blanks, method blank, laboratory method spike) needed for QA/QC and evaluation purposes is shown in Appendix J. The data satisfies all QA/QC requirements. Analytical data for the test samples were extracted from that report and are shown in Table 6-4. The concentrations of PCDDs and PCDFs were very low and similar to concentrations (background levels) found in ambient air in other studies by AREAL

TABLE 6-2. TOTAL ORGANIC CARBON MEASUREMENTS AREAL VS. GLNPO (ug/m3)

DATE	GLNPO TOC	AREAL TOC	ORGANIC CARBON COARSE	ORGANIC CARBON FINE	ELEMENTAL CARBON COARSE	ELEMENTAL CARBON FINE	TOTAL CARBON COARSE	TOTAL CARBON FINE	TOTAL
9/1/89	8.3	3.9	1.3	2.6	0.1	0.3	1.4	2.9	4.3
9/7/89	5.8	4.1	0.9	3.2	0.0	0.3	0.9	3.5	4.4
9/13/89	2.3	2.3	1.1	1.2	0.1	0.3	1.2	1.5	2.7
9/19/89	4.7	5.2	1.6	3.6	0.2	0.5	1.8	4.1	5.9
9/25/89	4.2	3.7	2.6	1.1	0.0	0.2	2.6	1.3	3.9
AVERAGE	5.1	3.8	1.5	2.3	0.1	0.3	1.6	2.7	4.2

TABLE 6-3. DIRECTIONAL PM DATA COMPARISON (SW QUADRANT)

DATE FROM	DATE TO	TSP/GLNPO (ug/m3)	TIME (hrs)	DCT/AREAL (ug/m3)	TIME (hrs)	TIME AVG HOUR MET DATA WAS FROM SW (hrs)	(%)
05-Sep-89	12-Sep-89	45.6	24.3	23.2	38	63	37.5
12-Sep-89	19-Sep-89	89.3	5.9	16.3	110	83	49.4
19-Sep-89	26-Sep-89	--	--	29.5	111	66	39.3
19-Sep-89	03-Oct-89	83.1	28.1	--	--		
AVERAGE		72.7	19.4	23.0	86.3	70.7	42.1

FIGURE 6-3
GREEN BAY TOTAL CARBON COMPARISON

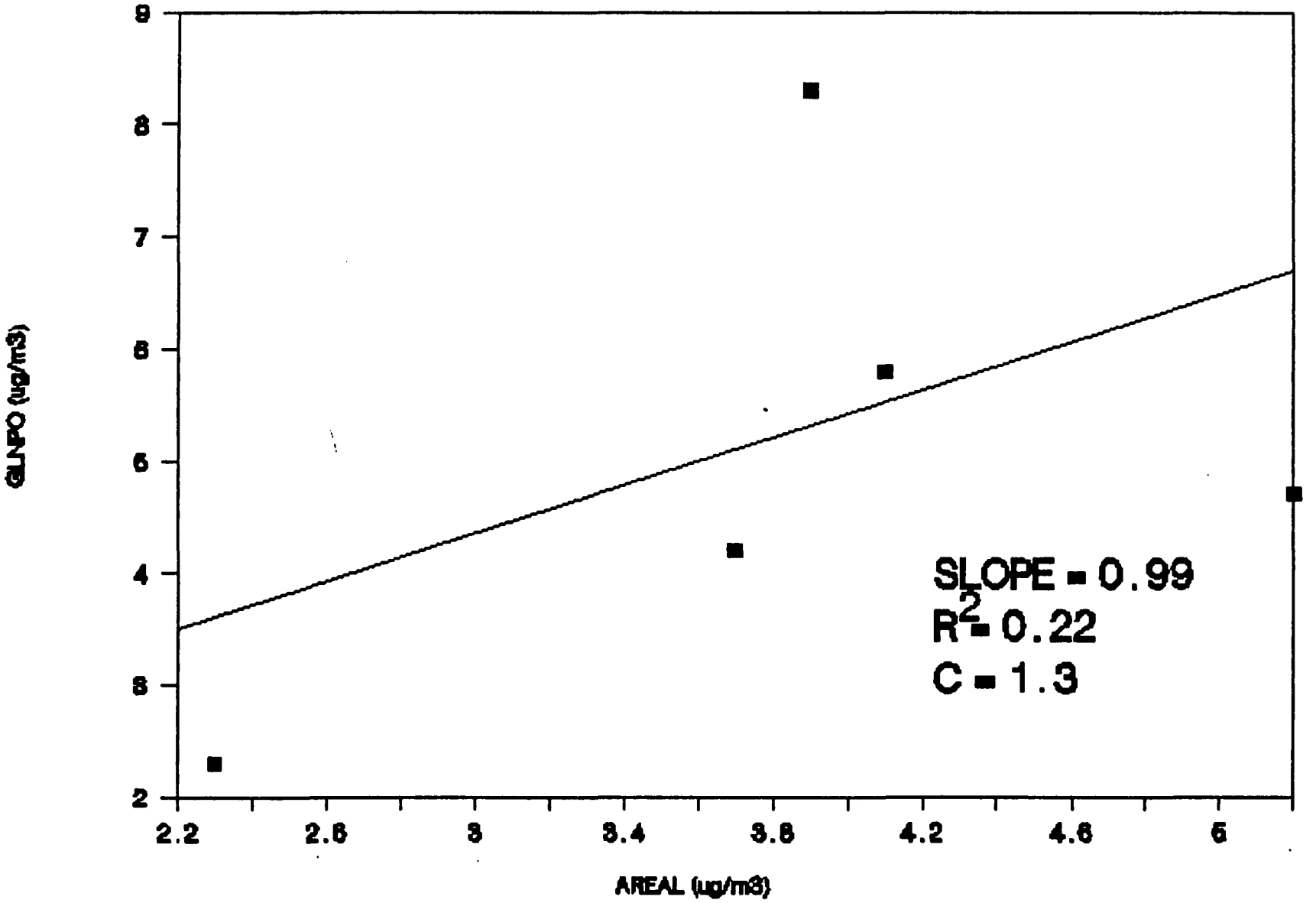


TABLE 6-4. DIOXIN-FURAN DATA FOR GREEN BAY

SAMPLE DATE	TPCDD (pg/m	TETRA CDD	PENTA CDD	HEXA CDD	HEPTA CDD	OCDD	TPCDFs (pg/m3	TETRA CDF	PENTA CDF	HEXA CDF	HEPTA CDF	OCDF
9/7/89	1.7	0.3	0.4	0.4	0.3	0.3	2.65	0.8	1.2	0.5	0.1	0.05
9/13/89	0.89	0.09	0.1	0.2	0.2	0.3	1.08	0.4	0.4	0.2	0.06	0.02
9/19/89	1.4	0.2	0.2	0.3	0.3	0.4	2.23	0.7	0.7	0.4	0.23	0.2
9/25/89	0.78	0.08	--	0.2	0.2	0.3	0.67	0.3	0.2	0.1	0.05	0.02

NOTE: ALL CONCENTRATIONS EXPRESSED IN PICOGRAMS PER CUBIC METER(pg/m3)

and other laboratories. The isomeric pattern of PCDDS and PCDFs detected in these samples indicate they were formed in combustion/incineration processes and released to the atmosphere predominately through stack gas emissions. Atmospheric transport is the major mode for widespread dispersal of these compounds throughout the environment. Several references are provided regarding PCDDs and PCDFs in ambient air, transport, deposition, and fate: *Chemosphere* , Vol. 17, No. 1, pp. 3-20, 1988; *Environmental Science and Technology*, Vol. 23, No. 11, pp. 1389-1395, and pp. 1396-1409, 1989; Chemosphere, Vol. 19, No. 1-6, pp 541-546, 1989; and Proceedings of the 1988 EPA/APCA International Symposium, Measurement of Toxic and Related Pollutants.

6.1.5 Polychlorinated Biphenyls and Organochlorine Pesticides

Both wind direction-controlled sequential sampling and 24-hour integrated sampling with PS-1 samplers were performed to determine PCBs and aldrin/dieldrin in ambient air. Eight collected samples, eight field blanks and seven blind spiked samples were analyzed by dual capillary gas chromatography (30 m DB-5 and DB-608 columns) with electron capture detection according to the EPA Contract Laboratory Program (CLP) protocols. Quartz-fiber particle filters and PUF plugs were extracted and analyzed separately. All extracts were analyzed using reference standards of aldrin, dieldrin, and Aroclors 1016, 1221, 1232,

1242, 1248, 1254, and 1260 supplied by the EPA Pesticides and Industrial Chemicals Repository. Recoveries from spiked samples ranged from 75 to 130%.

When PCBs were evident in the initial analysis, an acid-treated five-fold diluted sample was analyzed to remove possible interferences. The PCBs identified in the field samples generally covered a broad range of PCB standard peaks. Accordingly, they were quantified as total PCBs in relation to 23 prominent standard peaks from a standard mixture of Aroclors 1016 and 1260. Quantitation was obtained by summing the areas of these peaks found in the sample and the corresponding peak areas in the Aroclor 1016/1260 standard. No PCBs were detected on any of the filter extracts.

Data from the pesticides/PCBs analyses are presented in Table 6.5. No aldrin or dieldrin was found at concentrations exceeding the quantitation limits (0.15 and 0.25 ng/m^3, respectively, for 24-hour samples collecting 325 m^3 of air). Quantitation limits were generally set at five times the minimum level of detection. PCBs were found in the PUF extracts from seven of the eight field samples at concentrations ranging from 3 to 6.5 ng/m^3. With exception of the one negative sample, for which there was no overlapping wind-directed sampling, the results of 24-hour integrated and 36- to 100-hour wind-directed sampling were in agreement.

TABLE 6-5. PCB-PESTICIDE DATA FOR GREEN BAY

SAMPLE DATES	SAMPLE TYPE	ALDRIN (ng/m3)	DIELDRIN (ng/m3)	PCB's (ng/m3)
Wind Directed Sequential:				
05-Sep-89 TO 12-Sep-89	PS-1(Filter+PUF)	ND	ND	6.18
12-Sep-89 TO 19-Sep-89	PS-1(Filter+PUF)	ND	ND	4.95
19-Sep-89 TO 26-Sep-89	PS-1(Filter+PUF)	ND	ND	3.15
24-hr integrated:				
01-Sep-89	PS-1(Filter+PUF)	ND	ND	ND
07-Sep-89	PS-1(Filter+PUF)	ND	ND	4.95
13-Sep-89	PS-1(Filter+PUF)	ND	ND	4.11
19-Sep-89	PS-1(Filter+PUF)	ND	ND	6.48
25-Sep-89	PS-1(Filter+PUF)	ND	ND	3.27

ND = Not detected above quantitation limit (0.15 ng/m^3 for aldrin, 0.25 ng/m^3 for dieldrin and 0.3 to 1.5 ng/m^3 for PCBs for 24-hour samples).

