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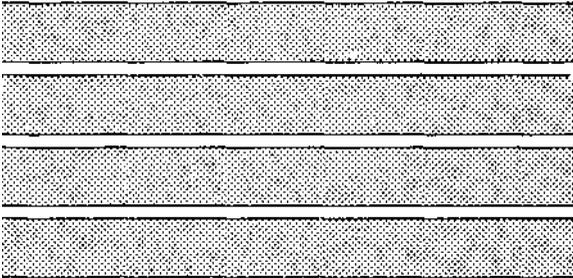
Atmospheric Deposition of Toxic Materials: A Component of the Green Bay Mass Balance Study

by Clyde W. Sweet, Stephen J. Vermette, and Donald F. Gatz
Office of Air Quality

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1. INTRODUCTION

1.1. BACKGROUND

Since high levels of polychlorinated biphenyls (PCBs) were discovered in certain Great Lakes fish in 1973, the impact of their presence in the Great Lakes on human and ecosystem health has been a topic of concern. Use and manufacture of PCBs were banned in the United States in the mid-1970s. It is difficult to determine trends in PCB levels since that time because the analytical and sampling methods for PCBs have changed so that recent data are often not directly comparable to older data. However, recent estimates of PCBs in lake water (Swackhamer and Armstrong, 1987) and in Great Lakes fish (Clark et al., 1984) are generally lower than those made in the early 1970s. In spite of these improvements, some Great Lakes fish still contain more than the 2 μg/g of PCBs allowed under current Food and Drug Administration rules. Current levels of PCBs are also suspected of decreasing the breeding success of many fish-eating birds on the shores of the Great Lakes (Kubiak et al., 1989).

There is good evidence based on a few temporally and spatially scattered measurements (Murphy and Rzeszutko, 1977; Swain, 1978; Strachan, 1985; Swackhamer et al., 1988; Chan and Perkins, 1989) that the atmosphere is an important source of PCBs in the Great Lakes. Based on data accumulated in the 1970s, Eisenreich et al. (1981) estimated that 60 to 90% of the PCBs entering Lakes Michigan, Huron, and Superior were due to inputs from the atmosphere. Even Lake Ontario, which has very significant inputs of PCBs from the Niagara River, is estimated to have received 33% of its annual PCB input from the atmosphere in 1965 (MacKay, 1989). Both wet deposition in rain and snow and dry deposition of airborne particles are important mechanisms for the movement of PCBs from the atmosphere into the lakes. Vapor phase PCBs can also enter the lakes in dissolved form in precipitation and by direct absorption at the water surface.

1.2. GOALS AND OBJECTIVES

The primary goal of the work reported here was to provide improved information on atmospheric loadings of PCBs and dieldrin to Green Bay as part of the U.S. Environmental Protection Agency's (U.S. EPA's) Green Bay Mass Balance Study.

A secondary goal was to develop improved sampling and analytical methods for measuring selected toxic organic compounds in air and precipitation in preparation for establishment of the Integrated Atmospheric Deposition Network (IADN) (IJC, 1988). The IADN is a cooperative effort by the United States and Canada in support of the Great Lakes Water Quality Agreement between the two nations.

Objectives in support of these goals included:

1)	Establishing and operating a master atmospheric deposition measurement station and two routine stations on the shores of Green Bay,

2)	Collecting and analyzing samples of air and precipitation from the three Green Bay sampling sites,

3)	Establishing an analytical laboratory at DePaul University (carried out by Dr. Tom Murphy under a separate but related grant), and

4)	Transferring the analytical technology developed under objective (3) to the Illinois State Water Survey at the end of the Green Bay Mass Balance Study.

In this report, concentrations of PCBs and dieldrin measured in air and precipitation between 1988 and 1989 around Green Bay are presented, and deposition into the bay from the atmosphere is estimated. Summaries are also presented of meteorological data and of atmospheric concentrations of total suspended particulate matter and total nonvolatile carbon.

## 2.	METHODS

## 2.1.	FIELD METHODS

### 2.1.1.	Sampling Sites

The locations of the three air and precipitation monitoring stations along Green Bay are shown in Figure 1. The southern site is on the University of Wisconsin - Green Bay (UWGB) campus, 2 km east of the city of Green Bay. A second site was located at Peninsula State Park, midway up the east shore of the bay in Door County, Wisconsin. The third site, at the northern end of the bay, was at Fayette State Park in Michigan's upper peninsula. At each site, air samples were collected when the wind was coming from predetermined sectors. Three sectors were sampled at UWGB: a northerly sector (300° -20°), sampling air coming off the bay; a southwesterly sector (210° -270°), sampling air that had passed over the urban/industrial zone of the city of Green Bay; and a southeasterly sector (110° -180°), sampling air from a rural inland area. At the Peninsula site, northwesterly (240° -30°) and southeasterly (60° -190°) sectors sampled air coming off the bay and air off the lake proper, respectively. Finally, at Fayette, northerly (300° -60°) and southerly (90° -270°) sectors were sampled, corresponding to lake and overland trajectories, respectively.

Fayette State Park (MI)

Peninsula State Park (WI)

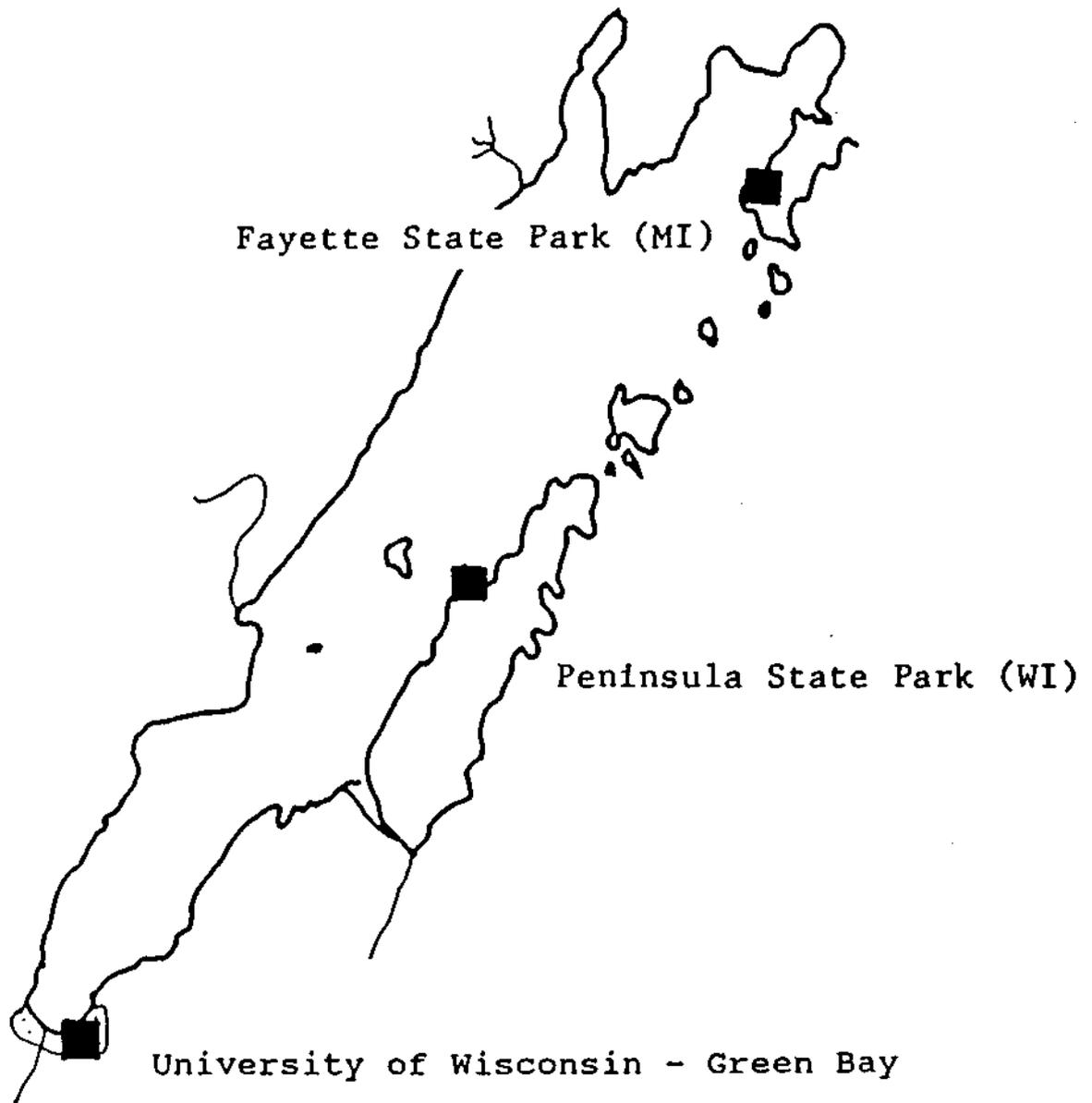University of Wisconsin - Green Bay

Figure 1. Map of sampling sites

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2.1.2. Sample Collection Methods

Table 1 summarizes the types and numbers of samplers operated at the sampling sites. This section describes the equipment and sampling methods. Copies of the site operators' instructions and a sample data sheet are attached in Appendix A.

Precipitation was collected using a commercial version (MIC, Thornhill, Ontario) of a wet-only sampler developed by the National Water Research Institute in Canada (Strachan and Huneault, 1984). It was modified for all-weather operation by enclosing and insulating the space underneath the sampler. The temperature in the enclosure was maintained at 10 to 15° C by a small space heater. This also provided sufficient heat to the Teflon™-coated catch basin to melt collected snow in the $0.212 \ m^2$ collection area. Rain or melted snow passes by gravity flow through a 30-cm column containing about 15 g of cleaned XAD-2 resin. Glass wool plugs before and after the XAD-2 resin trap the particles in the sample. The end of the outlet tube from the column was held at a position above the level of the XAD-2 resin so that the resin remained wet throughout the sampling period. The sampler is illustrated in Figure 2. Samples were taken at 14-day intervals. Early in the project, the collection surfaces were rinsed with methanol. Later, deionized water was used for the rinse, and the collection surface was also wiped with a small piece of glass fiber filter to remove any adhering particles. These rinsings were added to the extracts of the resin and glass wool plugs.

Air samples were collected using a standard high-volume sampler (General Metal Works, model GS2310, Village of Cleves, Ohio) modified with an aluminum tube behind the filter holder and ahead of the motor (Figure 3). This tube holds a stainless steel cartridge 8.7 cm in diameter and 4.4 cm thick containing 45 g of cleaned XAD-2 resin. The standard motor was replaced with a two-stage Lamb motor (Ametek-Lamb, model 115937, Kent, Ohio) that maintained a flow rate of 34 m^3/hr through one or two resin cartridges. These samplers were also fitted with automatic filter covers (General Metal Works, Sample Saver, model G8550). Particles were collected on glass fiber filters (Whatman EPM 2000) or using a four-stage cascade impactor (Andersen Samplers, model 234, Atlanta, Georgia). These samplers only operated when the wind was blowing from a predetermined sector. Typically samples were collected over a 14-day period. A sampler was activated when the wind was within the sector for at least 1 minute and the wind speed was above 1.5 (km/hr). Sample sizes were generally 1000 to 5000 m^3, and all were greater than 200 m^3.

Samples of airborne particles were also taken using a standard high-volume sampler at a flow rate of 68 m^3/hr for determination of total suspended particles (TSP) and nonvolatile organic and elemental carbon (NVOEC).

Table 1. Samplers Operated at the Green Bay Monitoring Sites

Sampler	Number (Master, Routine)	Sampling Frequency	Sample Duration	Sampling Media	Analysis
MIC	3,1	1/14 days	14 days	XAD-2	PCB's, dieldrin
TSP Hi- vol	1,1	1/6 days	24 hrs	8x10 GFF	Mass, NVOEC
Modified Hi-vol	3,2	1/14 days	14 days (wind directed)	8x10 GFF XAD-2	PCBs, dieldrin
Cascade Impactor	1,1	1/3 mos.	14 days	Impactors GFF	Particle sizing, PCBs, dieldrin
Wind speed/ direction	1,1	continuous	continuous	—	—
Temp., RH, SR	1,1	continuous	continuous	—	—
Rain	1,1	continuous	continuous	—	—

Note: RH = relative humidity, SR = solar radiation, GFF = glass fiber filter, NVOEC = nonvolatile organic and elemental carbon, MIC = Meteorological Instruments Co. (precipitation collector).

The first figure in the "number" column is the number of samplers at the Green Bay site and the second figure is the number of samplers at the Fayette and Peninsula sites.
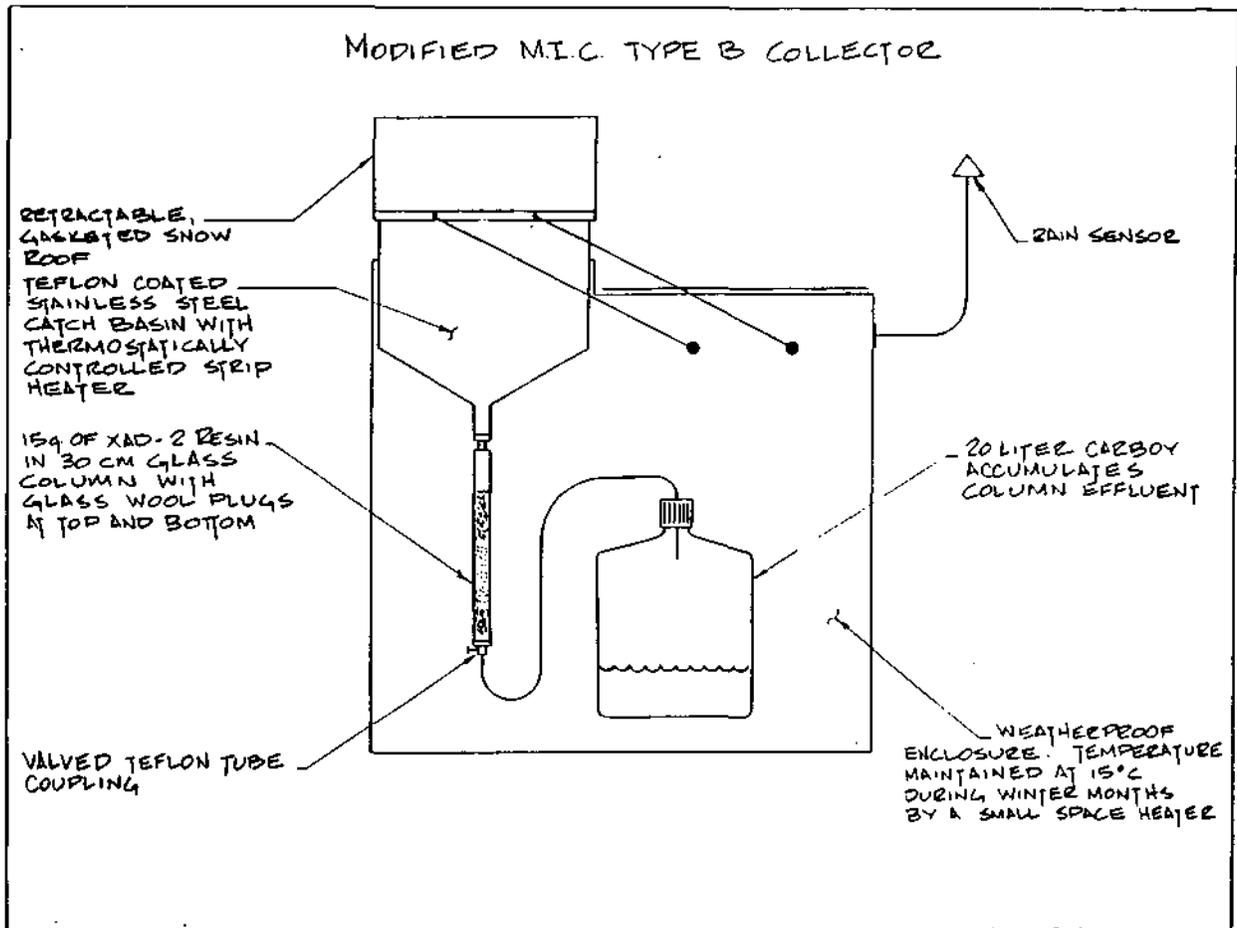
Figure 2. Schematic diagram of MIC precipitation collector

Modified Andersen High Volume Air Sampler

Whatman N° EPM 2000 Glass Microfiber Filter Positioned in an Andersen Model 43000 Filter Paper Cartridge.