The absence of detectable air levels of aldrin and dieldrin is not surprising. These pesticides have not been used in agriculture in the United States in many years. Dieldrin levels in the atmosphere in the Great Lakes region have generally been found to be below 0.1 ng/m^3 (Thomas J. Murphy, DePaul University, Chicago, IL, personal communication, March 1990; Terry Bidleman, University of South Carolina, Columbia, SC, personal communication, March 1990). It should be noted that aldrin is oxidized to dieldrin during the sampling process (R. G. Lewis, A. R. Brown, and M. D. Jackson, *Analytical Chemistry 49*, 1668-1672 [1977]).

Airborne PCB levels found in this study appear to be higher than expected. The most recent published data (J. L. Baker and S. J. Eisenreich, *Environmental Science & Technology*, *24*, 342-352 [1990]) show a range of 0.6 to 1.8 ng/m^3 (avg

1 ng/m^3) for Northern Wisconsin in the summer of 1984. However, 1983 data from an island in Lake Superior showed a range of 1.5 to 5.2 ng/m^3 (avg. 3.2 ng/m^3), which is comparable to AREAL findings. Recent personal communications with Steven Eisenreich of the University of Minnesota, Minneapolis, and Thomas Murphy (March 1990) suggest that PCB air concentrations rarely exceed 1 ng/m^3 in the Green Bay area. Results of collocated sampling by Dr. Eisenreich's laboratory during the AREAL monitoring period will be available for comparison by mid-April 1990. Their analytical results, as Dr. Murphy's, will be quantified against an EPA Grosse Ile Laboratory reference standards of Aroclors 1232, 1248, and 1262, a mixture similar to the Aroclors 1016/1260 standard used by the AREAL contract laboratory (Southwest Research Institute, San Antonio, Texas).

6.1.6 Precipitation Metals

Table 6.6 contains the mean and standard deviation (=.8865*Range) of two ICP analyses of each of the six samples received by AREAL. Absence of an entry or of an element which appears in Table 6-7 (Detection Limits) means that results were smaller than the Table 6-7 values.

TABLE 6-6. AREAL RESULTS FROM GREEN BAY PRECIPITATION SAMPLES#
(micrograms/liters)

	*FM 890822		FM 890815		*GM 890815		FM 890829		*GM 890718		GM 890822	
	Avg	St Dev	Avg	St Dev	Avg	St Dev	Avg	St Dev	Avg	St Dev	Avg	St Dev
Al	16.1	4	9.0	2	53.3	7	9.1	2	43.9	2	10.2	0.9
Ba	1.4	0.3			3.6	1			2.0	1		
Ca	136.9	0.1	117.7	0.00	1194	11	62.0	0.2	32.4	0.1	120.1	2
Cd	2.1	0.1	1.0	0.3	0.8	0.2	0.7	0.4	0.7	0.1		
Cu	4.1	0.6	1.6	0.02	1.7	1	1.1	0.1	1.2	0.1		
Fe	19.5	2	9.2	1.0	69.6	1	9.9	0.04	37.3	0.7	8.2	0.7
Mg	37.7	0.6	23.7	0.2	401	2	17.9	0.3	102.1	0.1	44.6	0.8
Mn	1.8	0.1	1.3	0.2	9.4	0.01	1.2	0.00	3.9	0.01	1.2	0.2
Ni	5.6	2	6.0	4								
Pb							17.0	0.8				
Sr					1.3	0.05						
Zn	103.9	8.2	24.0	1.4	46.4	1.3	1140	5	117.8	4.4	53.1	91

* Sample contained substantial foreign material.
\# If no entry, one or both analyses were below detection limit.

If element missing, but appears in Table 2, no reportable results were found.

TABLE 6-7. ESTIMATED DETECTION LIMITS FOR PRECIPITATION SAMPLES
(micrograms/liters)

Are these estimated detection limits correct?

Al	7	Co	2	Mn	0.3
As	9	Cr	2	Na	100
B	3	Cu	0.9	Ni	4
Ba	1	Fe	0.4	Pb	10
Be	0.3	K	580	Sr	0.8
Ca	0.7	Li	28	V	1.5
Cd	0.4	Mg	0.6	Zn	0.5

Several reference materials whose compositions were known to the analyst were analyzed along with the samples. They cover a wide range of concentrations and the analytes of interest. Recovery data are shown in Table 6-8. The unexceptional conclusion is that, except for the alkali metals, recoveries are reasonable until detection limits are approached.

Table 6-9 contains recoveries from two samples whose composition was unknown to the analyst. The interpretation of these data is similar to those from the solutions of known composition in Table 6-8.

Earlier, other portions of these samples were analyzed by the Central Regional Laboratory. As reported by CRL, elements were quantified using an ICP (Jarrell Ash Model 1160 ICPAES using PC based software). Data from these CRL analyses, but only for those elements which appear as finite values in the AREAL analyses, are presented in Table 6-10.

A comparison of the AREAL and CRL analyses (Tables 6.6 and 6.10) show generally good agreement for zinc. The AREAL values for zinc tend to be much higher than those from CRL. There could be zinc contamination in either the polyethylene bottles used to ship the samples to AREAL or somewhere in the AREAL analysis system. However, there was no evidence of problems in the AREAL analysis of standard solutions (Table 6-8).

A comparison of the CRL results from spiked and unspiked samples (Tables 6-10 and 6-11) shows most notably an almost complete erasure of aluminum in the unspiked samples. Variations for other metals seem to be random, and the heavier metals do not show systematic losses across all samples as might have been

TABLE 6-8. RECOVERIES FROM STANDARD SOLUTIONS OF KNOWN COMPOSITION (percent)SO*T

	EMSL/Cin1	SRM2 1/100	SRM2 1/1000	HiQC3	LoQC4
Al	103.5	100.4	99.6	103.6	112.9
As	104.0	101.2	100.9	106.9	200.6
B	95.5			98.6	124.4
Ba	100.7	101.9	128.4	97.9	127.8
Be	95.3	100.8	98.8	101.6	99.4
Ca	103.7	108.9	128.5	102.7	110.9
Cd	99.1	101.4	100.3	101.3	94.7
Co	96.8	101.1	103.4	97.0	110.9
Cr	99.9	99.6	102.4	100.0	98.9
Cu	104.8	106.0	104.3	100.3	100.7
Fe	97.0	99.1	97.9	96.2	116.9
K	97.5	108.5	165.2	93.4	BD
Li				97.9	504.8
Mg	102.6	101.8	101.7	100.0	104.4
Mn	101.4	100.0	100.5	98.2	108.0
Na	118.0	110.9	132.4	101.1	300.1
Ni	103.0	101.5	105.3	100.0	123.6
Pb	100.8	103.5	114.7	103.3	272.5
Sr		99.4	99.2	98.2	98.5
Ti	98.9			100.0	106.0
V	99.9			102.6	98.8
Zn	108.5	100.3	105.8	103.5	182.4

*Single column lists used for two samples if elements differ.

1EMSL/Cin ICP Quality Control Samples ICAP-19 and ICAP-7, Lot WP988
Concentration range: ICAP-19 1000 mg/liter
ICAP-7 890-10,000 mg/liter

2NIST Standard Reference Materials 3171 and 3172
Concentration range: 1/100 100 - 5000 mg/liter
1/1000 10 - 500 mg/liter

3HiQC ASB preparation from non-calibration standard stocks
Concentration range: Ca,Mg,K,Na 5000 mg/liter
All others 500 mg/liter

4LoQC ASB preparation from non-calibration standard stocks
Concentration range: 5 -200 mg/liter

TABLE 6-9. AVERAGE RECOVERIES FROM ONE ANALYSIS EACH OF TWO BLIND SAMPLES FROM EACH SERIES
(Percent)

	Series 4	Series 5
Cd	102	105
Cu	104	98
Fe	101	87
Mn	112	91
Ni	128	120
Pb	127	126
Zn	110	109

	Series 1	Series 2	Series 3
Ca	106	100	114
K	1084	156	1074
Mg	108	98	99
Na	165	112	137

* Based on tentative accepted values

TABLE 6-10. REGIONAL LABORATORY RESULTS FROM GREEN BAY PRECIPITATION SAMPLES#*
(micrograms/liter)

	FM08A22	FM08A15	GM08A15	FM08A29	GM07A18	GM08A22
Al	12.75	7.0	57.15	14.63	17.38	12.75
Ba	0.3	0.06	2.36	0.54	1.03	0.3
Ca	107.8	103.6	1100.0	52.67	166.4	107.8
Cu	0.07	1.75	0.91	0.91	1.89	0.07
Fe	3.74	11.22	59.34	7.93	13.01	3.74
Mg	41.90	21.74	382.0	15.6	61.04	41.90
Mn	0.7	0.96	8.62	0.65	1.91	0.7
Sr	0.24	0.09	1.35	0.12	0.57	0.24
Zn	5.36	10.77	7.72	2.72	8.60	5.36

*Elements contained in Table 6-6 only.

TABLE 6-11. REGIONAL LABORATORY RESULTS FROM GREEN BAY (UNSPIKED) PRECIPITATION SAMPLES
(micrograms/liter)

	FB08S22	FB08S15	QM08S15	FB08S29	QM07S18	QM08S22
Al	2.51	1.57	1.26	2.82	-1.6	-1.33
Ba	0.54	0.15	1.17	0.76	0.84	0.20
Ca	97.43	96.60	925.	244.0	329.3	67.32
Cu	2.08	4.41	0.04	3.34	0.39	-0.29
Fe	3.84	2.41	2.07	10.22	2.41	1.53
Mg	26.37	21.86	301.8	84.73	97.59	19.92
Mn	1.22	0.77	2.35	2.02	3.4	0.49
Sr	0.22	0.15	0.99	0.38	0.47	0.15
Zn	19.63	32.22	22.88	8.56	6.29	12.10

Three types of sampling equipment were used to obtain the composition of gases and fine and coarse particles at the UW-GB monitoring site. Table 4-1 contains the types of samplers used and chemical species analyzed. The low volume dichotomous sampler used 2 μm pore size Teflon filters to collect the fine and coarse particles. From these filters the mass, elemental and microscopy data were obtained. The low-volume dichotomous sampler was equipped with a well-defined PM_{10} inlet, while the high volume dichotomous sampler was equipped with the conventional gabled roof inlet. The size range of the coarse particles (>2.5 μm) that are collected by this sampler is dependent on wind speed and direction.

6.2.3 Mass, XRF and Ion Chromatography Correlations

Table 6-12 contains the average composition of the fine and coarse particles collected between September 1, and September 27, 1989 at the UW Green Bay site. Appendix K contains the XRF data for all the sampling periods. Figure 6-4 shows the fine and coarse mass concentrations plotted as a function of time for that period.

Tables 6-13 and 6-14 contain the carbon and inorganic ionic species data for fine and coarse particles collected on quartz filters in the high volume dichotomous samplers.

TABLE 6-12. AVERAGE COMPOSITION OF AEROSOL AT GREEN BAY, WI, from September 1-27, 1989

	Units	Fine	Coarse
Mass[a]	$\mu g/m^3$	17.1	6.18
Cv	$\mu g/m^3$	2.22	1.29
Ce	$\mu g/m^3$	0.27	0.05
NO_3^{1-}	$\mu g/m^3$	0.22	0.32
SO_3^{2-}	$\mu g/m^3$	0.57	0.12
SO_4^{2-}	$\mu g/m^3$	6.13	0.22
Al	ng/m^3	70 (26)[b]	480 (152)
Si	ng/m^3	50 (12)	617 (158)
S	ng/m^3	1754 (154)	71 (38)

hypothesized. If analysis for metals in rainwater is to continue, some attention must be focused on sample handling and quality control.

Table 6-9 contains recoveries from two samples whose composition was unknown to the analyst. The interpretation of these data is similar to those from the solutions of known composition in Table 6-8.

Earlier, other portions of these samples were analyzed by the Central Regional Laboratory. As reported by CRL, elements were quantified using an ICP (Jarrell Ash Model 1160 ICPAES using PC-based software). Data from these CRL analyses are presented in Table 6-10 but only for those elements which appear as finite values in the AREAL analyses,

6.1.7 VOC Measurement

The VOC data were not reported due to a sampling problem discussed earlier. Although most of the values seemed reasonable and no outliers were present in the data set, the data could not be independently validated.

The validation could not be done because of the potential contamination from the pump. Therefore, we are unable to state that the data are either good or biased by contamination. As a result no VOC data are being reported.

6.2 Modeling and Measurement Results

6.2.1 Introduction

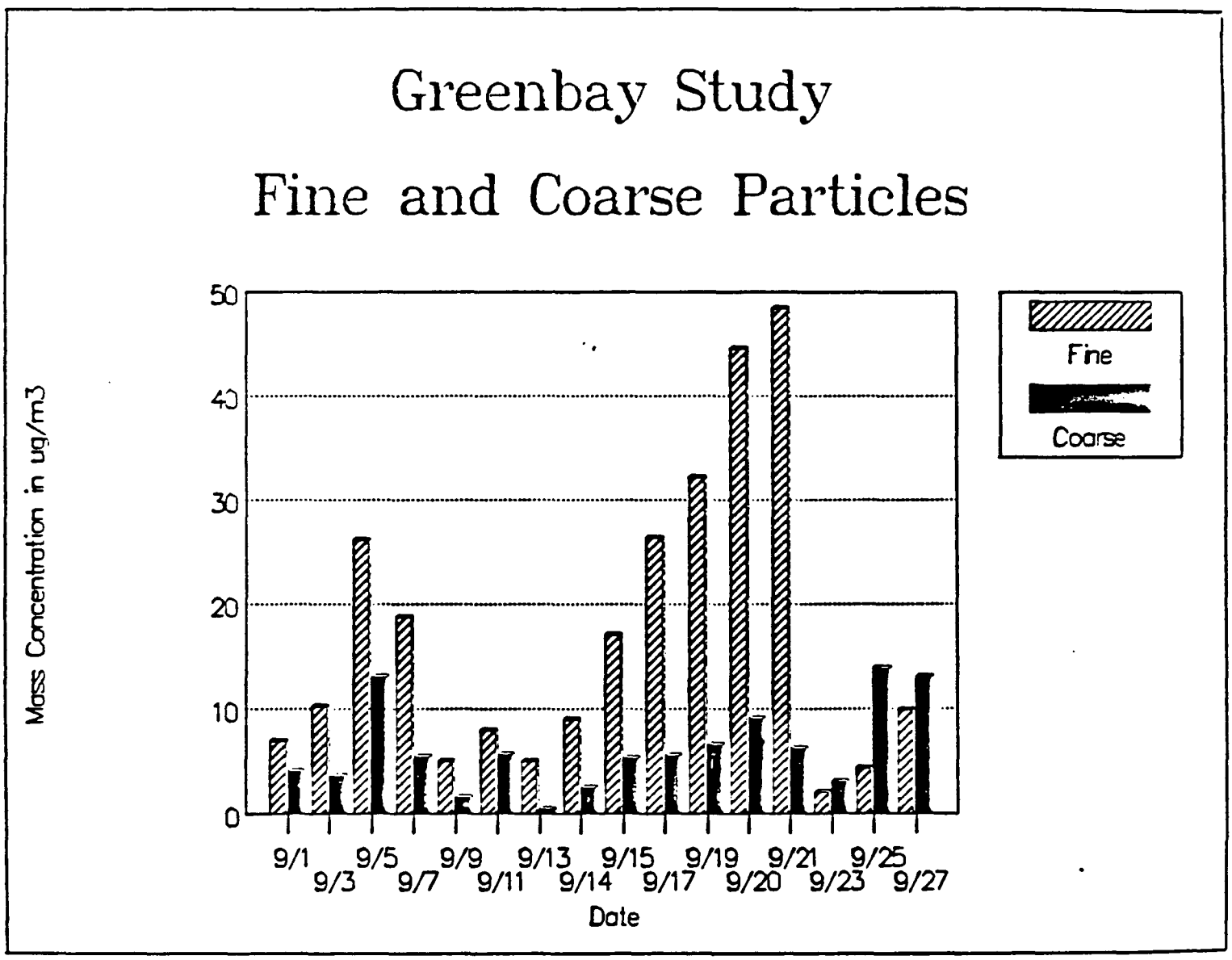
This section presents a discussion of the results of the sample analyses. The sampling systems and chemical analysis procedures used provide information on the chemical and physical properties of the air toxic gases and aerosols that impact the Green Bay area. The primary sampler used to collect these samples (the high-volume virtual impactor - HVVI) is based on virtual impaction principles which separates the coarse particles (>2.5 μm) from the fine fraction (<2.5 μm). The separation and subsequent analysis of these two fractions provided a complete assessment of physical and chemical properties, sources, and transport mechanisms of air toxic pollutants to the Green Bay.

6.2.2 Gas and Aerosol Samplers

Cl	ng/m^3	14 (3)	18 (3)
K	ng/m^3	45 (4)	83 (10)
Ca	ng/m^3	33 (3)	376 (36)
Ti	ng/m^3	1.1 (2.4)	12 (3)
V	ng/m^3	-0.2 (1.6)	0.5 (1.5)
Mn	ng/m^3	3.9 (0.6)	3.6 (0.6)
Fe	ng/m^3	48 (5)	122 (13)
Ni	ng/m^3	0.3 (0.3)	0.3 (0.3)
Cu	ng/m^3	3.0 (0.5)	1.9 (0.4)
Se	ng/m^3	1.1 (0.3)	0.1 (0.2)
Br	ng/m^3	2.1 (0.4)	0.2 (0.2)
Pb	ng/m^3	10.7 (1.4)	1.2 (0.6)
Zn	ng/m^3	19 (2)	5 (1)

[a]Mass, Carbon (Cr and Ce) and ionic data refer to samples collected by Hi vol sampler.
[b]XRF data for dichotomous sampler. Average uncertainty is given in parentheses.

Figure 6-4. Time series of fine and coarse particle mass for the Green Bay site. The fine mass exceeds the coarse on most days but the last sampling period.



'TABLE 6-13. MASS CONCENTRATION, IONIC SPECIES AND CARBON FOR FINE PARTICLES COLLECTED IN GREEN BAY, SEPTEMBER 1-27, 1989

1989	Mass Conc. $\mu g/m^3$	NO_3 $\mu g/m^3$	SO_3 $\mu g/m^3$	SO_4 $\mu g/m^3$	Total SO_4 $\mu g/m^3$	Org. C $\mu g/m^3$	Elem.C $\mu g/m^3$
9/1	6.85	0.20	0.48	1.28	1.85	2.55	0.30
9/3	10.21	0.12	0.69	2.25	3.08	1.76	0.10
9/5	26.09	0.10	0.59	9.10	9.80	2.98	0.28
9/7	18.76	0.08	0.86	8.23	9.25	3.23	0.34
9/9	4.92	0.13	0.49	1.19	1.78	1.33	0.06
9/11	7.97	0.09	0.45	3.05	3.59	1.41	0.19
9/13	5.02	0.29	0.50	1.35	1.95	1.18	0.26
9/14	8.99	0.24	0.41	2.55	3.04	1.21	0.19
9/15	17.03	0.27	0.62	3.41	4.18	2.49	0.37
9/17	26.40	0.08	0.44	9.25	9.78	2.60	0.24
9/19	32.20	0.10	0.46	10.00	10.55	2.83	0.42
9/20	44.52	0.10	0.48	17.88	18.45	3.59	0.49
9/21	48.39	0.10	0.51	24.50	25.11	4.50	0.51
9/23	1.96	0.32	0.51	0.75	1.36	0.81	0.03
9/25	4.31	0.38	1.02	1.58	2.81	1.08	0.16
9/27	9.80	1.02	0.56	1.67	2.34	2.03	0.33
Average	17.09	0.23	0.57	6.13	6.81	2.22	0.27

TABLE 6-14. MASS CONCENTRATION IONIC SPECIES AND CARBON FOR COARSE PARTICLES COLLECTED IN GREEN BAY, SEPTEMBER 1-27, 1989

Date 1989	Mass Conc. $\mu g/m^3$	NO3 $\mu g/m^3$	SO_3 $\mu g/m^3$	SO_4 $\mu g/m^3$	Total SO_4 $\mu g/m^3$	Org.C $\mu g/m^3$	Elem.C $\mu g/m^3$	Carb.C $\mu g/m^3$
9/1	4.00	0.05	0.11	0.19	0.35	1.34	0.09	0.16
9/3	3.59	0.14	0.16	0.18	0.39	0.79	0.04	0.11
9/5	13.06	0.54	0.15	1.24	1.42	1.64	0.00	0.14
9/7	5.43	0.16	0.21	0.26	0.52	0.90	0.00	0.11
9/9	1.56	0.06	0.08	0.12	0.21	0.95	0.00	0.01
9/11	5.63	0.33	0.21	0.12	0.37	1.26	0.01	0.09
9/13	0.44	0.06	0.07	0.06	0.14	1.13	0.05	0.10
9/14	2.47	0.18	0.17	0.11	0.32	0.60	0.06	0.09
9/15	5.32	0.39	0.16	0.09	0.28	1.29	0.08	0.26
9/17	5.53	0.81	0.13	0.26	0.41	0.77	0.06	0.15
9/19	6.55	0.50	0.14	0.14	0.31	1.59	0.15	0.37
9/20	9.09	0.78	0.19	0.15	0.38	1.62	0.11	0.25
9/21	6.24	0.43	0.09	0.44	0.55	1.18	0.11	0.19
9/23	3.08	0.07	0.03	0.03	0.07	0.79	0.00	0.11
9/25	13.88	0.27	0.02	0.10	0.12	2.58	0.00	0.31
9/27	13.06	0.29	0.03	0.07	0.11	2.18	0.05	0.77
Average	6.18	0.32	0.12	0.22	0.37	1.29	0.05	0.20

Figure 6-5 is plot of XRF data for fine particle sulfur expressed as sulfate vs. sulfate obtained from IC analysis of comparable filters from the high volume dichotomous sampler. One data point appears to be an outlier. The slope (0.98) and correlation coefficient (R^2 = 0.99) derived from this plot indicate very good agreement between the sampling systems.