Aluminum All-Weather Shelter

Resin Cartridge, Motor Mount and Detachable Air Duct designed by The Ministry of the Environment, Toronto, Ont, Canada

Stainless Steel Resin Cartridge with 45g of XAD-2 Resin

Ametek Lamb Mod 115437 Vacuum Motor. The System Flow Rate is 20 CFM and is Controlled by an Andersen Mod. 313 Flow Controller
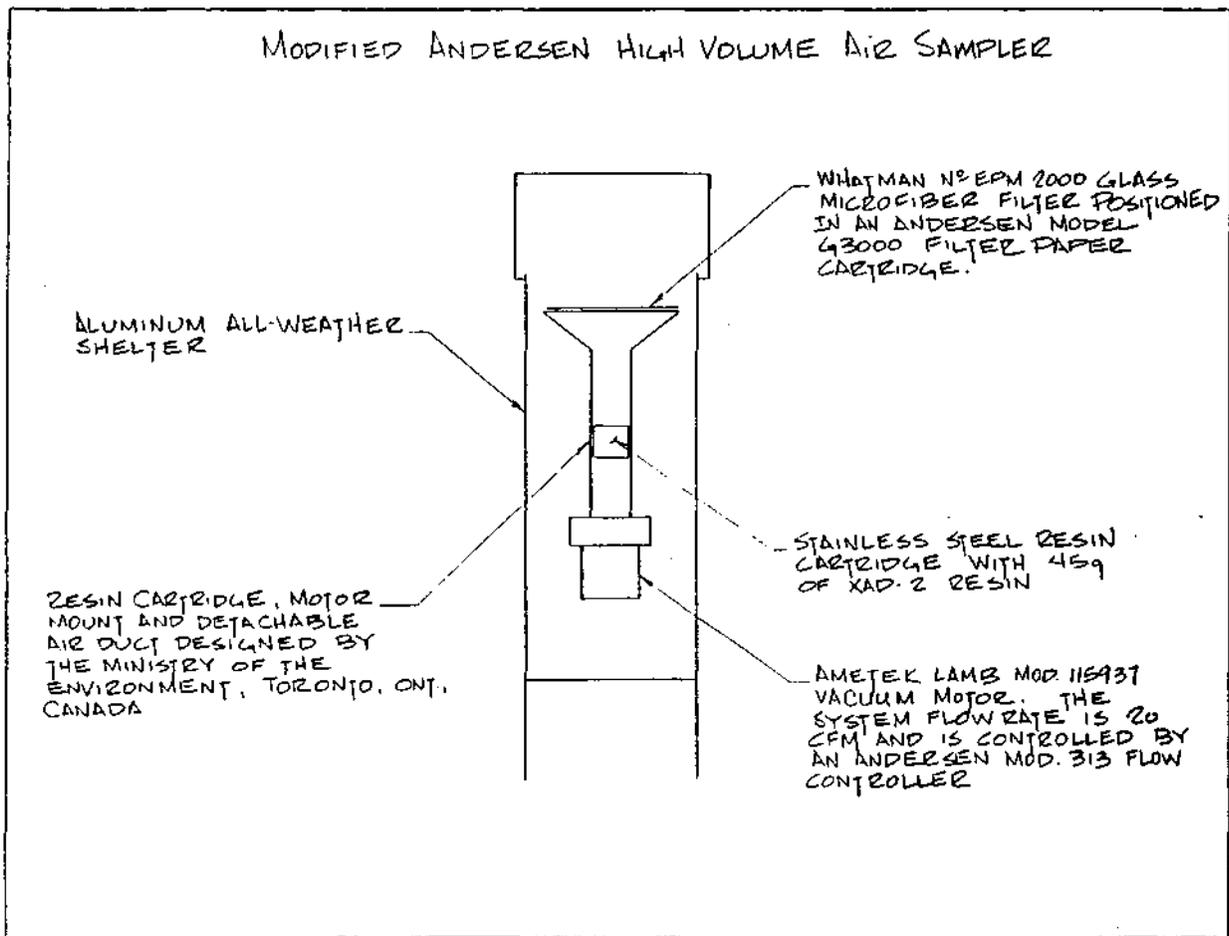
Figure 3. Schematic diagram of modified high volume air sampler

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2.1.3. Sampling Schedule

This section describes operation of the three-site network from November 1988 until May 1990. The sites were operated on a biweekly sampling schedule. All resin columns, air cartridges, and air filters were changed every other Tuesday when the meteorological data tape was also changed.   The buckets on the Belfort rain gauges were emptied weekly, if needed.   The TSP/NVOEC sampler took a 24-hour sample on the six-day U.S. EPA schedule, and the cascade impactor sample collected a seven-day sample on an occasional basis (approximately quarterly).

The three MIC samplers at the master site were used to take biweekly duplicate and field blank samples. The modified high-volume samplers were operated on a wind-directed basis by the Campbell data logger.   Each sampler operated only when the wind direction was from a predetermined sector.

2.1.4. Calibration and Quality Control

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

The air sampling equipment was operated and calibrated according to the manufacturer's recommendations.   Flow rates of the high-volume samplers were calibrated quarterly using a standard General Metal Works manometer. The samplers with resin cartridge vapor traps were set at 566 L/min (20 ft^3/min), and the TSP/NVOEC high-volume sampler was set at 1133 L/min (40 ft^3/min).   A small reference manometer was used as a qualitative check to verify normal operation between calibrations. The meteorological monitoring equipment was calibrated during the initial set-up. The meteorological sensors on the meteorological tower (solar radiation, wind speed, wind direction, temperature, and relative humidity) were returned to the manufacturer annually for recalibration. Where standard methods have been established, such as for TSP and NVOEC measurements, the standard procedures of the American Society for Testing and Materials (ASTM, 1990) were followed.

2.1.5. Meteorological Observations

2.1.5.1. Instrumentation and Schedule

Aside from the high-volume and MIC precipitation samplers, each of the three sites (Green Bay, Peninsula, and Fayette) was equipped with meteorological instrumentation. The purpose of this instrumentation was to develop a site-specific weather database, as well as to control the wind-directed air samplers (based on wind speed and direction), to verify the proper operation of the MIC precipitation collector, and to determine the state of precipitation (rain or snow). Equipment mounted on a 10 m tower included a solar radiation sensor (LI 200S pyranometer, LI-Cor,

Lincoln, Nebraska), temperature and humidity sensors (Campbell Scientific, Logan, Utah) and wind speed and direction sensors (Met-One cup anemometer and wind vane, Grants Pass, Oregon). Each site was also equipped with a standard Belfort rain gauge (Belfort Instrument Co., Baltimore, Maryland), and a Belfort rain gauge fitted with a Nipher wind shield. Sensor outputs, including the rain gauges, were automatically recorded every six seconds by a Campbell 21X data logger (Campbell Scientific, Logan, Utah) which also calculated and recorded hourly averages. Stored information on the data logger was accessed bi-weekly on cassette tapes.

2.1.5.2. Calibration and Quality Control

The meteorological equipment was calibrated during the initial set-up and recalibrated either quarterly or yearly. The cup anemometer, wind vane, and pyranometer were returned to the manufacturer for calibration once a year. Relative humidity and temperature sensors were tested quarterly in a humidity chamber. Humidity was controlled using saturated solutions of salts with a humidity range of 25 to 99%. Belfort rain gauges were calibrated quarterly using the manufacturer's calibration-weight sets and instructions in the Belfort manual. Aside from the routine calibrations, operators made routine field checks to identify potential problems, such as the wind vane not pointing into the wind or the cup anemometer not rotating freely.

Beside the routine calibrations and field checks, the meteorological data were screened biweekly. The initial screening procedures ensured that the data were reasonable. For example, solar radiation should be zero between sunset and sunrise; relative humidity should not exceed 100% or be less than 30%; temperatures should be within seasonal ranges; and wind direction should be variable. The first screening identified any abnormalities that needed further evaluation. Further evaluation included reviewing site operator notes and data comparisons between sensors and sampling sites. For example, electronic data were routinely compared with chart data for precipitation. Data comparisons were also made between the standard gage and Nipher- shielded gage. An example of a useful, albeit unorthodox approach, was the use of the rain gauge charts to confirm periods of high winds. The rain gauge housing offers sufficient resistance during high winds to cause a vibration that is apparent on the recorded ink trace. Meteorological data that appeared unreasonable and could not be confirmed were treated as missing data.

2.1.5.3. Data Configuration

Meteorological data are maintained in a fixed field Rbase database on a personal computer. The fixed fields include:

>   Julian Date
>   Time (CST)
>   Year
>   Station I.D.
>   Temperature (degrees F)
>   Relative Humidity (%)
>   Solar Radiation (langleys)

Wind Speed (mph)
Wind Direction (degrees)
Precipitation   - Standard Belfort (inches)
                 - Nipher Shielded (inches)

Data are available as hourly averages and have been routinely distributed as monthly reports. A complete meteorological database is available on disk.

2.2.   ANALYTICAL METHODS

Between May 1988 and August 1989, all resin preparation and most of the sample analysis were done at DePaul University as part of a companion project (Murphy et al, 1991). After March 1989, the precipitation samples were analyzed at the University of Minnesota. Airborne particle and vapor samples collected between September 1989 and May 1990 were analyzed at the Water Survey laboratory. The methods described below were those used at DePaul University with a few minor modifications made at the Water Survey.

2.2.1. Materials

All chemicals, solvents, and materials used in the work-up of the samples were certified free of interfering contaminants or were cleaned up before use. Pesticide grade solvents (Burdick-Jackson or Omnisolve™) were used as received for all steps and procedures where solvent residues could be incorporated into the sample. Sodium sulfate, silica, and glass wool were baked at 450° C overnight before use.

The XAD-2 resin (2% cross-linked polystyrene, 16-50 mesh, Rohm and Haas, Philadelphia, PA) was used as the absorbent for both air and precipitation samples. The material comes wet from the manufacturer and contains salts and organic compounds that interfere with sample analysis. The first step in the clean-up procedure was to thoroughly rinse the XAD-2 resin with water to remove fine particles, salts, and other water-soluble contaminants. A soxhlet extractor holding about 0.8 L of XAD-2 resin was used. The water-rinsed XAD-2 resin was extracted for 24 hours each by the following pesticide-grade solvents in sequence: methanol, acetone, hexane, methylene chloride, hexane, acetone, and methanol. At least two blank determinations were run on each batch of XAD-2 resin. For air cartridges, the XAD-2 resin was oven dried at 65° C and stored at 4° C. For precipitation columns, it was exchanged to Milli-Q water and stored in amber bottles at 4° C.

2.2.2. Media and Sample Handling

Airborne particles were collected on high purity glass fiber filters (Whatman EPM 2000, Whatman Ltd., Maidstone, UK). For precipitation sampling, about 15 g of purified XAD-2 resin was packed in a 30-cm glass column. For air sampling, the water was drained off and about 45 g of resin was packed in cylindrical stainless steel cartridges, 8.6 cm in diameter and 4.2 cm high. Packed precipitation columns were sealed with Teflon™ caps, and air cartridges were

wrapped in aluminum foil and sealed in air-tight metal cans. Shipment of samples between the laboratory and field sites was by surface mail (2-5 days). Each sample was accompanied by a data sheet. After processing at the laboratory, samples were logged in and stored in air-tight containers at -18° C until analysis.

2.2.3. Work-up Procedures

The cartridges for the air samplers held about 40 g of XAD-2 resin. After exposure in the field, the XAD-2 resin was poured into a cellulose thimble. The recovery standard mixture was added, and the thimble was placed in a 500 mL soxhlet. The XAD-2 was extracted with 300 mL of a 1:1 mixture of hexane and acetone for 24 hours at about 10 minutes/cycle. The extract was concentrated by rotary evaporation to about 3 mL and then solvent exchanged to hexane with rotary evaporation.

The concentrated extract, about 3 mL, was chromatographed on 3% deactivated silica to remove most of the nontarget, interfering compounds. The PCBs were eluted in hexane and dieldrin in 40% methylene chloride in hexane. The volume of each fraction was reduced from 0.3 to 1 mL by rotary evaporation and nitrogen blowdown. The quantitation standard was added to the concentrated extract and the sample transferred to a gas chromatography (GC) vial and capped.

The wet XAD-2 resin from the precipitation samples was placed in a cellulose thimble with the recovery standard and soxhlet extracted with 300 mL of the hexane:acetone mixture for 24 hours. The water layer that forms during rotary evaporation of these samples was back-extracted three times with hexane. This extract was added to the solvent layer and further reduced in volume as described above.

At the Water Survey lab, another method for extraction of precipitation samples was used. Bulk precipitation samples were shipped to the Water Survey and extracted using C-18 Empore extraction disks (Analytichem International, Harbor City, CA). In this method, a recovery standard dissolved in methanol was added to the precipitation sample, and additional methanol was added to give a final concentration of 1%. After equilibration for 30 min, the sample was slowly (25 mL/min) passed over a Nuclepore™ filter impregnated with C-18 bonded phase silica. Both particulate matter and dissolved organics were removed by this process. The filters were extracted with hexane and then methylene chloride. Subsequent solvent removal, concentration and work-up steps were essentially the same as those described above. This method had a lower blank than the resin extraction method.

The retention time and response factor for each compound identified was based on the results from a standard mixture of 3 Aroclors™ (250 ng/mL of Aroclor 1232, 180 ng/mL of Aroclor 1248, and 180 ng/mL of Aroclor 1262) obtained from the U. S. EPA Environmental Monitoring and Systems Laboratory, Cincinnati. The composition of this standard mixture was specified by Mullin (1985). The sum of the PCB congeners in this mixture was 640 ng/mL. This mixture was used to determine the relative response factor for each of the PCB congener peaks. Dilutions of this standard were used to determine the linear range of the analyses and to determine the

instrumental detection limit. This standard together with the quantitation standard was injected with each group of samples as a daily check. A recovery standard mixture containing PCB congeners #14 (22.19 ng), #65 (4.74 ng), and #165 (4.76 ng) was added to each sample before the clean-up procedure to measure sample recovery.

2.2.4. Gas Chromatography

The samples were analyzed on a Hewlett-Packard (HP) 5890A gas chromatograph. All separations used 30 m, 0.25 mm i.d. silica capillary column with a 0.25 μm bonded silicone phase (DB-5, J&W Scientific, Ranch Cordova, California). The chromatographic conditions were optimized to get at least 50% resolution between International Union of Pure and Applied Chemistry (IUPAC) compounds #18 and #17. Typical conditions were: injector temperature (all temperatures are Celsius), 240°; detector temperature 375°; split flow, 50 mL/min; purge flow, 2 mL/min; CH_4/Ar make-up flow, 40 mL/min; He carrier flow, 1.32 mL/min at 80°; and injection volume, 1 μL. The temperature program was: initially 80°, 107min to 160°, and 2.5°/min to 280° held for 19 min.

The data were collected and reduced with an HP 3393A computing integrator. Compounds identified and quantitated via a calibration table using the method of internal standards, with the PCB congener IUPAC #204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) as the internal standard. The following were used as additional time reference standards: 1,3,5-tribromobenzene, IUPAC #30 (2,4,6-trichlorobiphenyl), and octachloronaphthalene. These four compounds constituted the quantitation standard (6 μL per sample), and the IUPAC #204 compound was present at 6 ng per sample for all GC injections. The data reports then listed the amount of each compound identified in the sample in ng per sample.

The retention time and response factor for each compound identified were based on the results from a standard mixture of 3 Aroclors™ (250 ng/mL of Aroclor 1232, 180 ng/mL of Aroclor 1248, and 180 ng/mL of Aroclor 1262) obtained from U. S. EPA/EMSL, Cincinnati. The composition of this standard mixture was specified by Mullin (1985). The sum of the PCB congeners in this mixture was 640 ng/mL. This mixture was used to determine the relative response factor for each of the PCB congener peaks. Dilutions of this standard were used to determine the linear range of the analyses and to determine the instrumental detection limit. This standard together with the quantitation standard was injected with each group of samples as a daily check. A recovery standard mixture containing 10 μg each of PCB congeners #14, #65, and #165 was added to each sample before the clean-up procedure to measure sample recovery.

2.2.5. Quality Control and Quality Assurance

A comprehensive set of quality control (QC) checks was performed regularly throughout the study. This included blanks on solvents and materials, recovery experiments for precipitation, air and filter samples, and second extracts of filters and resin to check extraction efficiency. The best measure of day-to-day quality assurance (QA) for the project were the XAD-2 blanks.

These blanks went through the entire analytical scheme: extraction, concentration, clean-up, concentration, and chromatography. They were meant to be a direct measure of the quality of the XAD-2 resin, but they were also a continuing, indirect measure of the quality of the analytical method. These blanks also serve as the best independent check of the performance of the recovery standards. The recoveries for congeners #14, #65, and #166 were $103 \pm 20\%$ (standard deviation), $92 + 18\%$, and $102 \pm 17\%$, respectively. In addition, the area ratio between the early eluting congener (#30) and the late eluting congener (#204) was monitored for changes indicative of discrimination in the injector or changes in the relative sensitivity of the detector. These changes would affect the accuracy of the internal standard calculations.

The results from the analysis of samples were invariably biased by the collection and analysis processes. These biases in the results need to be corrected. The two most important biases are losses during the work-up of the sample and contamination of the sample during the whole process of media preparation, sample collection, and sample work-up. The losses during work-up were accounted for by the use of the recovery standard discussed above. The best measurements of the contamination bias were the results of measurements on field blanks (Keith et al., 1983). For 95% confidence that a compound is present in a sample, its level must be above the limit of detection (LOD) for that compound. The LOD is the field blank + 3 , where a is the sample standard deviation (S.D.). The LODs based on field blanks in this project were a factor of 50 higher than field blanks based on the sensitivity of the GC detector system. The limit of quantification (LOQ) for the samples was defined as the field blank + 10 .