Similar results were obtained for the fine particle mass collected by the two samplers: The slope was 0.95 and the correlation coefficient (R^2) was 0.99. The correlation for the coarse particle mass collected by the two samplers was less impressive. Figure 6-6 shows the correlation for mass concentrations for the low and high volume dichotomous samplers. The poor correlation between the two sets of coarse particle data (slope = 0.73, intercept = 2.04 $\mu g/m^3$, and R^2 = 0.77) is associated with the different inlet geometries for the samplers. For example, during the last period of the study the wind speeds increased to 10-15 m/s from 3-6 m/s, which caused substantial amounts of coarse particles to be suspended in ambient air. Because the low volume sampler inlet has a d_{50} cutpoint of 10 μm, while the high volume sampler d_{50} is nearer to 25 μm, a good correlation for coarse particles is not expected between the two samplers.

6.2.4 Carbon Measurements

Three types of carbon measurements were obtained from the fine and coarse particle fractions collected in this study. The C_v measurements refers to organic carbon species in the aerosols that can be volatilized from the quartz filter in a N_2 atmosphere at 600°C; the C_e refers to the elemental or so-called black carbon that can be converted to CO_2 at 650°C in the presence of O_2 doped N_2 after the C_v has been removed from the sample aliquot. The carbonate carbon data shown in Table 6-15 refers to the carbon species (carbonates) that can be converted to CO_2 through the addition of strong acid to an aliquot of the quartz filter. These definitions of the types of carbon although arbitrary, are generally accepted by groups performing and reporting these analyses.

Figure 6-5. Plot of low-volume versus high-volume dichotomous sulfate data for the Green Bay site. Low-vol data were derived from XRF while hi-vol data were obtained from IC analysis. The slope of the regression line is 0.98 and correlation coefficient, R^2, is 0.98.

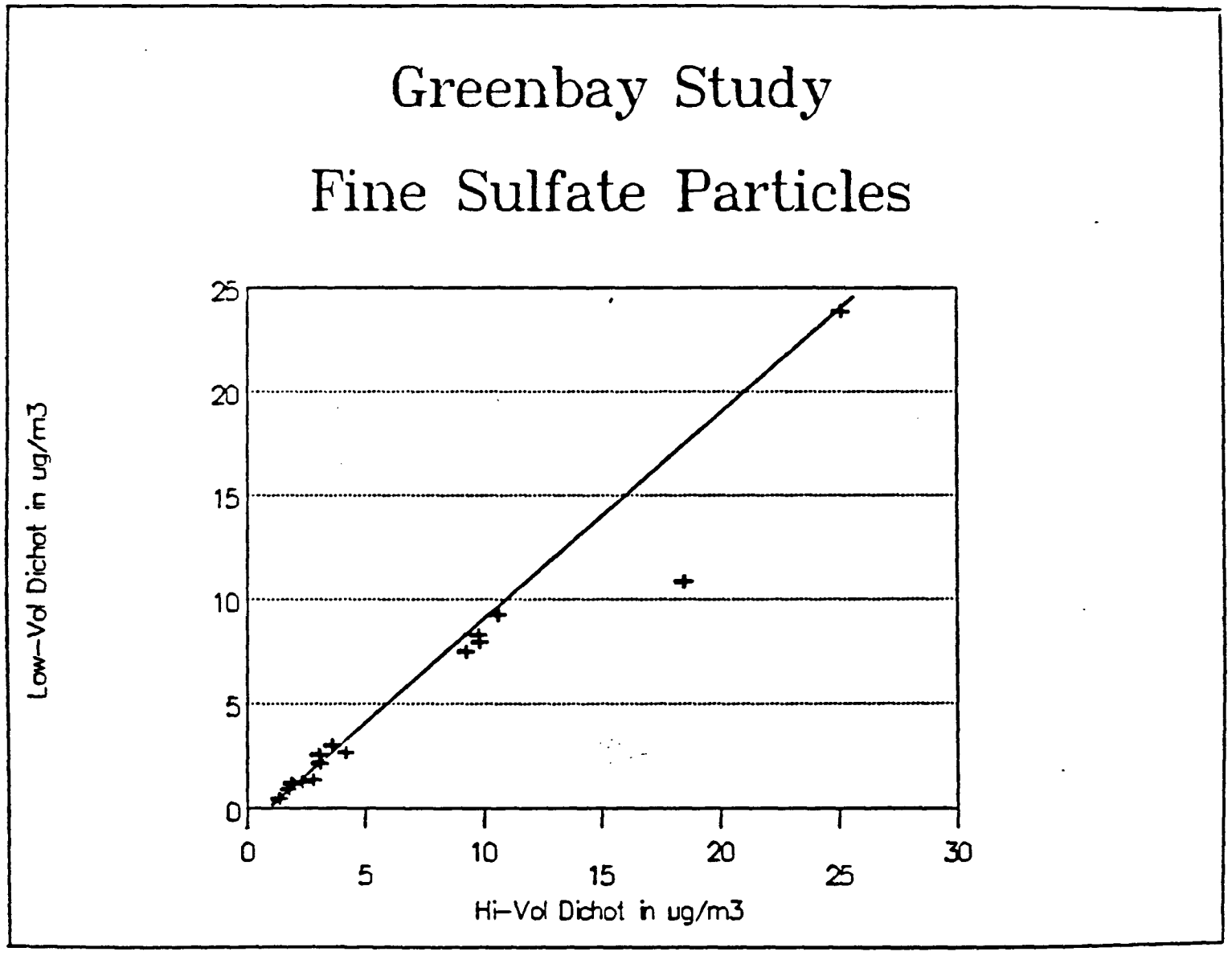


Figure 6-6. Plot of low-volume versus high-volume dichotomous mass concentration. The slope of the regression line is 0.73, intercept 2.04 $\mu g/m^3$ and $R^2 = 0.77$.

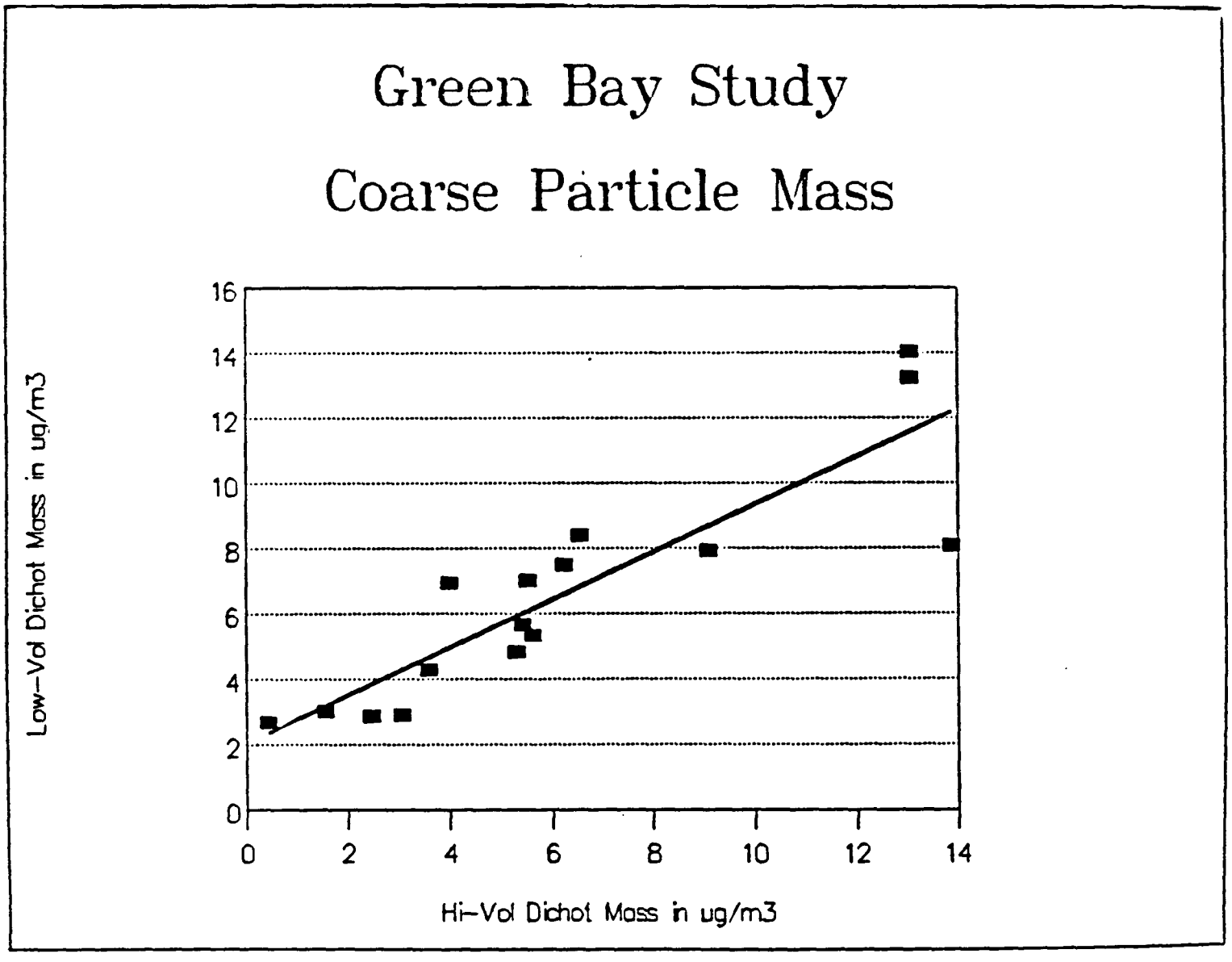


Figure 6-7 is a time series plot of the organic carbon present in the fine and coarse particles. There was about 1 1/2 times more organic carbon in the fine fraction than in the coarse fraction. However, during the last two sampling periods the coarse organic carbon exceeded the fine. This variation in organic carbon distribution between the fine and coarse fraction suggests the organic carbon in the fine and coarse particles may be from different sources. A substantial portion of coarse particle carbon is of a biological origin, as will be shown later in the microscopy analysis section.

Elemental carbon was 1/8 of the concentration of the organic carbon in the fine fraction. Elemental carbon in the coarse fraction was almost non existent. No carbonate carbon was present in fine fraction, since soil particles are the principal source of the carbonate carbon and soil is primarily found as coarse particles.

6.2.5 Ionic Composition

The ionic composition data for the sulfate, sulfite and nitrate for the fine and coarse particles are shown in Figures 6-8 and 6-9. Sulfate ion concentrations dominated the composition of the fine aerosols. Sulfite ions were found in both the fine and coarse particles. These are the first ambient air samples analyzed by AREAL that contain measurable amounts of sulfite. We assume sulfite is associated with the emission from the pulp and paper processing industry in the Green Bay area. Nitrate concentrations were relatively low and averaged 0.2 $\mu g/m^3$ for the fine and 0.3 $\mu g/m^3$ for the coarse particles.

Figures 6-10 and 6-11 show the relative concentration of the chemical species present in the fine and coarse particle fractions. In the fine fraction the dominate species was sulfate (36%), while in the coarse fraction minerals (45%) dominated. Organic carbon was the next highest in abundance in both fractions. However, coarse particle organic carbon was different than the fine particle organic carbon in that there was a substantial amount of biological particles (spores, pollen etc.) in the coarse fraction, wherease organic carbon in the fine fraction consisted of combustion products.

Figure 6-7. A time series of the organic carbon present in the fine and coarse fraction.

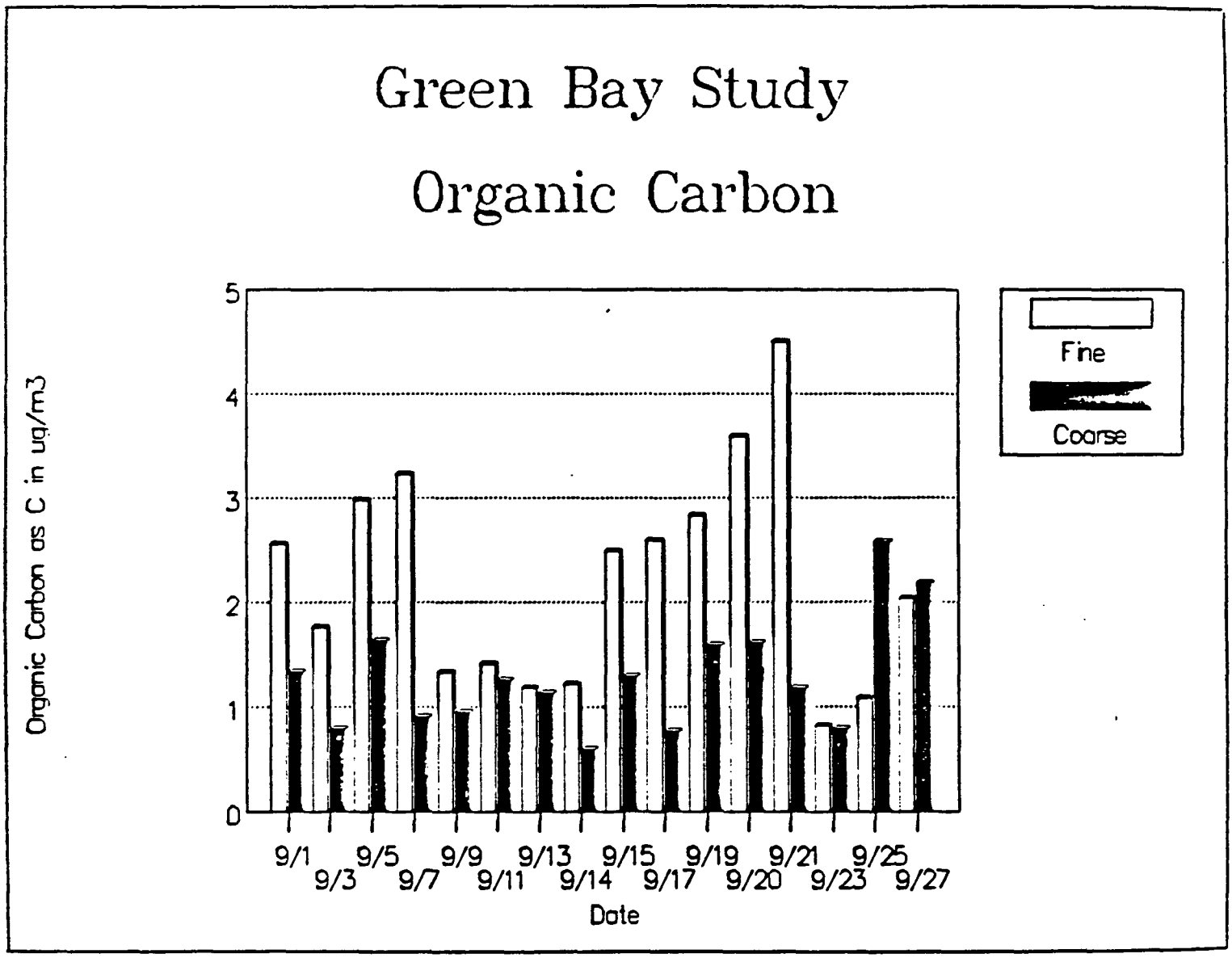


Figure 6-8. Ionic composition data for the sulfate, sulfite and nitrate for fine particles.

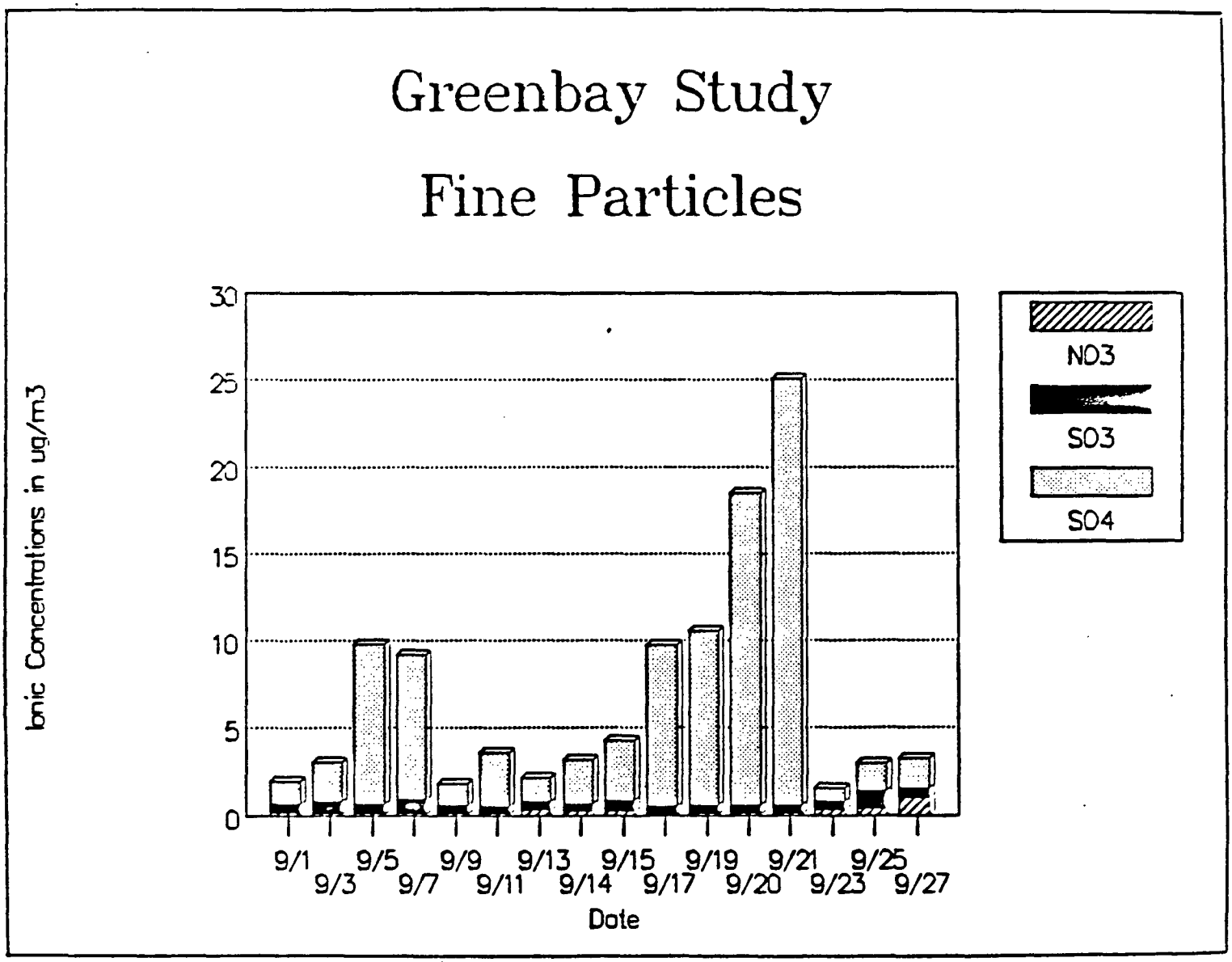
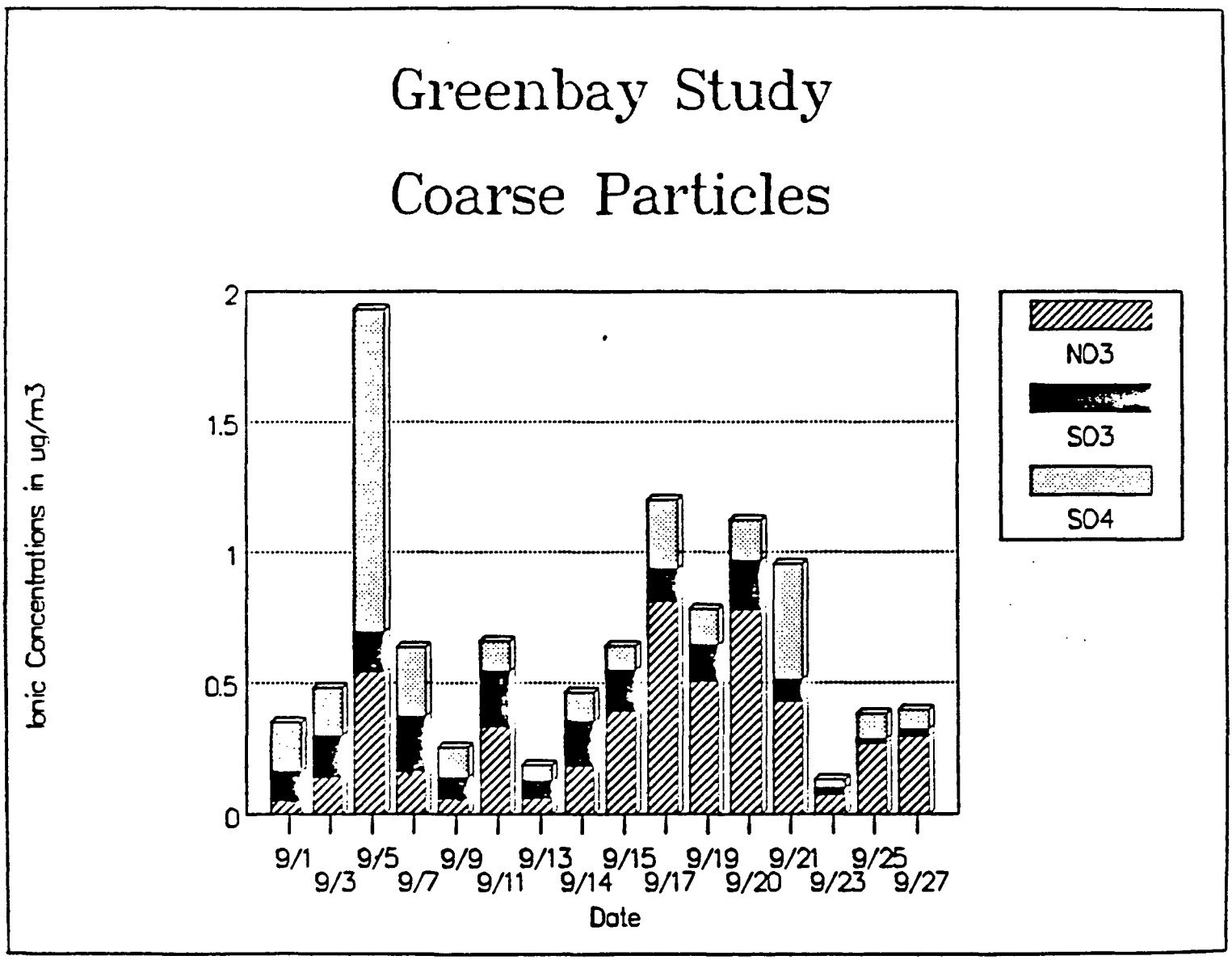


Figure 6-9. Ionic composition data for the sulfate, sulfite and nitrate for coarse particles (note the scale is different from that of Figure 6-8).