Field blanks were obtained for both precipitation and high-volume air samples. In each case, XAD-2 resin was installed in the samplers for the normal sampling period but was not exposed to precipitation or high-volume air flow. The precipitation field blank also included a rinse of the collector surfaces to check for contamination by dry-deposited material that might have penetrated the cover and seal on the precipitation collector. In addition storage blanks were run on the precipitation columns. These blanks were exposed to all storage and shipping procedures but were not opened in the field. The average concentrations of PCBs in the field blanks were used to calculate the LOD and LOQ as described above. The storage blanks often showed as much PCB contamination as the field blanks even when initial concentrations of PCBs in the freshly cleaned resin were quite low, which indicates a slow release of PCBs from the resin during storage. This was the impetus for initiating the longer clean-up scheme described earlier.

An additional QC experiment used an MIC precipitation sampler installed at DePaul University in Chicago. One of the possible problems with the XAD-2 resin extraction system used with this sampler was the loss of PCBs associated with atmospheric particles, the source of most of the PCBs in precipitation. It was assumed that the particles are collected on the glass wool plugs. Top plugs were normally black or gray in most samples. Often the bottom plugs were also discolored, indicating that some particles passed through the trap. It was determined that the combination of glass wool filter plugs and XAD-2 resin in the column retained more than 90% of the PCBs in the precipitation samples from Chicago, where PCB levels are much higher than near Green Bay. This indicates that there is no significant loss of dissolved PCBs or PCB-bearing fine particles through the column.

Finally, eight experiments at the Green Bay site also evaluated analyte breakthrough during air sampling. Two cartridges were mounted in series, and the sampler was operated under normal flow rate and total volume conditions (up to 2200 m^3). Most of these experiments occurred during the summer when temperatures were highest and breakthrough problems would be most likely. Under these conditions, the top cartridge held between 90 and 99% of the total PCBs collected.

2.2.6. TSP and NVOEC Analyses

Filters were weighed for TSP and NVOEC determinations after equilibration at 50% relative humidity for 24 hours. Circles 1.9 cm^2 in area were removed for NVOEC determinations. These circles were treated with a small amount of 3M HCl to remove carbonate and heated for one hour at 90° C to remove the excess HCl. Analysis was carried out in a total carbon analyzer (Dohrmann, Santa Clara, California) by combustion at 850° C and measurement of the resulting CO_2 by infrared absorption.

3. RESULTS

3.1. SAMPLE ANALYSES

The results reported here are from analyses on samples collected between May 1988 and May 1990 when all three sites in the network were operating. Precipitation samples collected between May 1988 and April 1989 were analyzed by Dr. Tom Murphy at DePaul University. Those collected between May 1989 and May 1990 were analyzed by Dr. Steve Eisenreich at the University of Minnesota. A few additional precipitation samples were analyzed after May 1990 at the Water Survey. Air samples were all analyzed at DePaul University before August 1989 and at the Water Survey between September 1989 and May 1990. All TSP and NVOEC analyses were performed at the Water Survey.

The Green Bay Mass Balance target compounds covered in this report are the PCB congeners and dieldrin. Lead and cadmium were analyzed in another laboratory and are not included here.

3.1.1. Precipitation

Prior to May 1989, precipitation samples were sent to DePaul University for analysis. Due to the low amount of precipitation during the drought year of 1988 and the high field and lab blanks, we can only report a maximum concentration for PCBs in precipitation based on the average amount found in the field blanks (25 ± 10 ng), the LOD (55 ng), and the average sample size (6.6 L). This is equivalent to a maximum concentration of 8.3 ng/L. Dieldrin concentrations were also below the LOD in precipitation samples. The maximum dieldrin concentration based on its LOD was 3.9 ng/L.

After April 1989, analysis of precipitation samples was performed at the University of Minnesota. During this period, 28 biweekly samples were collected at each of the three sites. Table 2 shows the average sample volumes. Preliminary data indicated an average concentration for total PCBs of about 2 ng/L from 18 samples made available to us from the Minnesota lab. A t-test indicated that the average amount of total PCBs in the samples (12 ± 5 ng) was not significantly different than the PCBs in the field blanks (10 ± 4 ng) at the 95% confidence level. The pattern of PCB congeners, however, was different in the samples compared to the field blanks with more of the heavier congeners in the precipitation samples (Eisenreich, 1990).

Four samples collected during the summer of 1990 were analyzed at the Water Survey using the Empore extraction technique to measure the amount of PCBs in the field blanks, about 5 ± 2 ng. Extraction of 2 to 4 L of precipitation gave total PCB amounts above the LOD (11 ng) in three out of four cases. The average concentration in precipitation (after subtraction of the blank) was 3.8 ± 1.9 ng/L. Figure 4 shows the congener pattern of the PCBs in these samples. As with the samples analyzed at Minnesota, the heavier congeners dominate. For comparison, typical congener patterns for airborne vapor and particles are shown in Figures 5 and 6.

Table 2. Average Biweekly Precipitation Volume at Green Bay Sites

Site	Average Volume*(L) (± S.D.)	Range
Green Bay	5.0 ± 4.8	0 - 15
Peninsula	4.4 ± 3.7	0 - 13
Fayette	4.5 ± 3.9	0 - 14

* 28 sample periods between 4/89 and 5/90

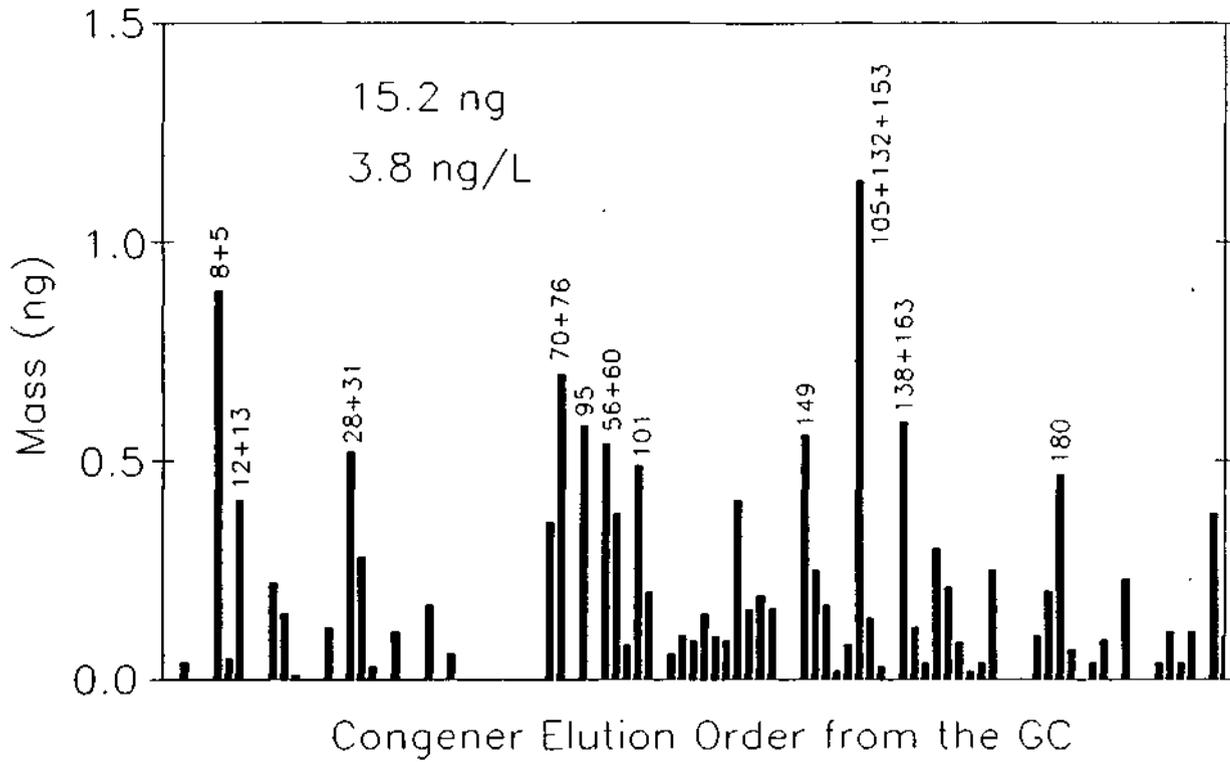PCBs in Precipitation (Green Bay 9/17/90)
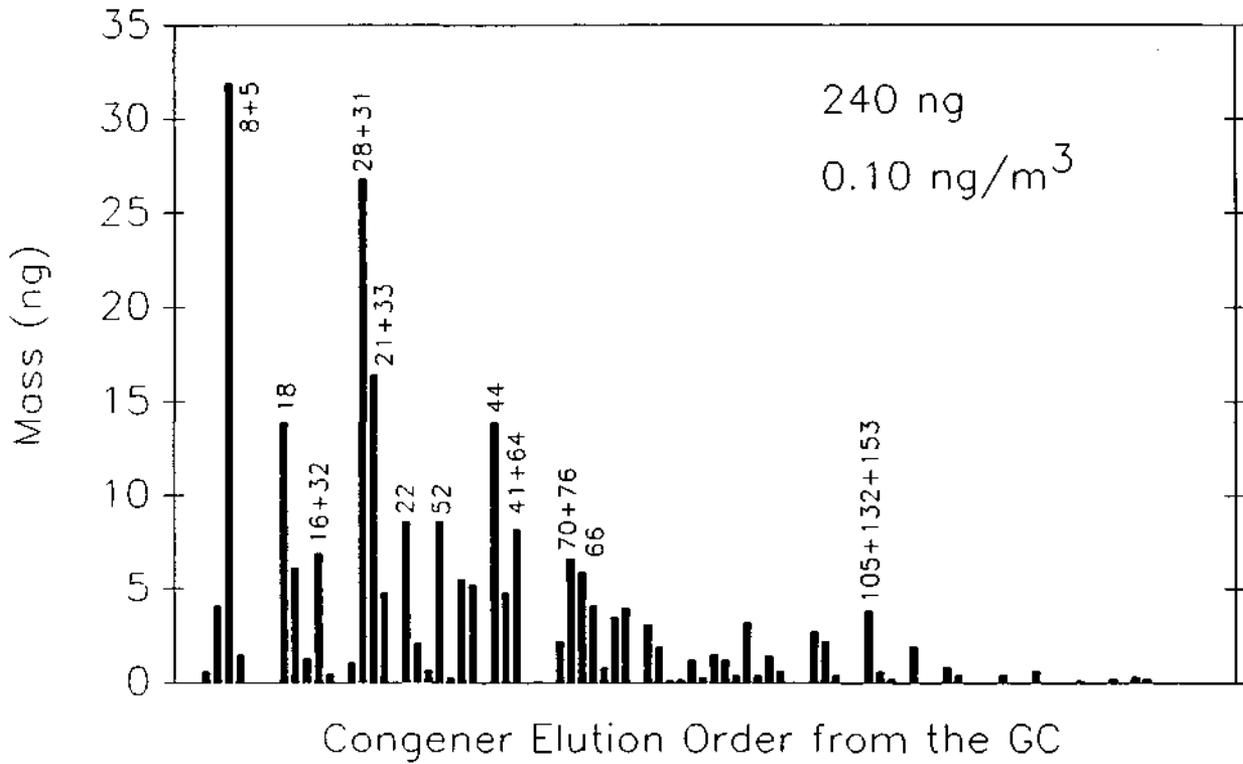
Figure 4. PCB congener pattern in precipitation

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Figure 5. PCB congener pattern in airborne vapor
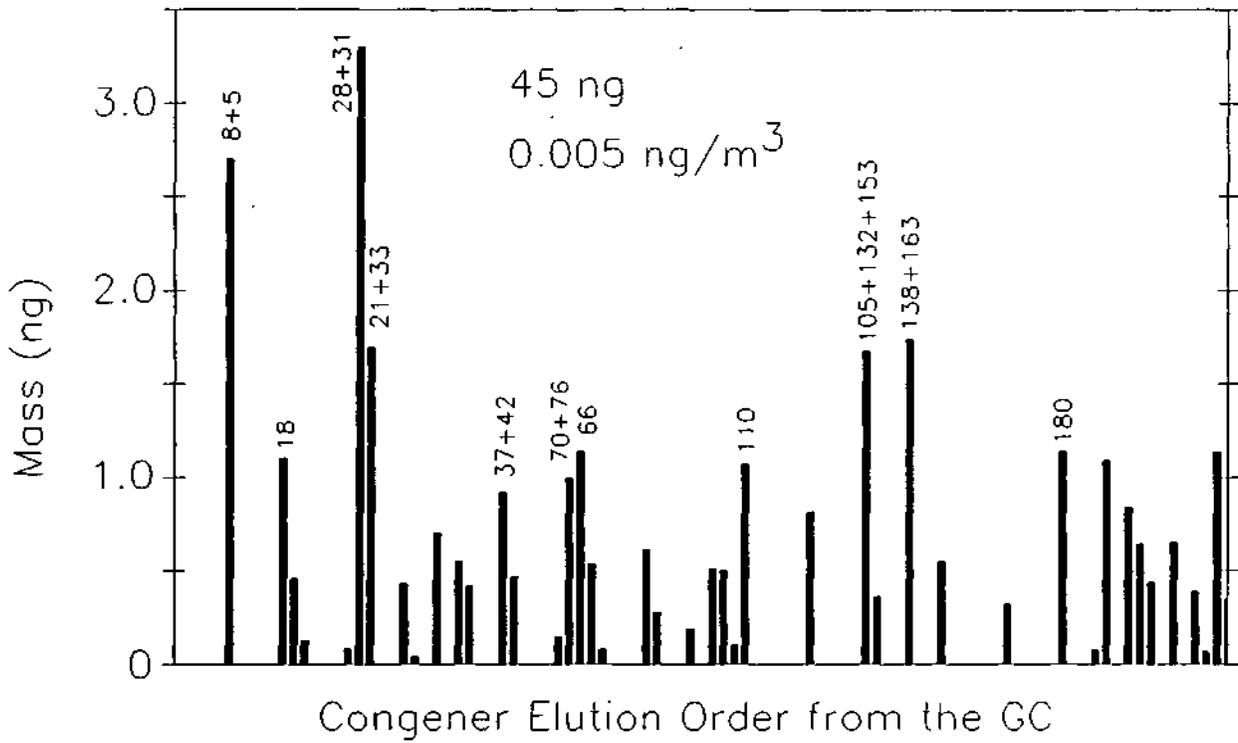
PCBs in Airborne Particles (Green Bay 1/90)

Figure 6. PCB congener pattern in airborne particles

3.1.2. Air Samples

Between May 1988 and August 1989, 95 sets of filters and cartridge vapor traps were collected at the Green Bay site, 36 sets at the Peninsula site, and 40 sets at the Fayette site. These samples were analyzed at DePaul University. After eliminating field blanks, samples with insufficient volume (<200 m^3), and samples lost because of mechanical problems with the sampler or laboratory accident, 60, 27, and 36 sets remained from the Green Bay, Peninsula, and Fayette sites, respectively. The sample volumes varied from 200 to 8000 m^3 depending on the wind direction during a particular sampling period. The average sample volume was 2450 m^3.

The samples collected between September 1989 and May 1990 were analyzed at the Water Survey. PCBs and dieldrin were analyzed in 44, 14, and 14 air cartridge samples collected at the Green Bay, Peninsula, and Fayette sites, respectively. The Peninsula and Fayette samples were all monthly composite samples. Filter samples run at the Water Survey were also monthly composite samples with three or four individual filters in each composite sample.

3.1.2.1. PCBs

Tables 3-6 list the results for total PCBs in the field blanks and samples. These values have been corrected for interferences and analytical recovery. For individual congeners whose analytical value was below the overall limit of detection (LOD), the actual analytical value determined was used to calculate total PCBs. This may introduce a high bias for those congeners with a high detection limit due to interfering compounds. In other words, the values for these congeners may reflect interferences rather than the actual PCB concentration. This bias primarily applies to filter samples where most of the congener concentrations are below the limit of detection. For vapor phase PCBs, the concentrations measured were mostly between the LOD and LOQ.

The data in Tables 4 and 6 indicate that average airborne PCB concentrations are significantly higher at the Green Bay and Peninsula sites compared to the Fayette site. At all three sites, PCBs associated with particles (filter samples) account for 2 to 10% of the total. There were no statistically significant differences in average PCB concentrations between wind directions at any of the sites. The average values from the two different labs covering two different years are almost identical. The higher maximum values appearing in the first data set (DePaul) probably reflect the fact that more of these samples were collected during the summer months.

Table 3. DePaul Field Blank Data for Total PCBs in Air (ng)

	Average	LOD	LOQ
Cartridge*	39	110	240
Filter*	25	52	110

*   based on 15 cartridge samples and 11 filter samples
     LOD = average field blank + standard deviation x 3
     LOQ = average field blank + standard deviation x 10

Table 4. PCBs in Air - DePaul Data

Site	Wind Direction	Number	Sample Type	Total PCB ± S.D. (ng/m^3)	Range (ng/m^3)
Green Bay	North	22	Cartridge	0.30 ± 0.30	0.02 - 1.28
			Filter	0.011 ± 0.025	0 - 0.12
	Southwest	26	Cartridge	0.30 ± 0.21	0.04 - 0.71
			Filter	0.030 ± 0.056	0 - 0.21
	Southeast	12	Cartridge	0.25 ± 0.20	0.08 - 0.86
			Filter	0.007 ± 0.01	0 - 0.04
Peninsula	All	27	Cartridge	0.19 ± 0.16	0.02 - 0.83
			Filter	0.007 ± 0.011	0 - 0.04
Fayette	All	36	Cartridge	0.081 ± 0.079	0.005 - 0.28
			Filter	0.005 ± 0.014	0 - 0.08

Table 5. Water Survey Field Blank Data for PCBs in Air (ng)

	Average	LOD	LOQ
Cartridge*	18	60	160
Filter*	12	30	70

* based on 10 cartridge samples and 5 filter samples
LOD = average field blank + standard deviation x 3
LOQ = average field blank + standard deviation x 10

Table 6. PCBs in Air Samples - Water Survey Data

Site	Wind Direction	Number	Sample Type	Total PCB ± S.D. (ng/m^3)	Range (ng/m^3)
Green Bay	North	15	Cartridge	0.24 ± 0.20	0.03 - 0.51
	Southwest	15	Cartridge	0.25 ± 0.11	0.12 - 0.45
	Southeast	14	Cartridge	0.24 ± 0.08	0.10 - 0.43
	All	15	Filters	0.007+ 0.004	0 - .015
Peninsula	All	14	Cartridge	0.18 ± 0.14	0.03 - 0.47
Fayette	All	36	Cartridge	0.085 ± 0.05	0.03 - 0.18
Peninsula and Fayette	All	20	Filters	0.005 ± 0.009	0 - 0.042

Dieldrin concentrations in the air samples analyzed by the Water Survey were 46 ± 79 pg/m^3 at Green Bay. At Fayette and Peninsula, the dieldrin concentrations in air were 15 ± 15 pg/m^3 and 20 ± 22 pg/m^3, respectively. Over 98% of the dieldrin was in the vapor trap at all three sites. Murphy et al. (1991) reported 1 to 5 pg/m^3 in the air samples analyzed at DePaul University.

Seasonal variations in total PCB concentrations are illustrated for the entire data set (1988 to 1990) in Figures 7-11. Air samples from the urban area (southwest winds) at Green Bay show no clear seasonal trend (Figure 7). In contrast, northerly airflow directly off the bay (Figure 8) exhibits a strong seasonal trend. Airborne PCB concentrations are lower during the December to April period when the bay was ice covered. These results suggest that the bay is a significant source of airborne PCBs at the Green Bay site during the wanner months. For airflow over land from the rural area (Figure 9), there is also some indication of higher PCB levels during the warmer months.

The data from the Peninsula site (Figure 10) show a similar pattern, again indicating that the bay is a source of airborne PCBs at this location. At the Fayette site (Figure 11), the overall PCB concentrations are much lower. While these data also show a seasonal trend with higher PCB concentrations in air coming off the water during the warmer months, the differences here are not as large. Higher PCB concentrations associated with southerly winds at the Fayette site may also mean that this wind direction corresponds to the influx of regional air masses from more polluted areas to the south.

The relative proportion of the different homolog groups (PCB congeners with the same number of chlorine atoms) is shown in Figure 12. For the majority of sample sets, the total amount of PCBs in the filter samples was below the detection limit. There were 12 filter samples, however, (nine from Green Bay, two from Fayette, and one from Peninsula) with total particulate PCBs above 83.4 ng, the LOD for total PCBs in filter samples. For each of these filter and cartridge sets, all of the congeners were checked against individual LODs; and those that were below the LOD were dropped from the analysis. In this way, the confounding effects of interfering compounds are mostly removed. This has little effect on the vapor samples where most of the congeners are above the LOD. Some homolog groups, however, may be underestimated in filter samples if most of the congeners in the group are below the LOD. The data shown in Figure 9 suggests that the vapor phase is relatively enriched in the lighter congeners with 70% of total PCBs in the tri- and tetrachloro-PCB homolog groups. Particle-bound PCBs, on the other hand, contain a higher proportion of heavier congeners. Over 50% of the particulate PCBs contain five or more chlorine atoms per molecule. Proportions of PCB homologs in precipitation are also included in this graph. For these samples, hexa- and heptachloro-PCB homologs are the predominant congeners.
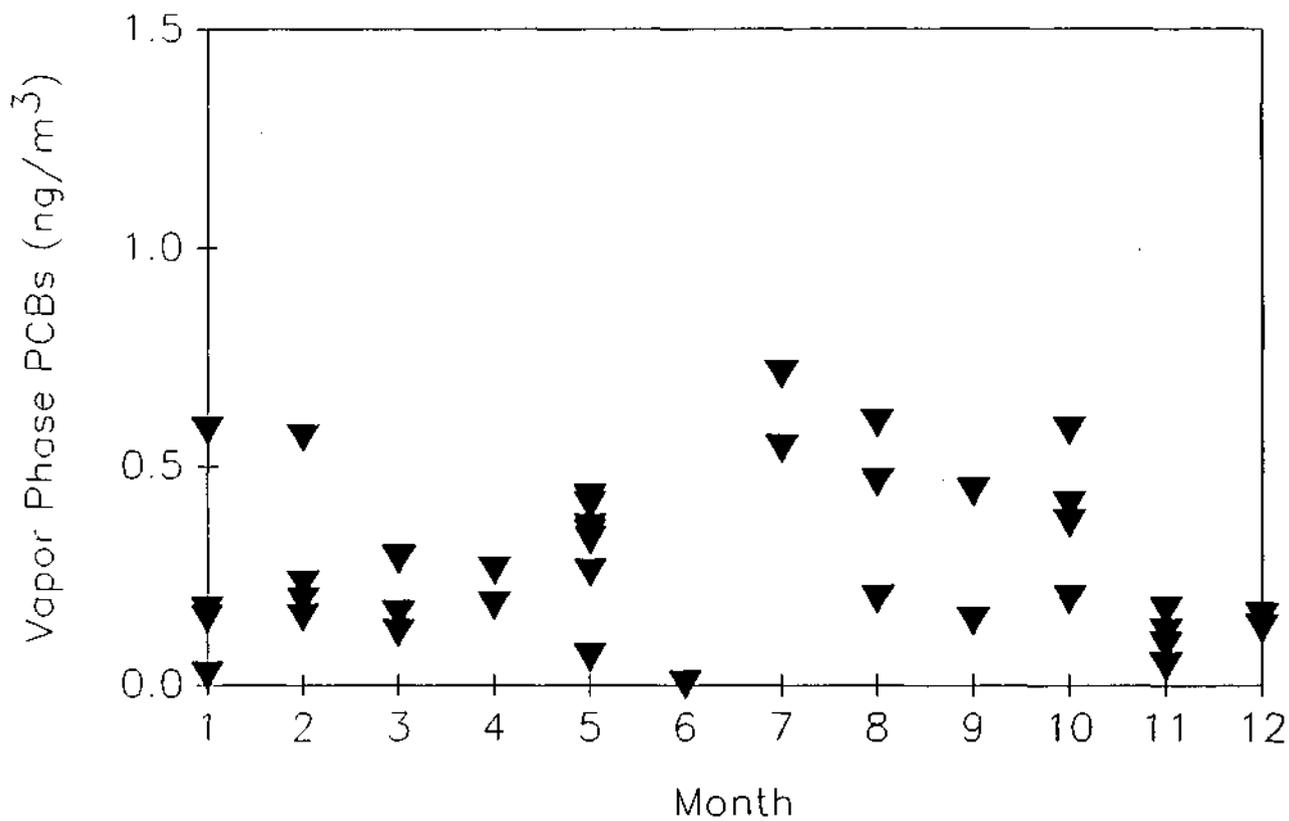
Figure 7. Seasonal variation in total PCB at Green Bay with airflow from urban areas (southwest winds)

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Figure 8. Seasonal variation in total PCB at Green Bay with airflow over water (north winds)

Figure 9. Seasonal variation in total PCB at Green Bay with airflow over land from rural areas (southeast winds)

Peninsula Site

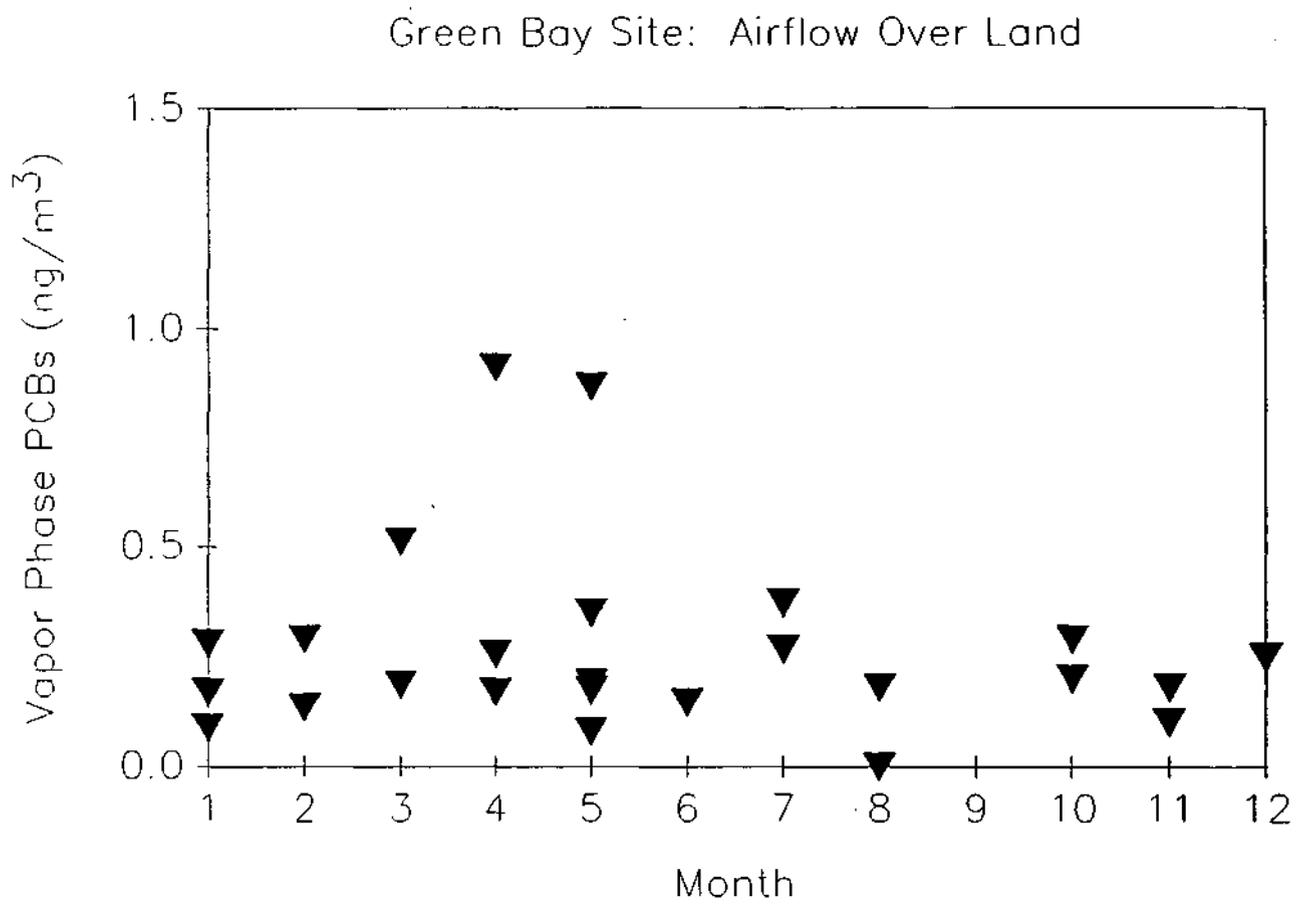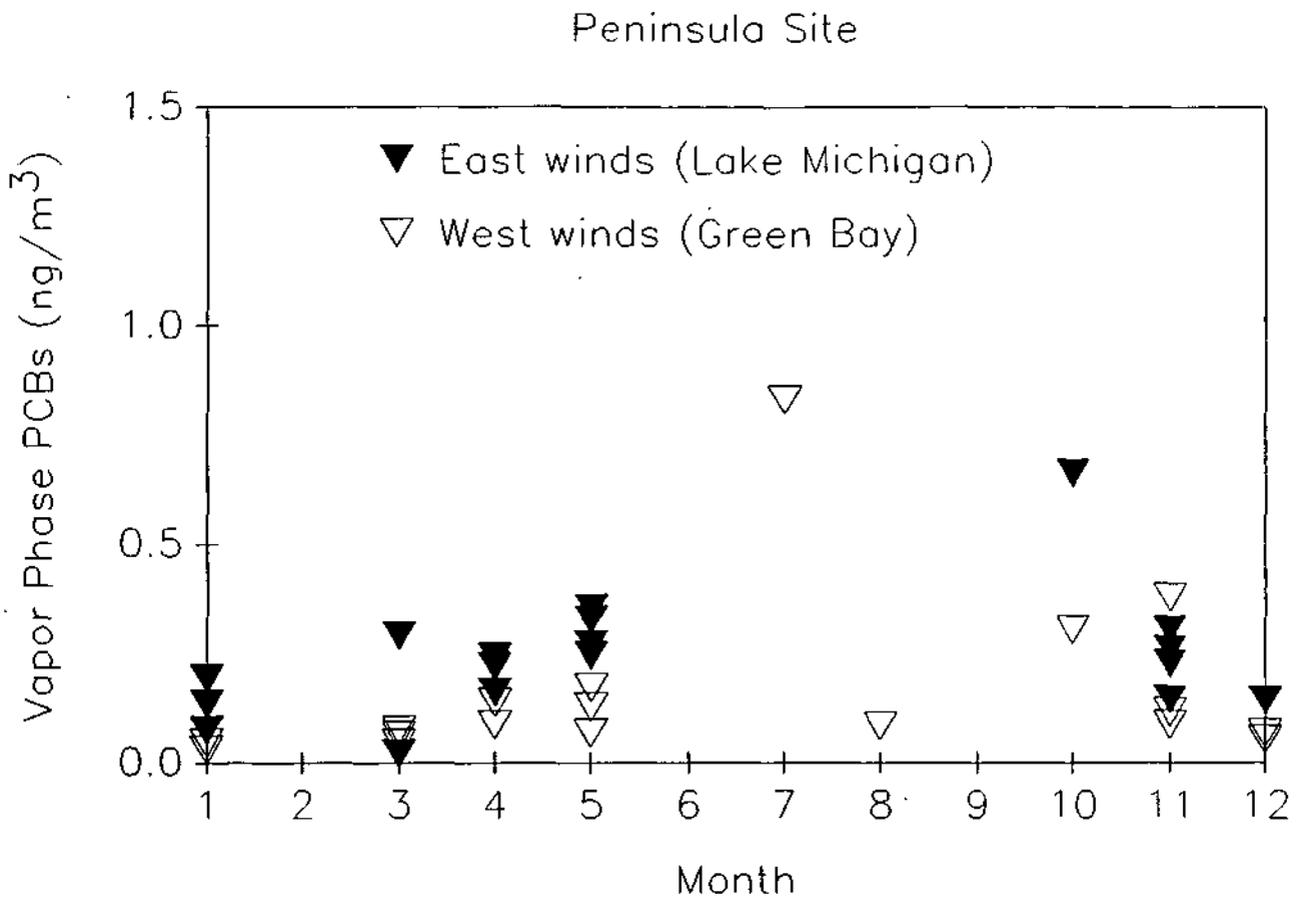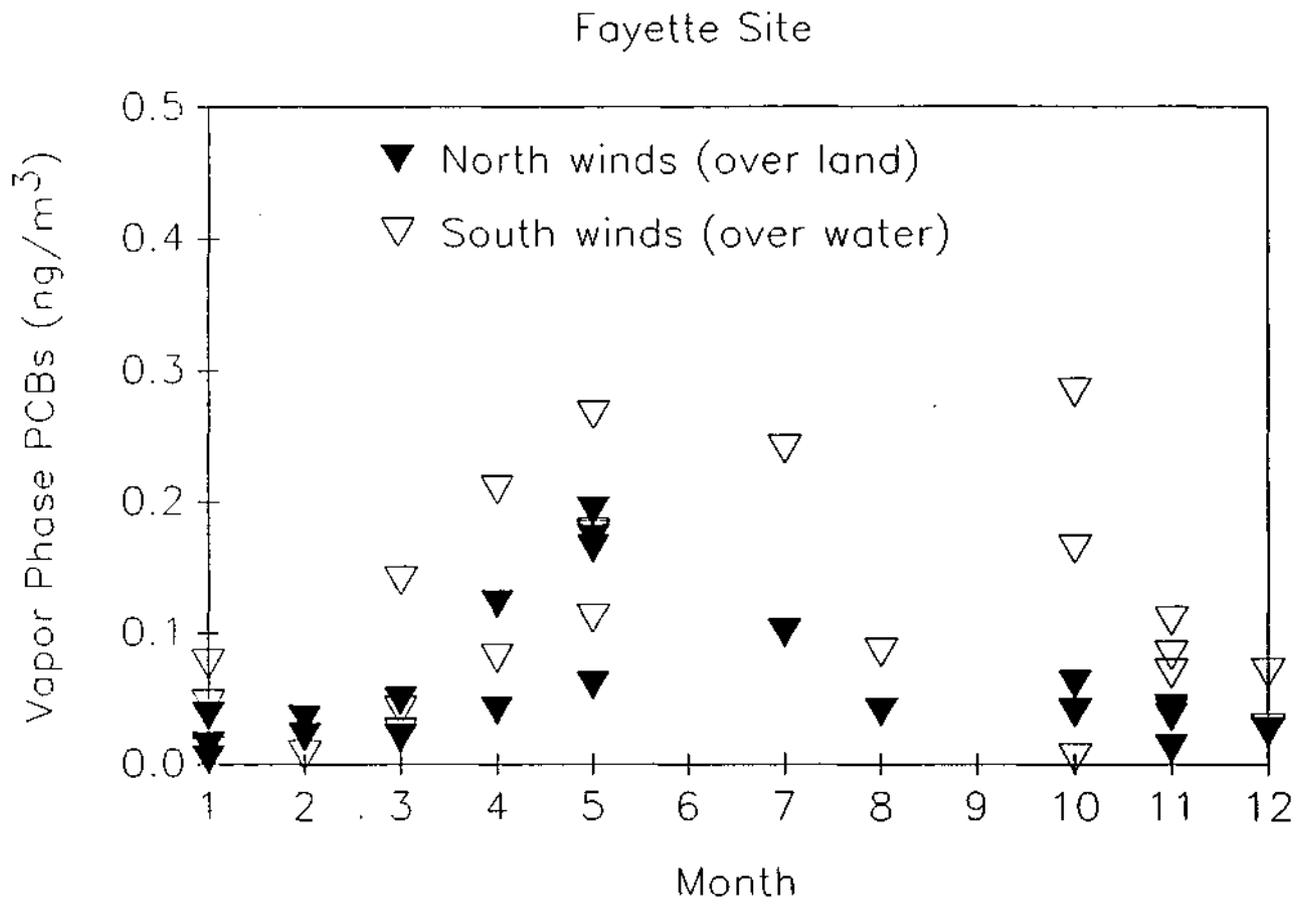Figure 10. Seasonal variation in total PCB at Peninsula State Park