6.2.6 Annular Denuder Measurements

Annular denuder samples were collected for two periods during the study. Sampling times and results derived from these samples are shown in Table 6-15. The results in the table are expressed as $\mu g/m^3$ and $nmole/m^3$. Comparison with data in Table 6-13 indicates that the fine particle sulfate concentrations measured with the HVVI and the denuder samplers were in good agreement even though they were collected over slightly different periods. However, as shown in Table 6-13, the nitrate concentrations measured with the high volume dichotomous sampler were only a small fraction of the nitrate measured with the annular denuder. This is consistent with evaporation of nitrate from the high volume dichotomous quartz filter during sampling. This loss of nitrate with this type of sampler has been observed in previous studies. The molar ratio of the SO_2 is nearly unity, suggesting nearby sources of SO_2. There was very little acidity present in the fine particle samples. The presence of a few $\mu g/m^3$ of NH_3 measured with the denuder is consistent with the absence of acidic particles.

TABLE 6-15. ANNULAR DENUDER MEASUREMENTS COLLECTED AT THE UWGB SITE

DATE	Sept. 4-5, 1989		Sept. 5-6, 1989	
SPECIES	$\mu g/m^3$	$nmole/m^3$	$\mu g/m^3$	$nmole/m^3$
Gases				
SO_2	8.29	130	10.0	157
HNO_2	6.21	132	1.01	22
HNO_3	0.46	7.3	1.56	25
NH_3	2.47	145	3.54	210
Particles (<2.5μm)				
$SO_4^=$	8.14	85	11.3	118
NO_3^-	2.0	32	4.8	78
H^+		4.0		11.4

Figure 6-10. Relative contribution of various species (measured and calculated) to the total mass in the fine fraction.

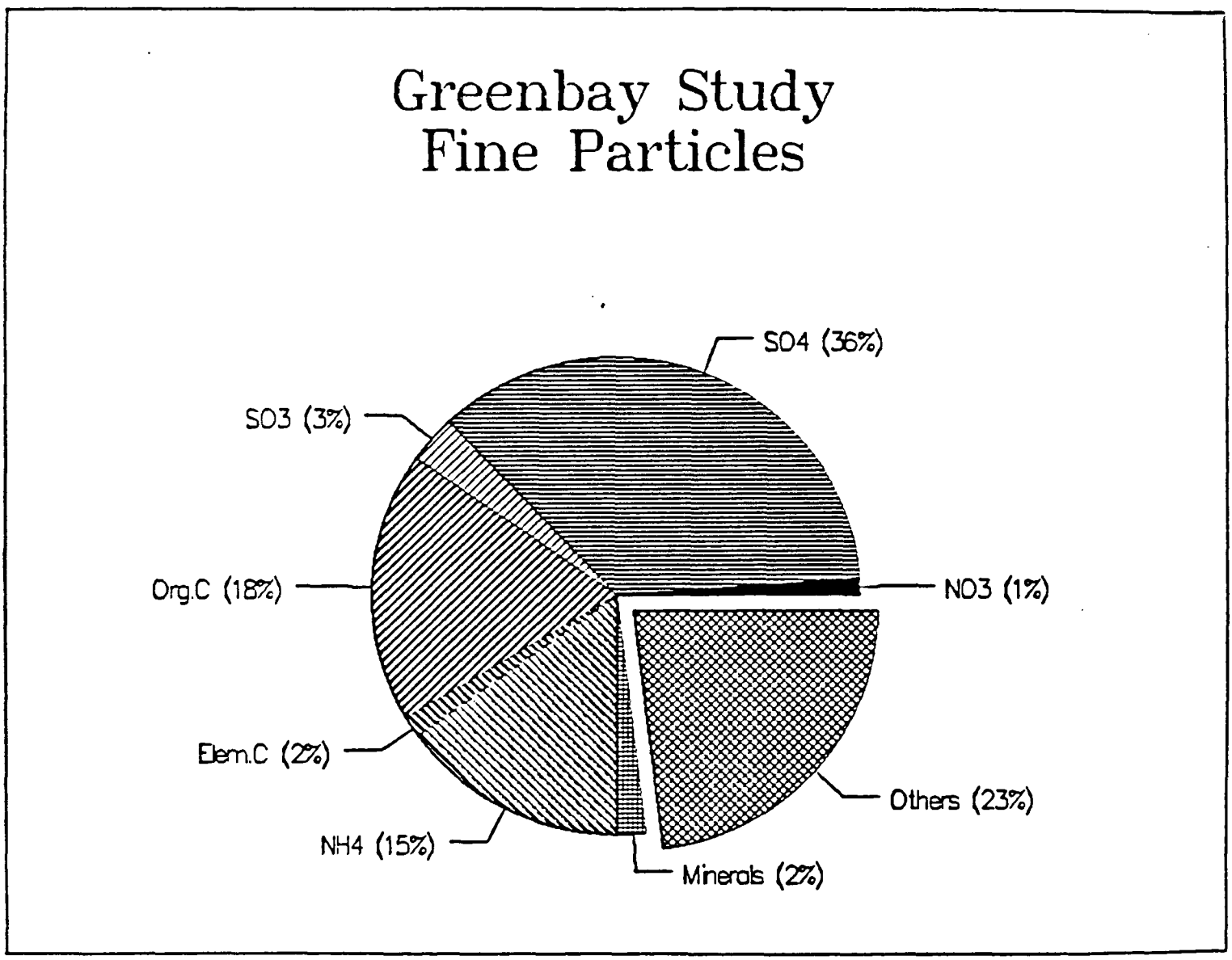
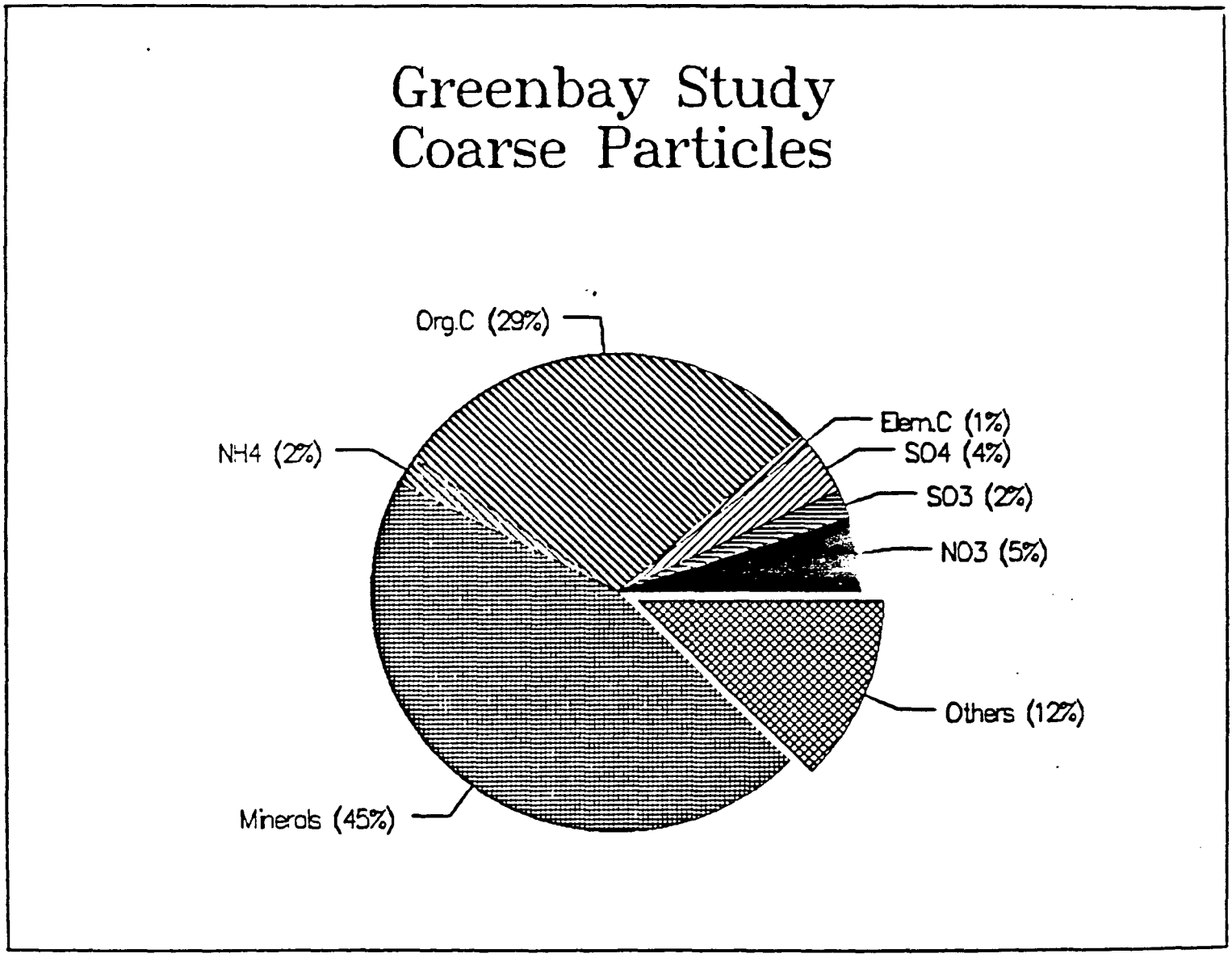


Figure 6-11. Relative contribution of various species (measured and calculated) to the total mass in the coarse fraction.



6.2.7 Scanning Electron Microscopy Analysis

Three sets of samples collected by a low-volume dichotomous sampler were analyzed using a scanning electron microscope (SEM) coupled with an x-ray energy dispersive analyzer (EDX). This analysis provides the size, morphology and elemental content of each individual particle within a defined field of view. The samples chosen represent different particle mass concentrations and meteorological conditions. For each sample, over 200 particles were analyzed in the coarse and fine fraction. Preliminary results for the Sept. 21, 1989 sample are presented in this report.

Figure 6-12 shows a typical field of view of particles in the coarse (top) and fine (bottom) fractions. Minerals and biological particles dominate the coarse fraction, while submicrometer sulfate particles completely dominate the fine fraction.