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Fayette Site

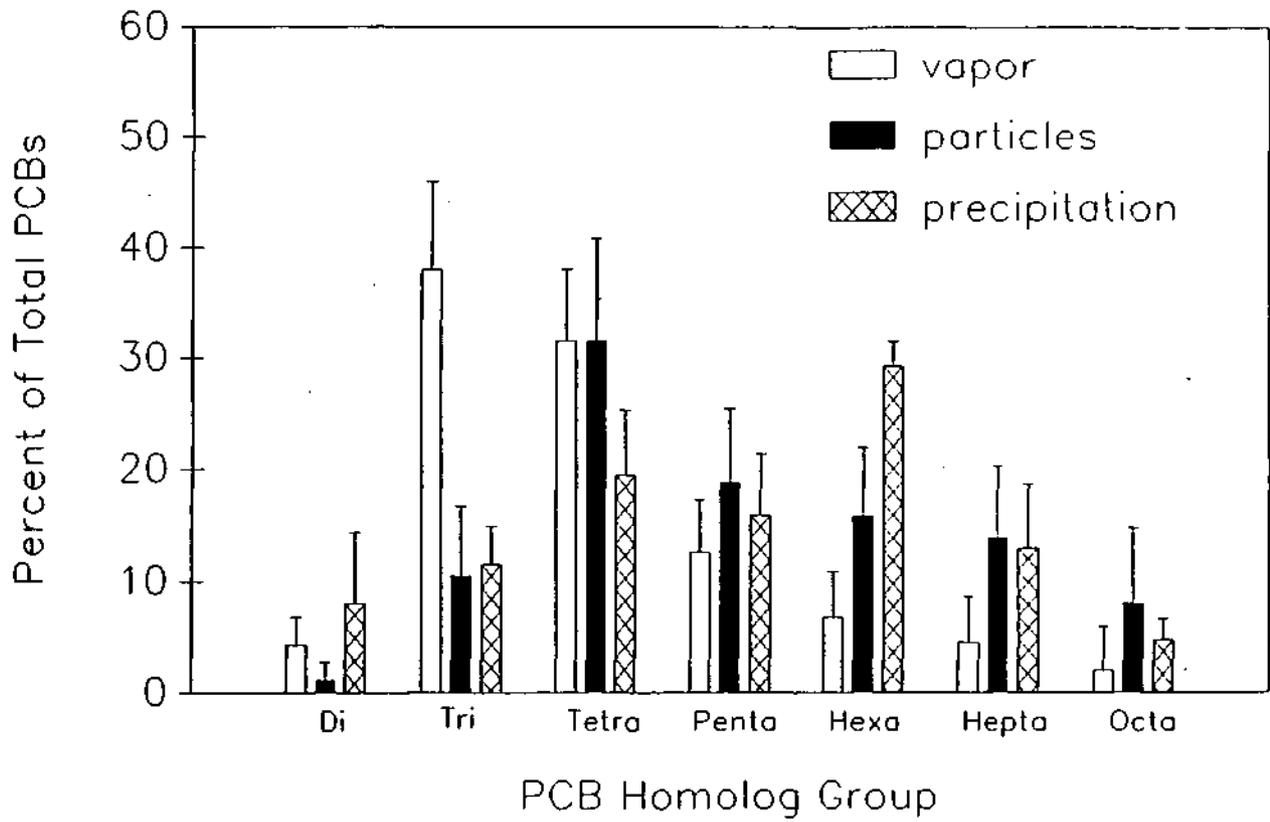Figure 11. Seasonal variation in total PCB at Fayette State Park

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Figure 12. Distribution of airborne PCBs by homolog group at Green Bay

Finally, the particle size distribution for PCBs was determined in four separate cascade impactor runs (two at Green Bay and one each at Fayette and Peninsula). To collect enough particle-bound PCBs, the high-volume sampler was run continuously for seven days to collect about 11,000 m^3 of air. The particles in this air sample were divided by the cascade impactor into five size fractions corresponding to stages 1-5 in Figure 13. For the Fayette and Peninsula samples, all of the PCBs were on the smallest particles (>1.4 μm in diameter). At the Green Bay site, cascade impactor results showed that as much as 50% of the particulate PCBs were associated with larger particles between 2 and 10 μm in diameter.

3.1.2.2. TSP and Total Carbon

Values for total suspended particles (TSP) and total airborne nonvolatile organic and elemental carbon (NVOEC) were determined on standard high-volume samples collected every six days on the U.S. EPA schedule. A time series of these determinations for 1989 and 1990 is given in Figures 14 and 15. TSP values at Green Bay are generally higher than at the other two sites, reflecting inputs of dust from the urban area. The average TSP value at Green Bay is 34.1 $\mu g/m^3$ versus 21.8 $\mu g/m^3$ at Peninsula and 24.5 $\mu g/m^3$ at Fayette. TSP levels tend to rise and fall in unison at the three sites, indicating that much of the TSP is associated with regional air masses affecting all three sites.

Total NVOEC values generally amount to 10 to 15% of TSP. The Green Bay levels are usually higher than the Fayette or Peninsula levels. Notable exceptions occur in the May-June period at these sites when the highest total airborne carbon values of the year were recorded. This period coincides with the release of pollen from pines and other vegetation in this area. In fact, some filters collected during May and June had a distinct yellow cast. Otherwise there seems to be no clear pattern in the NVOEC measurements.

An attempt was made to correlate TSP, NVOEC, and the ratio of NVOEC to TSP with PCB levels in the samples. No correlations were found. This may be due to the fact that for most of the filter samples PCB concentrations were well below the LOD.

3.2. METEOROLOGICAL DATA

Tabulated summaries of the collected meteorological data are presented in Tables 7-9. Summary values are presented for individual years (1988, 1989, and 1990) and season. When comparing data between sites or between years, it should be noted that the start-up times for 1988 vary between sites, that the 1990 data do not represent a full year, and that the winter season includes December from the previous year. Wind direction and speed are presented for selected sectors, as percent-time and mph, respectively. These sectors vary between sites and are the same as those identified earlier for collection of air samples (wind-directed high-volume samples).
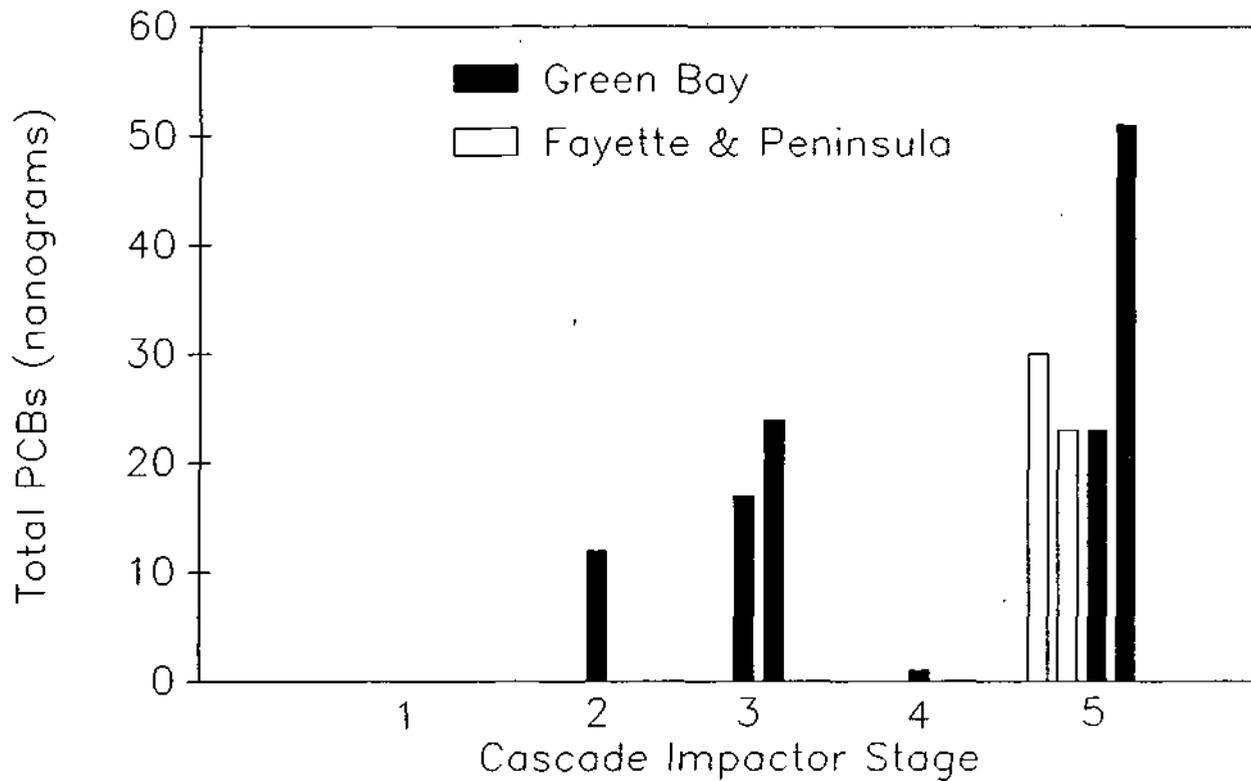
Figure 13. Particle size distribution of PCBs at the Green Bay sites. Cascade impactor size ranges are: stage 1 = >10.2 μ m, stage 2 = 4.2 to 10.2 μ m, stage 3 = 2.1 to 4.2 μ m, stage 4 = 1.4 to 2.1 μ m, and stage 5 = <1.4 μ m.
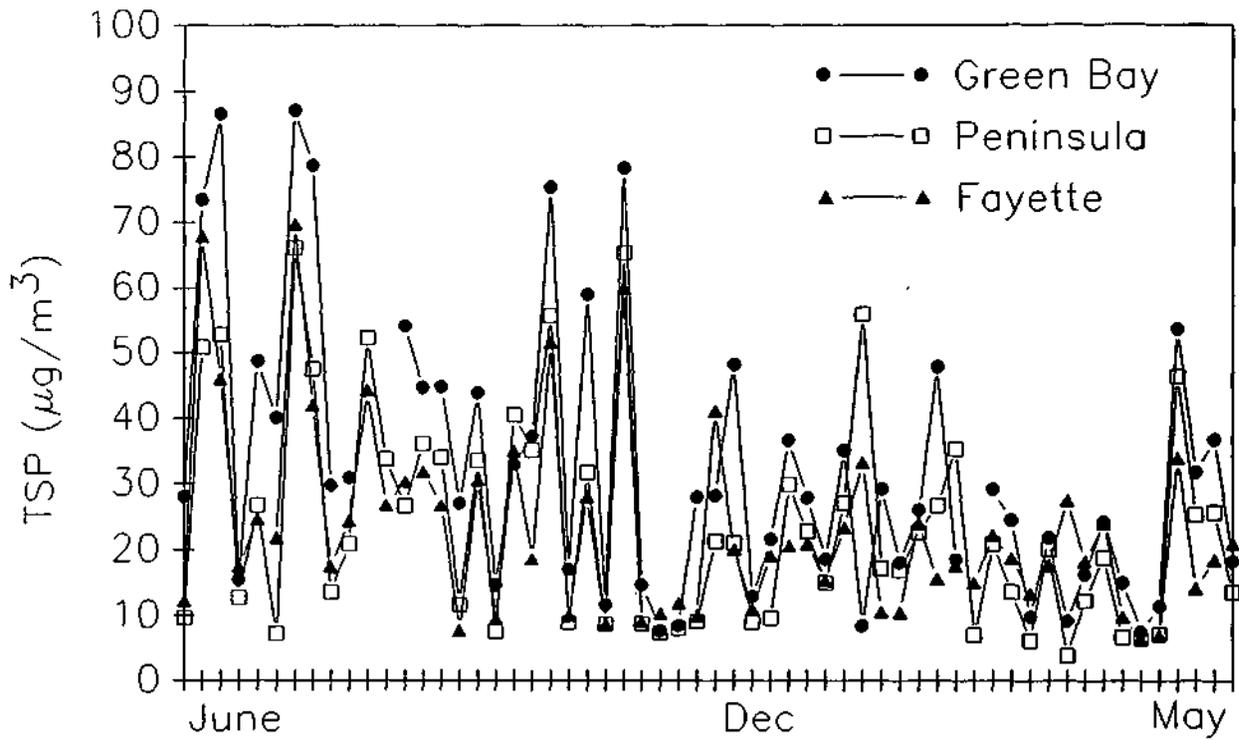
Figure 14. Seasonal variation in TSP at three Green Bay sites
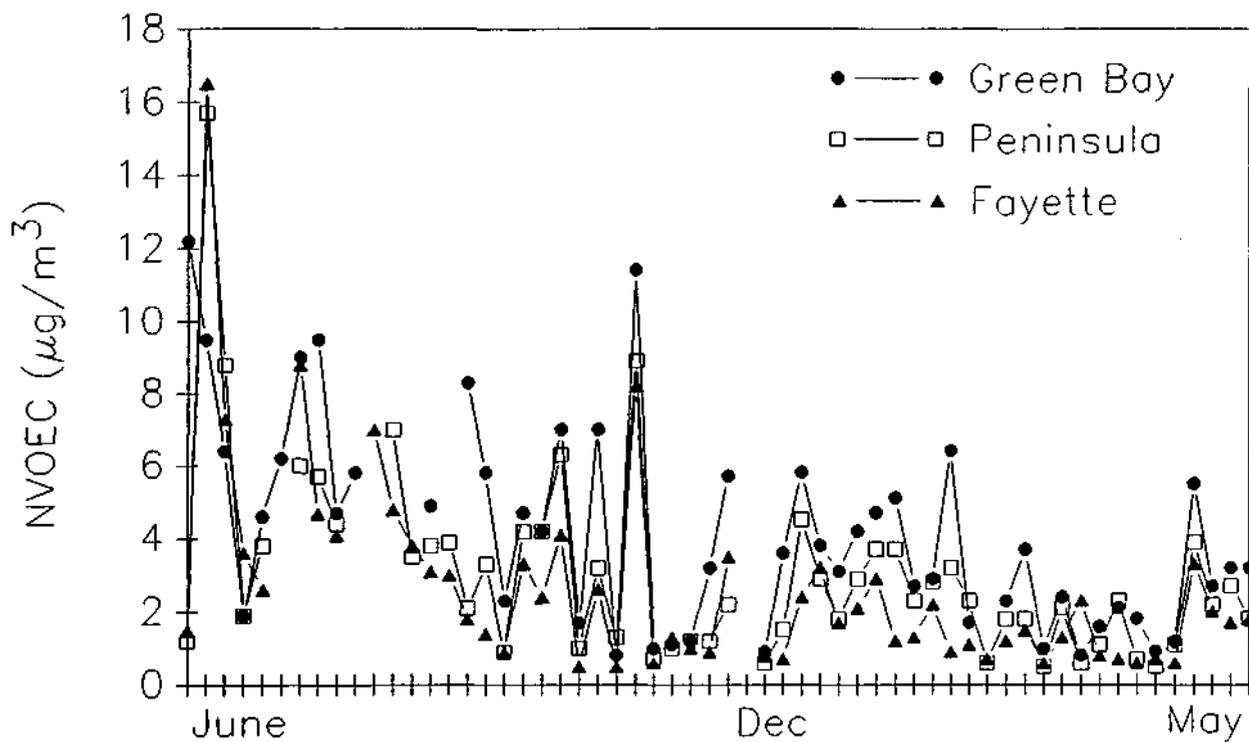
31

Figure 15. Seasonal variation in NVOEC at three Green Bay Sites

Table 7. Green Bay Meteorological Summary (12/87 - 5/90)

Year/Season	Mean Temp. (° F)	Total Precip. (inches)	Mean R.H. (%)	Mean Daily Solar (langleys)	Wind Direction (%)			Wind Speed (mph)		
					South 110° -180°	West 210° -270°	North 300° -020°	South 110° -180°	West 210° -270°	North 300° -020°
1988 (1/88-12/88)	45	20.58	73	354	5.6	14.0	15.3	7.1	10.9	10.5
Winter (12/87-2/88)	14	2.11	77	160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Spring (3/88-5/88)	45	3.01	65	431	6.0	8.2	13.1	6.7	12.1	8.8
Summer(6/88-8/88)	72	6.74	64	539	5.3	14.2	9.0	6.3	9.9	7.8
Autumn (9/88-11/88)	47	8.70	85	210	6.5	12.3	21.1	7.6	10.8	11.8
1989 (1/89-12/89)	44	21.62	78	315	6.8	12.7	20.7	6.7	9.9	10.3
Winter (12/88-2/89)	21	1.48	82	160	2.7	25.6	15.5	6.9	11.9	10.6
Spring (3/89-5/89)	40	7.62	75	367	8.4	8.7	24.9	7.2	9.8	9.6
Summer (6/89-8/89)	69	5.81	82	498	5.7	7.0	14.5	5.7	7.8	7.8
Autumn (9/89-11/89)	48	7.44	76	233	10.3	11.8	23.2	7.0	9.4	12.0
1990 (1/90-5/90)	36	9.38	70	294	6.4	13.6	20.6	7.4	11.4	10.7
Winter (12/89-2/90)	21	2.69	78	159	4.0	15.9	24.2	6.6	9.9	10.7
Spring (3/90-5/90)	44	6.73	66	373	7.4	12.2	19.4	7.8	11.8	10.8
Study Period (1/88-5/90)	43	51.58	75	325	6.3	13.3	18.8	7.0	10.6	10.4
Winter (1988-90)	19	6.28	79	160	3.3	20.7	19.8	6.7	11.1	10.7
Spring (1988-90)	43	17.36	69	387	7.5	10.0	20.4	7.3	11.2	10.0
Summer (1988-89)	71	12.55	73	518	5.5	10.8	11.4	6.0	9.2	7.8
Autumn (1988-89)	47	16.14	80	221	8.4	12.1	22.2	7.2	10.1	11.9

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Table 8. Peninsula Meteorological Summary (9/88 - 5/90)

Year/Season	Mean Temp. (° F)	Total Precip. (inches)	Mean R.H. (ft)	Mean Daily Solar (langleys)	Wind Direction (%)		Wind Speed (mph)	
					East 060° -190°	North 240° -030°	East 060° -190°	North 240° -030°
1988 (9/88-12/88)	36	7.48	82	125	12.6	46.1	5.8	8.2
Autumn (9/88-11/88)	42	6.21	83	139	15.2	41.8	5.4	8.3
1989 (1/89-12/89)	43	20.73	76	301	7.1	26.3	5.1	6.5
Winter (12/88-2/89)	22	3.24	77	141	5.8	44.8	6.4	7.3
Spring (3/89-5/89)	39	6.07	72	384	13.4	24.7	5.4	5.8
Summer (6/89-8/89	66	6.23	80	465	4.3	7.7	4.2	4.5
Autumn (9/89-11/89)	47	5.75	76	220	7.1	30.3	5.0	7.3
1990 (1/90-5/90)	34	9.51	76	279	8.6	28.1	5.6	6.5
Winter (12/89-2/90)	21	5.00	80	132	2.8	33.5	5.6	6.5
Spring (3/90-5/90)	40	5.22	73	374	12.5	28.7	5.6	6.3
Study Period (9/88-5,90)	40	37.72	77	268	8.3	29.9	5.4	6.9
Winter (1988-90)	22	8.24	79	137	4.3	39.2	6.2	7.0
Spring (1988-90)	40	11.29	72	379	13.0	26.5	5.5	6.0
Summer (1988-89)	66	6.23	80	465	4.3	7.7	4.2	4.5
Autumn (1988-89)	45	11.64	79	187	10.4	35.0	5.2	7.8

Table 9. Fayette Meteorological Summary (4/88 - 5/90)

Year/Season	Mean Temp. (º F)	Total Precip. (inches)	Mean R.H. (%)	Mean Daily Solar (langleys)	Wind Direction (%)		Wind Speed (mph)	
					South 090º -270º	North 300º -060º	South 090º -270º	North 300º -060º
1988 (4/88-12/88)	44	9.87	80	159	32.1	19.6	6.9	7.7
Spring (4/88-5/88)	45	n.a.	71	n.a.	n.a.	n.a.	n.a.	n.a.
Summer (6/88-8/88)	63	n.a.	71	378	27.1	6.0	5.3	6.0
Autumn (9/88-11/88)	47	8.16	86	165	34.0	21.7	6.8	7.5
1989 (1/89-12/89)	40	22.17	78	300	25.3	19.9	6.3	5.9
Winter (12/88-2/89)	20	4.47	79	132	32.2	18.7	6.8	6.9
Spring (3/89-5/89)	38	6.75	73	385	32.8	27.2	6.4	5.8
Summer (6/89-8/89	64	6.53	77	498	12.9	13.3	4.8	4.5
Autumn (9/89-11/89)	45	5.24	81 .	216	27.5	18.8	6.6	6.8
1990 (1/90-5/90)	31	10.16	79	276	32.7	17.7	6.5	6.6
Winter (12/89-2/90)	20	4.46	84	121	23.3	17.9	6.3	6.2
Spring (3/90-5/90)	37	6.57	76	372	34.6	18.2	6.6	6.6
Study Period (4/88-5/90)	39	42.20	79	266	28.3	19.4	6.5	6.4
Winter (1988-90)	20	8.93	81	126	27.8	18.3	6.6	6.6
Spring (1988-90)	38	13.32	74	379	33.6	23.1	6.5	6.1
Summer (1988-89)	64	6.53	76	488	14.1	12.7	4.9	4.6
Autumn (1988-89)	46	13.40	83	191	30.7	20.2	6.7	7.2

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Temperature and precipitation summaries (as presented in Tables 7 and 8) were compared with long-term averages, calculated as 30-year normals (1951 to 1980). For Green Bay, yearly and seasonal temperatures were near normal (± 10%), with the exceptions of a cold winter in 1988 (80% of normal) and a warm winter in 1989 (120% of normal). Total precipitation was approximately 70% of normal. Notable anomalies include the spring of 1988 and the winter of 1989 (40% of normal precipitation) and the autumn of 1988 (122% of normal precipitation). For the Peninsula site, the data comparisons are similar to Green Bay, with yearly and seasonal temperatures being near normal (± 10%) and total precipitation being approximately 70% of normal. A notable exception was the winter of 1989, with 120% of normal precipitation.

3.2.1. Wind Direction and Speed

Wind roses are presented as an average for the study period and seasonal periods (Figures 16-20). The wind roses for Fayette show a suspicious minimum in the frequency of surface winds from the west-southwest (WSW) sector. Plotting wind direction by one-degree increments (not shown) reinforced the presence of an anomaly. A review of the site description revealed the presence of a hill to the west of the site, with treetops above the 10 m tower. The distance between the hill and sampling site is believed sufficient so as not to obstruct obliquely falling precipitation; however, it appears to offer an obstruction to surface winds. By way of explanation, the obstruction appears to have redirected airflow around the hill, accentuating surface winds from the west-northwest (WNW) and south-southwest (SSW) sectors. An examination at the other two sites showed no obstructions to airflow.

Examination of the wind roses for the full study period (Figure 16) shows an increased frequency of winds   10 mph at Green Bay, compared to the other two locations. The greater frequency of high winds can be attributed to the open area around the Green Bay site in comparison to the forested area of the other two sites. Examination of wind roses by season shows a cycle of wind direction and speed likely related to climate and local siting. In the winter (Figure 17), westerly surface flows prevail at each of the three sites, with a greater frequency of high winds at Green Bay. In the spring (Figure 18), surface winds from the east, especially the north-northeast (NNE) and south-southeast (SSE), occur almost as frequently as from the west, and there is an increased frequency of calm conditions at Fayette. In the summer (Figure 19), no one wind direction prevails and calm conditions increase at the Peninsula and Fayette sites. Increased calm conditions likely reflect a denser tree canopy. Finally, in the autumn, (Figure 20), easterly flows give way to a return to a prevailing westerly surface flow and the frequency of calm conditions decreases.
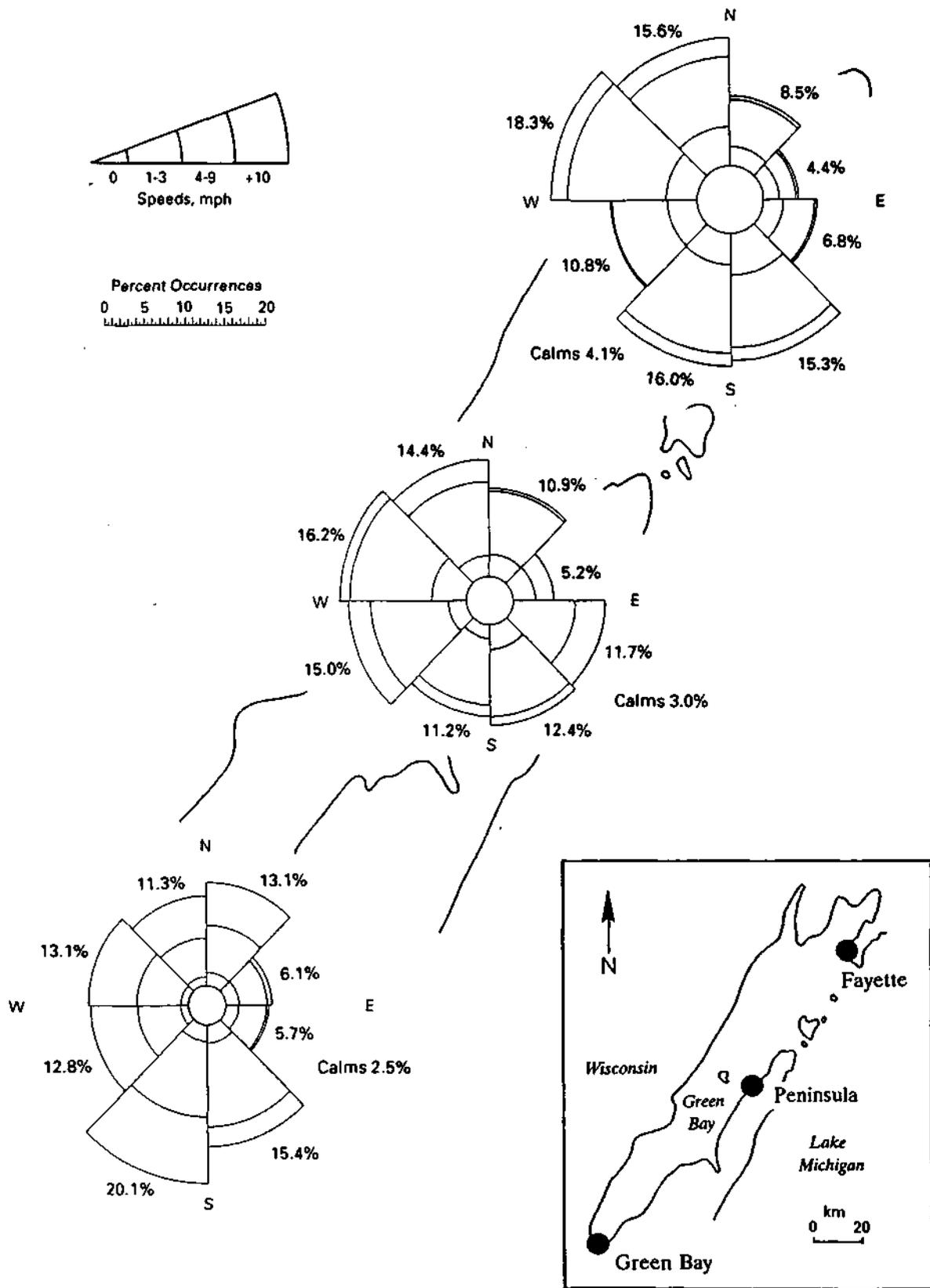
Figure 16. Wind roses for the full-study period (Green Bay: 1/88-5/90, Peninsula: 9/88-5/90, Fayette: 4/88-5/90).