Table 6-16 shows the distribution of the coarse particles as a function of size and chemical composition. Based on particle counts silicates (alumino-silicates and quartz) represent 27% of the coarse particles and calcium containing particles represent another 25%. Some of the calcium particles were of anthropogenic origin (based on particle morphology). Particles that contain carbon, excluding calcium carbonate, (listed under minerals as Ca rich particles) include biological particles (17%) and non-volatile organic particles (9%). Particles of combustion source origin included sulfates, incinerator particles, fly ash, aluminum and iron-rich particles from metal industries. The presence of iron-rich particles in such large percentages is quite unusual for particles collected in this remote location. Figure 6-13 is a close-up photomicrograph of an iron sphere and spores (biological). The submicrometer particles lying on the Teflon filter fibers are fine sulfate particles (0.1-0.5 μm) that are also collected by the coarse filter. Figures 6-14 and 6-15 are spectra of the iron sphere and the submicrometer sulfate shown in Figure 6-10. SEM analysis provided evidence that the carbon (excluding the carbon associated with mineral particles) in the coarse fraction is mostly associated with biological materials. On the

Figure 6-12. Photomicrographs of typical fields of view for coarse (top) and fine (bottom) fraction collected on Sept. 21, 1989. Note that magnifications are different.

TABLE 6-16. CHEMICAL-SIZE DISTRIBUTION OF COARSE PARTICLES COLLECTED ON SEPTEMBER 21, 1989, IN GREEN BAY

Particle Category	Particle Size Distribution <-1.5 μm	<-2.1 μm	<-3.1 μm	<5.1 μm	<-7.1 μm	<-10 μm	Total Count
Minerals:							
Al-Si		4	21	11	6	1	43
Quartz		2	8	11	4		25
Ca		5	4	6	2		17
Ca+Mg		1	6	17	1	1	26
Ca-S		4	9	5	1		19
Others			1	2		1	4
Biologicals		2	12	18	9	1	42
Organics	1	6	6	8	1		22
Fly ash	2	2		1	1		6
Al-rich			1	1	1		3
Fe-rich	7	7	5	5			24
Incinerator		1	2	1			4
Sulfates	1	4	4				9
Others	2		2				4
Total	13	38	81	86	26	4	248

.icrograph of coarse particles showing an
pores linked to each other.

← Correct Picture(s)

Figure 6-14. X-ray spectra of the iron sphere shown in Figure 6-13.

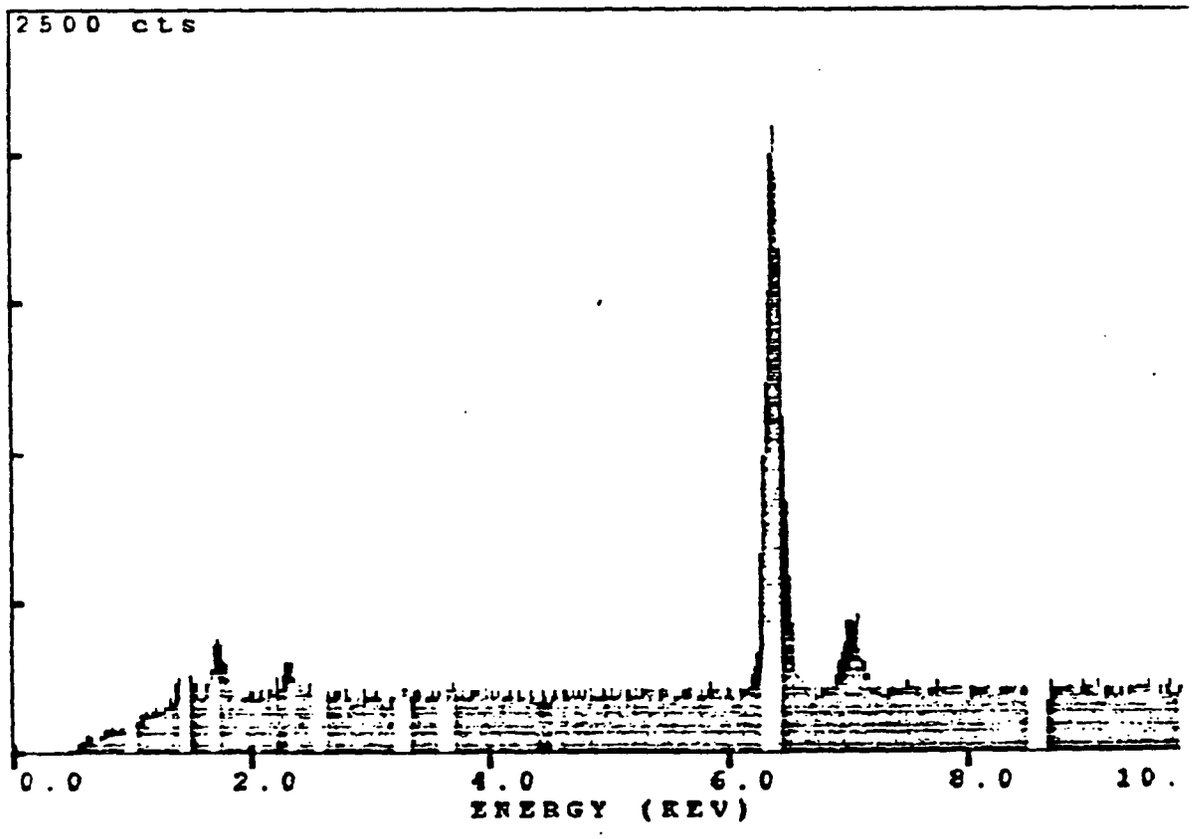
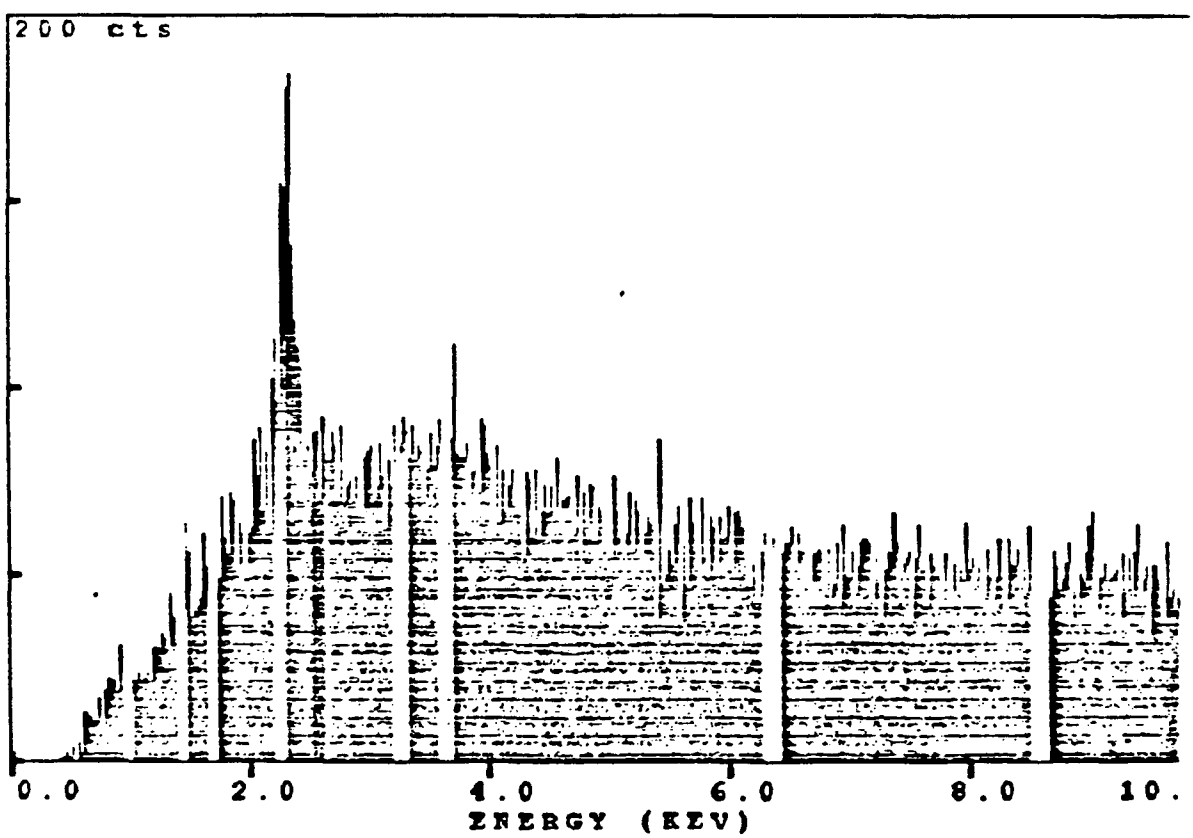


Figure 6-15. X-ray spectra of a submicrometer sulfate (round greyish particles lying on the Teflon fibers) particles shown in Figure 6-13.



other hand the carbon in the fine fraction is linked to emissions from combustion sources.

6.2.8 Source Apportionment by CMB

The chemical mass balance model for source apportionment was applied to chemical species data obtained by XRF and pyrolysis. In this model, the measured concentration C_i of species i is represented as the sum

$$C_i = \Sigma S_j A_{ij} + \epsilon_i$$

where A_{ij} is the abundance of species i in the emission from source j, S_j is the mass concentration due to emissions from source j, and ϵ_i is the residual that represents the difference between the measured and calculated concentrations. This equation is solved for S_j by minimizing v^2 in the expression

$$v^2 = \Sigma \epsilon_i^2 / E_i^2$$

where E_i^2 is the effective variance, which represents uncertainty in both C_i and A_{ij}. The species used in the v^2 minimization were C_v, C_e, Si, S, Ca and Zn. In years past Pb was also included in such CMB analyses because it was an excellent tracer for vehicle exhaust. However, due to recent laws that mandate the reduction of Pb in gasoline, Pb is no longer a useful tracer for vehicle exhaust.

I don't believe their Zn values

The CMB model was applied to data for the average of all samples from September 2-27, 1989, and was also applied to samples collected on September 19-21, when Zn concentrations were unusually high. The following components were included in the CMBs for fine particles: regional background, vehicle exhaust, sources of volatilizable carbon, incinerator emissions and soil. The signatures (A_{ij}) for these components are described below.

? *The analysis of all 6 Zn samples done by RTP for the acid spiked samples were biased high when compared to our data.

<u>Regional Background</u>: This component represents a regional background that is rich in sulfate and related anions and is the predominant constituent

of fine particles in the eastern half of the U.S. The species abundances for this component represent the average fine particle composition measured at six rural sites: Great Smoky Mountains; Shenandoah Valley; Deep Creek Lake, MD; and three rural sites along the Ohio River in Kentucky, Indiana, and Ohio. The source profile includes S, Cl, K, Mn, Zn, Se, and crustal elements (Al, Si, Ca, Ti, and Fe). The source profile does not include species from vehicle exhaust (C_v, C_e, Br and Pb).