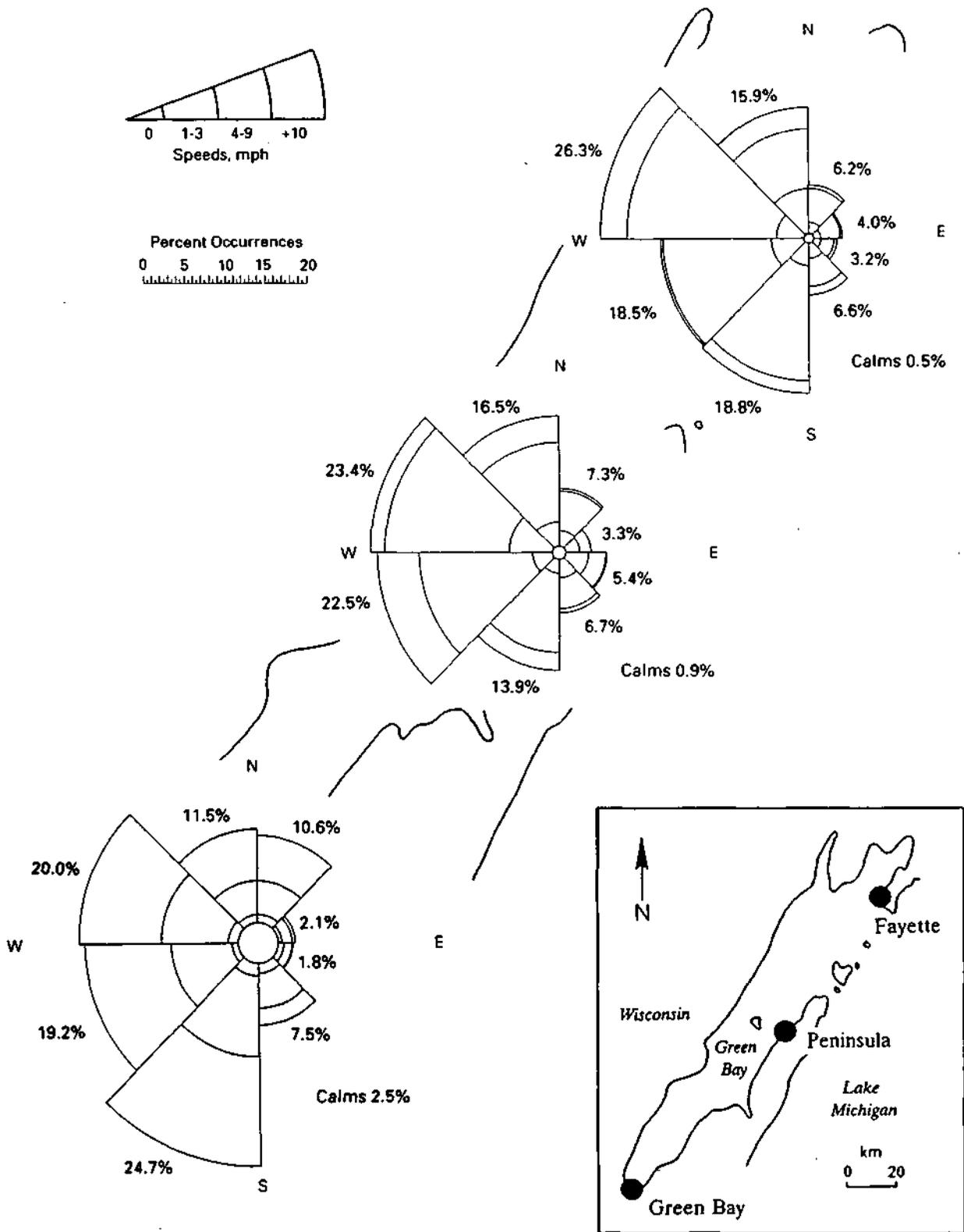Figure 17. Wind roses for accumulated winter seasons (December, January, February).
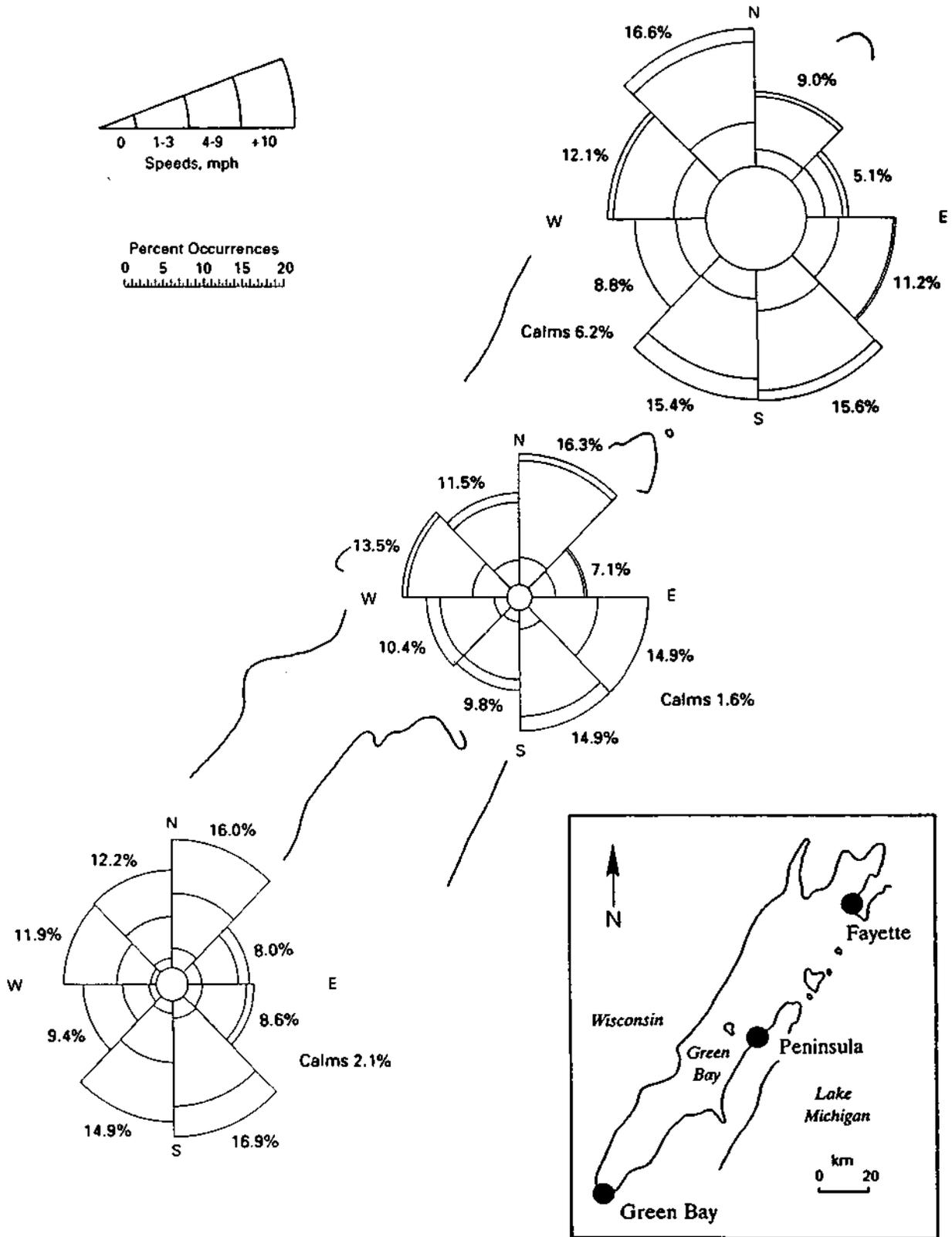
38

Figure 18. Wind roses for accumulated spring seasons (March, April, May).
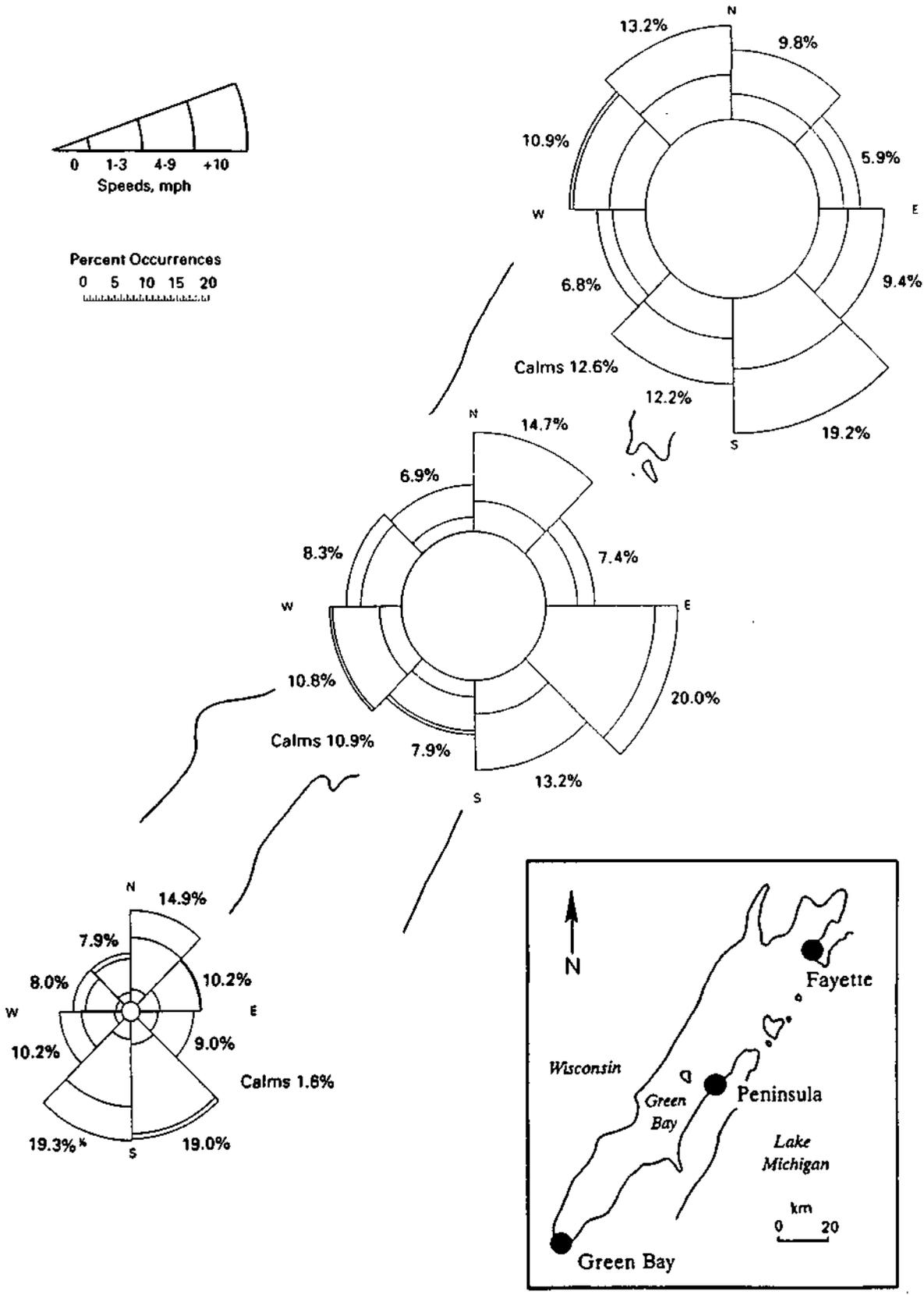
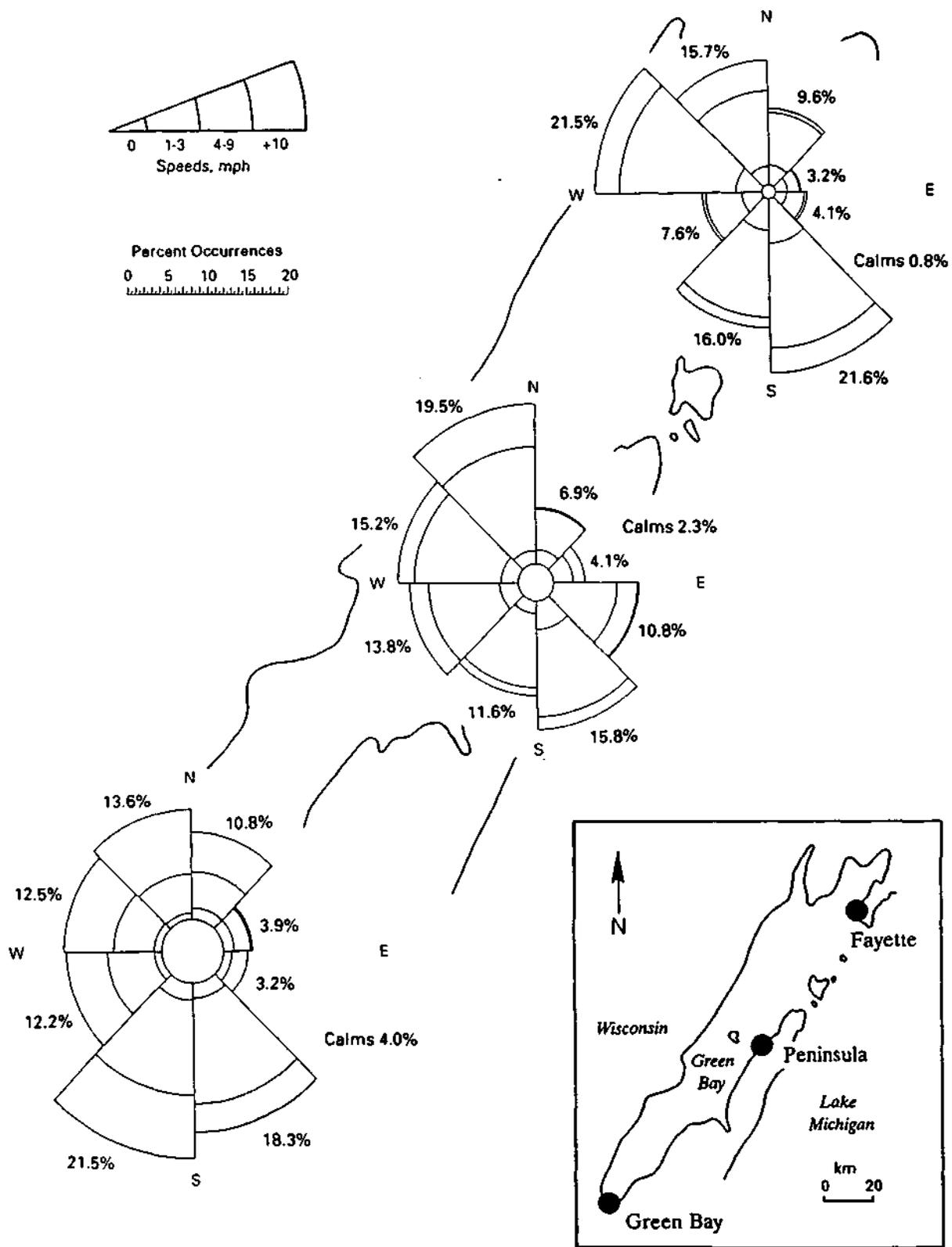Figure 19. Wind roses for accumulated summer seasons (June, July, August).

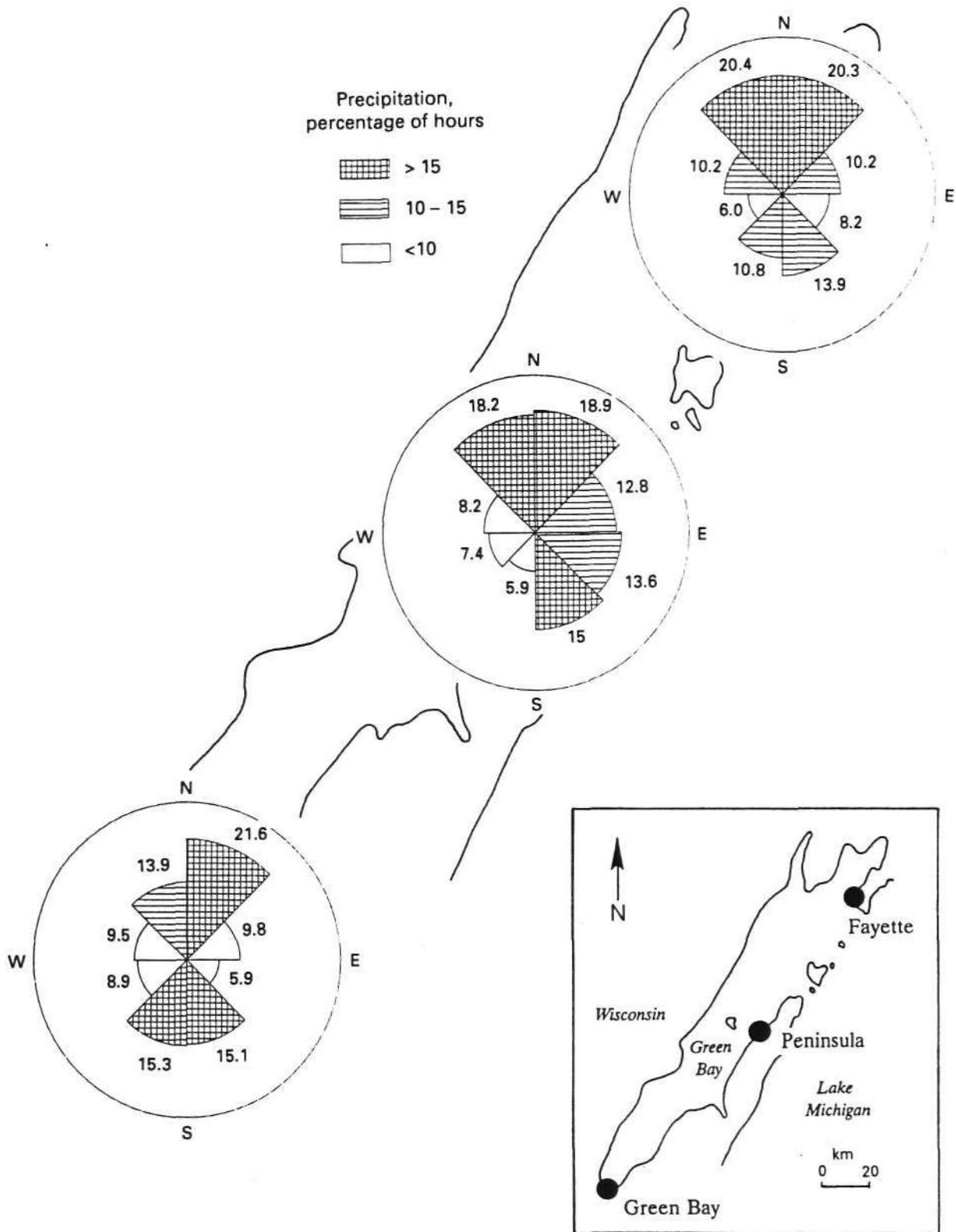Figure 20. Wind roses for accumulated autumn seasons (September, October, November).

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Figure 21. Percentage of hours with precipitation, by surface wind direction.

3.2.2. Precipitation

Precipitation data were collected by Belfort and Nipher-shielded Belfort rain gauges operated in parallel at each of the three sites. During periods of snow, especially when accompanied with high winds, the Nipher shield is designed to provide the Belfort rain gauge with a more efficient catch. Analysis of parallel data sets substantiates this claim (Table 10). During the summer when only rain falls, there is no substantial difference between the two collectors. In the winter months with snowfall, however, there is a substantial difference and the Nipher-shielded gage exhibits the higher catch -- an average increase ranging from 23 to 111%. The catch efficiency of the unshielded Belfort rain gauge is thought to deteriorate with higher wind speeds, thus the higher percent catch for Green Bay, in relation to the other two sites, can be attributed to higher average wind speeds. By way of specific example, a snowstorm with average wind speeds of 18 mph (gusting to 22 mph) gave a Nipher-shielded catch of 0.60 inches, a threefold increase over the catch of the unshielded Belfort rain gauge (0.19 inches). In a separate snowfall, with average wind speeds of only 3 mph, no difference in snow catch occurred between gages. The precipitation summaries presented in Tables 7-9 used data obtained from the unshielded gage for the spring, summer, and autumn precipitation totals, while values obtained from the shielded gage were used for the winter totals.