Incinerator Emissions: On three of the sampling days (September 19-21) the ambient concentrations of Cl, K, and Pb in fine particles were 2 to 3 times higher than their average values. These elements are characteristic of incinerator emissions. Confirmation that one or more incinerators produced such a combination of elements was provided by SEM analysis, which detected these elements in individual particles collected on September 21. The CMB signature used was Profile Number 17108 from EPA's Addendum to the Air Emissions Species Manual (EPA-450/2-88-003c), which represents emissions from a large municipal incinerator in Philadelphia measured in 1982.

Soil: A global average for crustal shale was used to represent the soil component.

Vehicle Exhaust: The source signature used was Profile Number 33011. This profile is a composite of several individual profiles and represents highway traffic that includes diesel and gasoline powered vehicles. The abundances of C_v and C_e were 41.3% and 46.5%, respectively. The C_v/C_e ratio is sensitive to the percent of diesel powered vehicles in the vehicle population.

Volatilizable Carbon Sources: Of all the signatures only vehicle exhaust has major amounts of carbon. Because the ambient data indicate that there is about eight times more C_v than C_e, the vehicle signature, for which the C_v and C_e abundances are about equal, cannot alone account for all of the carbon. Therefore, two other signatures with high C_v abundances were considered. One was Profile Number 42306, which represents slash burning of conifers in the smoldering burn phase. Such emissions would have been present if there were a construction site in Green Bay where pine trees were recently cleared and were

being burned in a pile. The other one considered was Profile Number 22301 in EPA's Receptor Model Source Composition Library (EPA-450/4-85-002), which represents emissions from a veneer dryer used in manufacturing plywood. It is even possible that the volatilizable carbon measured in Green Bay was from vehicles. That would be the case if the composite profile that we used included too many diesel and too few gasoline powered vehicles.

CMB Results. Since it was not known which types of sources contributed to the volatilizable carbon measured in Green Bay, two separate CMB analyses were made for fine particles. In the first the slash burn signature was used to represent volatilizable carbon, and in the second the veneer dryer signature was used. The results were averaged and are shown in Figure 6-16. Due to ambiguity in the origin of the component for volatilizable carbon, vehicle exhaust and volatilizable carbon emissions are shown in Figure 6-16 as a single component that accounts for 25% of the measured fine particle mass concentration.

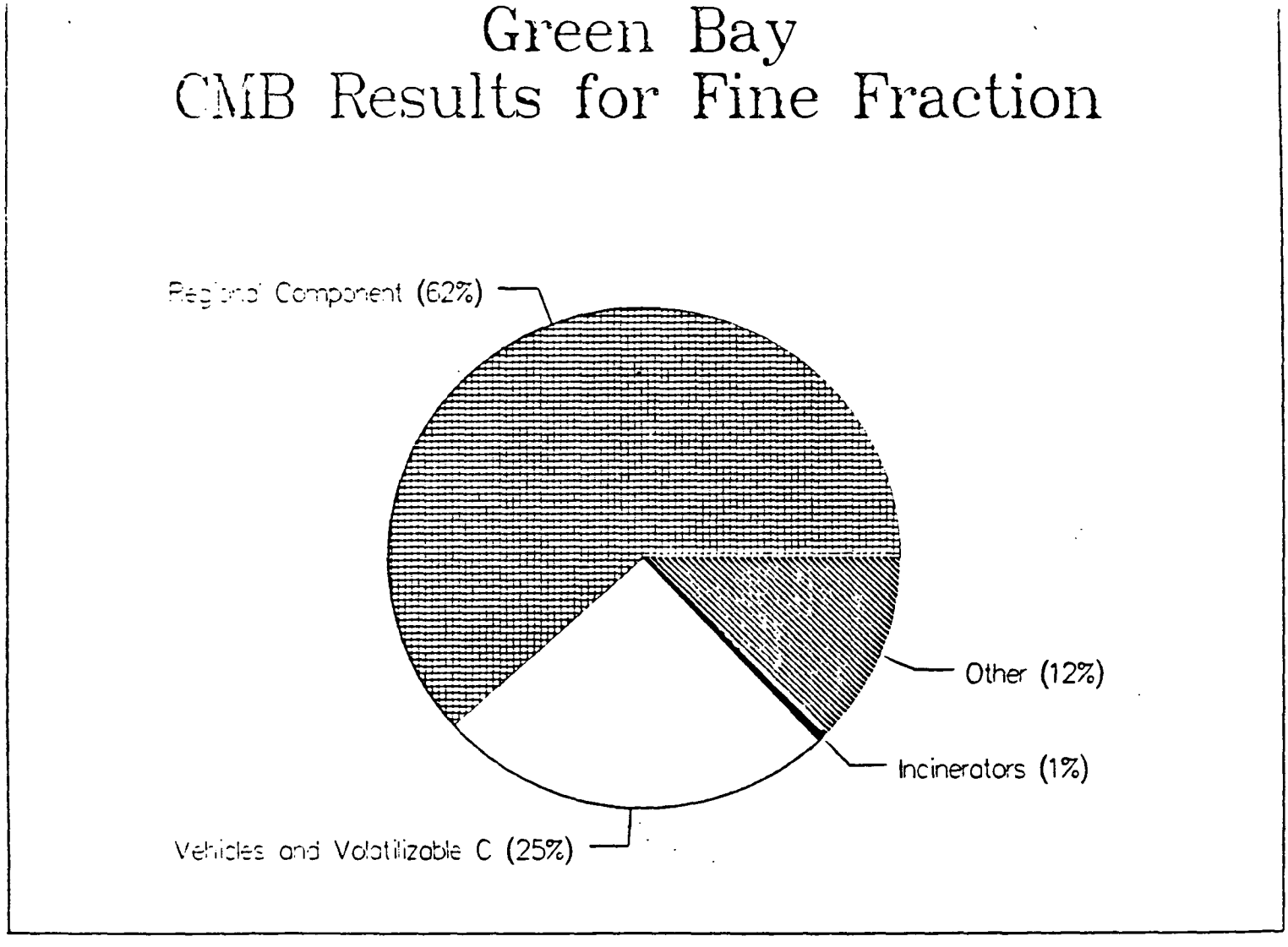
The large regional component accounts for 61% of the measured fine particle mass. It is unlikely that local sources contribute significantly to this component. The amount of crustal elements in the regional component was sufficiently large that the separate soil component was not detected in the CMB analysis. Even though there were several incinerators in the Green Bay area, (the closest on to the sampling site is a municipal sludge incinerator 5 miles distant) the incinerator component contributed only 1% to the average measured mass. The component labeled "other" represents the difference between the measured and calculated fine fraction mass.

Source Apportionment by Multiple Linear Regression (MLR)

A frequently used alternative to CMB source apportionment is MLR. The MLR approach attempts to express the measured mass concentration M_k for sampling period k as a sum

$$M_k = \Sigma a_j C_{jk} + \epsilon_k$$

Figure 6-16. Components of average fine fraction mass deduced by CMB model for samples collected from September 1 to 27, 1989.



where C_{jk} is the measured concentration during sampling period k of a species which is a tracer for the emissions from j, $1/a_j$ is the abundance of the tracer in the emissions from source j, and ϵ_k is the residual that represents the difference between the measured and calculated mass concentrations. Each term in the sum is the product of two factors (one measured and one unknown), and is the calculated contribution to M_k from each source. Each term a_jC_{jk} directly corresponds to the quantity S_j in the CMB approach. The equation is solved for the a_j values by minimizing a v^2 expression similar to the one used in CMB.

Only limited success was realized in applying the MLR approach to the Green Bay data set. The reasons are readily identified:

1. Only 16 sampling periods of complete data were available. Experience has shown that approximately three times this number are needed to obtain stable results with MLR.

2. The sampling periods were of 24-hr duration, whereas experience has shown that 12-hr durations are better suited to the MLR method. This is because variability between samples (upon which multivariate methods depend) tends to be increased by diurnal conditions.

3. The measured species did not include enough tracers of the sources of interest. For example, until very recently Pb or Br were reliable tracers of mobile source emissions, even for those vehicles which did not use leaded gasoline. The virtual disappearance of leaded gasoline from the U.S. market however, which has occurred in recent months, has dramatically changed this so that other sources are now likely to dominate these elements. Indeed, when these two elements were alternatively tried in MLR analyses of the data set there was no consistency between the two analyses.

Similarly, for the incinerator component, it was not possible to identify any measured species that was uniquely associated with this source category for use as a tracer.

The one species that seemed to be a useful tracer was sulfate ion, as a tracer of the "regional" component discussed in the CMB analysis. While not surprising, neither is it a trivial result. That is, when sulfate was used as a tracer species, the impact of the regional component (the product of the measured sulfate concentration and its regression coefficient) was similar to the 61% found in the CMB analysis. This was consistently the case whether sulfate was the only tracer in the MLR or whether other tracer variables were used with it.

The measurement of sulfite (SO_3) in the fine particle mass was a significant finding, marking the first time we have seen this ion in consistently measurable amounts in ambient air. This is very likely a result of sulfite emissions from the several pulp and paper plants in the Green Bay area. In principle, sulfite should be a possible tracer for this category of emissions. In practice, however, sulfite is unstable (in comparison with sulfate) both in the atmosphere and after it is collected in a sampler, so that the amounts reported can only be considered a lower limit for what existed in the atmosphere. Steps can be taken to preserve the integrity of sulfite samples, and any future work contemplated for this region should implement the necessary sampling and analytical changes to accomplish this.

Finally, a better quantification of the motor vehicle impact would require a comprehensive volatile organic compound (VOC) sampling component. Recent work in our laboratory has shown the usefulness of several particular VOC species as motor vehicle tracer replacements for Pb and Br. Measurement of VOCs is of course also needed to assess the organic burden which this air pollutant category places on the Great Lakes through deposition.

APPENDICES

APPENDIX A. AREAL Sampling Procedure for Dichotomous Samplers

APPENDIX B. AREAL Sampling Procedure for Hi-Volume Virtual Impactor

APPENDIX C. AREAL Sampling Procedure for PUF/PS-1

APPENDIX D. AREAL Sampling Procedure for VOC Samplers

APPENDIX E. AREAL Sampling Procedure for Hi-Vols

APPENDIX F. List of VOC Compounds Analyzed

APPENDIX G. Dioxin/Furan Analysis Procedures and QA Plan

APPENDIX H. Results of ISWS Lab Audit

APPENDIX I. Results of CRL/Bionetics Lab Audit

APPENDIX J. Dioxin/Furan Analysis and QA/QC Results

APPENDIX K. XRF Analysis Results

XRF data for all fine and coarse particle samples collected at the Green Bay site during September 1989.

XRF DATA FOR GREEN BAY
SEPTEMBER 1, TO 27. 1989

Input files for this run of LSQDRX

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BLANK  #1 -  \XDATA\BLANK\SB1215.BF1

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SHAPES #3 -  \XDATA\SHAPE\SHAPES.SH3
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SHAPES #4 -  \XDATA\SHAPE\SHAPES.SH4
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Fine attenuation file    :  \XDATA\ATTEN\ATFINE.DAT
Coarse attenuation file  :  \XDATA\ATTEN\ATC.DAT
X11 data file            :  XLL.DAT
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