The precipitation data are further summarized by frequency of events, intensity of events, and relationships with wind direction. An event is defined in this summary, as an hourly recorded total ≥ 0.02 inch of precipitation. This value of 0.02 inch represents a conservative estimate of collected precipitation, as values of 0.01 inch cannot always be distinguished from data logger noise.

The frequency of hourly precipitation ≥ 0.02 inch at each of the three sites ranges from 4.3 to 6.2% of total sampling hours. An upper limit, which includes possible data logger noise, gives a range of 9.5 to 10.0% (Table 11). Summer months account for the fewest hours with precipitation, while autumn and spring months account for the largest number.

An interesting characteristic of the hourly precipitation data is the greater frequency of light precipitation (≤ 0.05 inch) during the winter months (82% of total events) as compared to the summer months (54%). There are obvious variations of hourly precipitation amount with season. The frequency of heavier precipitation events increases during the warm months (Table 12). For example, events exceeding 0.35 inch occur almost exclusively in the summer months. This pattern is characteristic of the more frequent localized convective storms that would be expected during the warm months. Using temperature as a means to determine the state of precipitation, analysis shows that 21.1% (Green Bay), 31.1% (Peninsula), and 33.5% (Fayette) of the precipitation fell as snow or frozen rain (≤ 32°F).

Table 10. Comparison Between Belfort and Nipher-Shielded Belfort Catch Efficiency

Site	Average Wind Speed (mph)	Belfort (inches)	Nipher-Shield Belfort (inches)	Nipher/Belfort (inches)
Summer: Rain				
Green Bay	5.8	5.78	5.81	1.01
Peninsula	3.3	6.23	6.22	1.00
Fayette	3.3	6.53	6.81	1.04
Winter: Snow				
Green Bay	10.1	1.31	2.76	2.11
Peninsula	6.2	4.32	5.32	1.23
Fayette	5.7	5.43	6.82	1.26

Table 11. Frequency of Precipitation Events

Site	Event Definition	Winter Hrs	Winter %	Spring Hrs	Spring %	Summer Hrs	Summer %	Autumn Hrs	Autumn %	Annual Hrs	Annual %
Gieen Bay	0.02	171	4.0	467	7.4	103	2.5	589	10.9	1330	6.2
	0.02*	292	6.8	868	13.7	212	5.1	687	12.7	2059	9.6
Peninsula	0.02	188	4.4	180	4.5	50	2.3	208	5.9	626	4.3
	0.01*	430	10.0	367	9.2	139	6.3	441	12.5	1377	*95*
Fayette	0.02	173	4.0	190	4.9	84	3.5	274	6.3	721	4.7
	0.01*	383	8.9	387	10.0	180	7.5	584	13.5	1534	10.0

* Recorded precipitation of 0.01 inches cannot always be distinguished from data logger noise.

Table 12. Distribution of Hourly Precipitation (hourly values > 0.02 inches)

Precipitation Intensity (in./hr.)	Site	Winter (%)	Spring (%)	Summer (%)	Autumn (%)
0.05	Green Bay	77	62	45	47
	Peninsula	87	68	56	56
	Fayette	82	63	62	67
0.10	Green Bay	22	24	23	29
	Peninsula	9	17	22	25
	Fayette	15	22	23	22
0.15	Green Bay	0	8	12	12
	Peninsula	3	7	6	11
	Fayette	3	9	6	6
0.20	Green Bay	1	4	5	6
	Peninsula	0	4	4	2
	Fayette	1	2	4	3
0.25	Green Bay	0	1	5	5
	Peninsula	1	2	0	2
	Fayette	0	1	0	2
0.30	Green Bay	0	0	1	1
	Peninsula	1	1	2	1
	Fayette	0	1	0	1
0.35	Green Bay	0	0	1	2
	Peninsula	0	1	4	1
	Fayette	0	1	1	0
0.35	Green Bay	0	0	9	1
	Peninsula	0	1	6	0
	Fayette	0	2	5	1

Surface winds were summarized during hours with precipitation (Figure 21). While surface winds do not indicate the movement of storm systems or long-range air trajectories, they do indicate short-range local air trajectories near the sampling sites. Analysis indicates that the largest percent of precipitation events (38%) occurred with surface winds from the north, while the smallest percent occurred with surface winds from the west (17%). For Green Bay, precipitation occurred mostly with northerly and southerly surface winds representing surface airflow from the southern basin of Green Bay and over land, respectively. Precipitation at Peninsula occurred preferentially with surface winds from the north and east. Geography dictates precipitation collected at Peninsula was associated with surface winds from the northern basin of Green Bay and from across Lake Michigan. For Fayette, precipitation occurred most frequently with winds from the NNW and NNE sectors (41%), which are trajectories over land.

4. DISCUSSION

The DePaul University laboratory was not able to quantitate the amount of PCBs in precipitation using XAD-2 resin. The concentrations of total PCBs measured by both the DePaul and Minnesota laboratories are below the field blank LODs for precipitation samples. The congener pattern in the precipitation analyzed at Minnesota, however, indicated that the higher molecular weight congeners predominate. This observation was confirmed by the results obtained at the Water Survey using the Empore extraction method in which hexa- and heptachloro-PCB congeners are the major components of the PCBs in precipitation.

Using the LOD-based maximum concentrations that can be derived from the data from DePaul (8.3 ng/L) and Minnesota (3.7 ng/L), and the quantified Water Survey data (2.6 ng/L), we estimate an average concentration of total PCBs in precipitation of 2 to 5 ng/L. This value compares reasonably well with other recent measurements of average total PCBs in precipitation around the Great Lakes of 5 to 8 ng/L (Chan and Perkins, 1989).

A problem that was discovered with the precipitation sampling method required a change in field operations. Originally the MIC samplers were rinsed with methanol to remove adhering PCBs from the Teflon-coated collection surfaces. Eisenreich (1990) reported that roughly 50% of the PCBs in precipitation collected by MIC samplers were in this methanol rinse. At the beginning of this project, Murphy et al. (1991) determined that large amounts of PCBs (50-200 ng) were present in the methanol rinse even when no precipitation had passed through the collector. This finding has since been confirmed at the Water Survey laboratory. The source of this artifact is uncertain. To avoid contamination of the sample with PCBs not derived from precipitation, we changed to a water rinse procedure to remove particles adhering to the collection surfaces. This rinse does not contain PCBs when no precipitation has passed over the collector.

Our finding that average total PCB concentrations in the air around Green Bay are only 0.3 to 0.1 ng/m^3 was unexpected. Recent estimates of airborne PCBs at remote sites in northern Wisconsin (Manchester-Neesvig and Andren, 1989) and at Isle Royale on Lake Superior (Swackhamer, et al., 1988) are 5 to 10 times higher than our Fayette data suggest. Atmospheric concentrations of PCBs have probably declined since the 1970s. Improvements in analytical methods and increased awareness of analytical interferences, however, have probably also contributed to the decline in PCBs reported for air and precipitation samples.

The use of congener specific analyses and LODs based on field blanks can also lead to lower estimates of PCBs in environmental samples. The mass detected by the gas chromatograph should not be included in the final sample if a particular congener is below the LOD. Even if the mass is above the LOD, subtraction of an average field blank value for each congener often produces a substantial reduction in total PCB mass for samples with a number of small peaks. Failure to subtract field blanks may be one reason PCB concentrations reported in some other air sampling studies are higher than those reported here.

There is a significant gradient in airborne PCB concentrations from the southern end of Green Bay to the northern end. The higher levels at the southern end can be attributed, in part, to the urban/industrial area of the city of Green Bay, a known PCB source. However, the bay itself is an important source of airborne PCBs.   Due to the relative fugacities of dissolved PCBs in surface waters and vapor phase PCBs in air, the net flux of PCBs in Green Bay should be to the air (Murphy et al., 1983; Swackhammer and Armstrong, 1986; Strachan and Eisenreich, 1988). The fact that this flux can make a significant contribution to airborne PCBs measured over land is demonstrated by wind sector sampling. At the Green Bay site, average concentrations and maximum PCB values are as high in air coming off the bay as in air coming from the industrial zone. This source of PCBs is shut off completely between December and April when the bay is ice covered. In addition, vapor phase PCBs from the sector over water during summer and fall are enriched in trichloro-PCBs compared to air coming from other sectors during this period (42.7 vs. 34.7%). A t-test indicated that this difference is significant at the 95% confidence level. The trichloro-homolog group made up over 60% of the PCBs in air collected directly over Lake Superior aboard ship (Baker and Eisenreich, 1990).

Particle-bound PCBs made up only 2 to 10% of PCBs in the atmosphere at all three sites. The vapor-particle distribution of semivolatile compounds like PCBs depends on vapor pressure, temperature, and the size, surface area, and organic content of particles in the atmosphere (Junge, 1977). The vapor pressures of most PCB congeners are such that they are predicted to exist almost entirely in the vapor phase in clean-air environments. It should be kept in mind, however, that the high-volume sampling technique used to collect particulate PCBs may underestimate the amount of particulate PCBs if they are "blown off the filter during sampling. This can occur if equilibrium conditions (especially temperature) change during sample collection.

The predominance of particulate PCBs on the smallest particles is consistent with long-range transport of the PCBs to the Fayette and Peninsula sites. During long range transport (> 100 km) through the atmosphere, particles larger than 1 μ m in diameter tend to settle out (Doran and

Horst, 1985). In addition, since most of the surface area and organic carbon on airborne particles is associated with submicron particles, semivolatile materials like PCBs will migrate to the smaller particles as they exchange between vapor and particle-bound phases. The cascade impactor results from Green Bay show some that of the particulate PCBs are associated with larger particles at this site. This indicates a nearby source of particulate PCBs. The Green Bay industrial area along the Fox River is about 2 km southwest of our Green Bay site is an area known to be a major source of PCBs to the lake. It seems likely that resuspended surface soil and urban dust from this area is contaminated with PCBs and is the source of large particle PCBs at our site.

The observed distributions of PCB congeners (Figures 4-6) indicate that a substantial amount of partitioning occurs during the transfer of PCBs between the interconnected environmental compartments of vapor, particles, and precipitation. Trichloro-PCBs are the dominant group in vapor samples but make up only about 10 to 15% of the PCBs in particles and precipitation. It has been shown that particle scavenging is the dominant source of PCBs in precipitation (Duinker and Bouchertall, 1989). Apparently this process results in a further depletion of low molecular weight PCB congeners in precipitation.

Airborne PCBs enter Green Bay from the atmosphere via three principal mechanisms: wet deposition in rain and snow, dry deposition of particles, and absorption of vapor at the surface. Based on our data, we estimate that the total average PCB concentration in precipitation over Green Bay is about 3 ng/L. Green Bay has an area of 4500 km^2 and annual precipitation of 0.75 m. Multiplying the volume of annual precipitation by the average concentration gives an annual wet deposition of total PCBs into Green Bay amounting to about 10 kg/yr. Since all dieldrin values were below the LOD, we can only estimate the <u>maximum</u> wet deposition of this compound. With an LOD-based maximum concentration of 3.9 ng/L, no more than 13 kg of dieldrin enters the bay annually in precipitation.

Dry deposition can be calculated by multiplying the average concentration of particulate PCBs, 0.01 ng/m^3, times the deposition velocity of submicron particles, 0.2 cm/sec (Strachan and Eisenreich, 1988), and the area of the bay, 4500 km^2. This results in about 3 kg deposited to the bay annually in dryfall. As with wet deposition, only a maximum dry deposition of dieldrin can be calculated. Based on the concentration measured at Green Bay, 0.001 ng/m^3, no more than 0.3 kg of dieldrin enters the bay in dryfall.

Inputs of vapor can be estimated based on the measured air vapor concentration. Liss and Slater (1974) developed a model to quantify the exchange of gases between the air and bodies of water (equation 1):

$$1/K_{OL} = 1/K_W + RT/HK_A \qquad (1)$$

where K_{OL} is the overall mass transfer coefficient, K_w is the water mass transfer coefficient, K_A is the mass transfer coefficient in air, R is the gas constant, T is the absolute temperature and, H is the Henry's Law constant. A K_{OL} of 2.53 x 10^{-6} m/sec for vapor exchange can be

determined using a wind-frequency-weighted K_w of 3.45×10^{-6} m/sec (Murphy et al., 1991), a K_A value of 10^{-3} m/sec (Mackay and Yuen, 1983), a temperature of $293°$ K and 23 Pa-m^3/mol for H. The flux of PCBs to Green Bay can then be calculated using equation 2:

$$FLUX = K_{OL} \times f_{PCB}/H \qquad (2)$$

where f_{PCB} is the average fugacity of PCBs in the air. For a concentration of 0.2 ng/m^3 and an average molecular weight of 266, the fugacity equals 0.2×10^{-8} Pa. The flux calculated using equation 2 is about 5.5 kg/yr into Green Bay.

Volatilization from the bay can be estimated using equation 3 (Strachan and Eisenreich, 1988):

$$FLUX = K_{OL} (C_{dis} - (C_v \times RT/H)) \times SA \qquad (3)$$

where C_{dis} is the concentration of dissolved PCBs in surface water, $0.7 \, \mu$g/m^3 (Swackhammer and Armstrong, 1987); C_v is the average vapor-phase concentration of PCBs in the atmosphere over the bay, $0.2 \times 10^{-3} \, \mu$g/m^3; and SA is the surface area of the bay. Using these values with the other parameters defined previously, an annual net flux to the atmosphere out of the bay of about 250 kg of PCBs can be calculated.

Using these figures, wet deposition of PCBs to the bay is 2.2 μg/m^2/yr and dry deposition (vapor and particle) is 1.9 μg/m^2/yr for a total deposition from the atmosphere of 4.1 μg/m^2/yr. This is slightly lower than the estimates of about 7 μg/m^2/yr for atmospheric deposition of PCBs to Lake Michigan made a few years ago (Swackhamer and Armstrong, 1986; Strachan and Eisenreich, 1988). This is primarily due to the lower levels of PCBs we measured in air and precipitation. The earlier studies also indicated that volatilization losses may be a major removal mechanism for PCBs from Lake Michigan. Currently volatilization losses from Green Bay seem to be even more significant than those calculated for Lake Michigan. This may be because atmospheric inputs are now relatively low there compared to other inputs.

ACKNOWLEDGMENTS

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APPENDIX A

ILLINOIS STATE WATER SURVEY

INSTRUCTIONS FOR XAD-2 COLUMN CHANGE WITH MIC SAMPLERS

1.   Make sure that all precipitation has passed through the column. If rain or snow has been recent and precipitation is still eluting from the column, wait until all the liquid has drained from the funnel. If the system is plugged, catch any standing liquid in a clean beaker and pass it through the column.

2.   Measure and record the total precipitation volume.

3.   Wearing plastic gloves, rinse the Teflon collection surfaces with about 400 ml. of deionized water while scrubbing with a piece of glass fiber filter (half of an 8x10 filter with serial no. removed) to remove deposited particles. Allow these rinsings to pass over the column until the water level is halfway between the top of the column and the top of the resin bed. Remove the column; cap both ends with Teflon plugs (make sure the black O-rings are in place). Seal the glass fiber filter in a sample jar; label and package the column and jar for shipment.

4.   Clean the collector surfaces by rinsing with 200 mL of pesticide-free methanol followed by approximately 5 liters of clean tap water with additional scrubbing. Use a test tube brush to clean the funnel outlet. This should be followed by another rinse with 400 mL of deionized water. Discard these rinsings.

5.   Install a new column making sure the top and bottom O-rings are in place. After opening the outflow valve and positioning the outflow tubing, add about 100 ml. of deionized water to the collection funnel. Make sure that this water flows through the system; then empty the receiving jug. Wrap the column tightly with aluminum foil to exclude light.

6.   Send the column and a data sheet for each sample to:

    Dr. Clyde Sweet   Phones:
    Illinois State Water Survey   Clyde Sweet 217-333-7191
    2204 Griffith Dr.   Paul Nelson 217-244-8719
    Champaign, IL 61820

8.   Sample code: nP-#(B)-YR MO DA

    n=site identifier: G=Green Bay
                            P=Peninsula
                            F=Fayette

    The date in the code is the date the sample is picked up; # refers the sampler number at sites where there are more than one sampler, include a "B" in this position if the sample is a blank; P refers to sample type (precipitation).

INSTRUCTIONS FOR FILTER CHANGE WITH HIGH-VOLUME SAMPLERS

1. Remove the filter holder from the sampler by loosening the 4 plastic hand nuts. Take it inside for the filter change.

2. Wearing plastic gloves, remove the exposed filter and fold it in half lengthwise with the deposit side facing in. Wrap the filter securely in aluminum foil, label and seal in a plastic bag.

3. Install a clean glass fiber filter for the TSP or cartridge samplers with the labeled side facing up. Wipe away any accumulated dirt from around the filter holder with a clean cloth and reinstall the filter holder on the sampler. Tighten the hand nuts securely to insure an air-tight seal.

4. For the cartridge samplers, remove the exposed cartridge wearing plastic gloves, wrap in Al foil and seal with tape in a labeled metal can. Replace a clean cartridge in the holder. When replacing the cartridge holder, make sure the o-rings are in place and tighten the nuts carefully to avoid cross-threading.

5. Record the counter reading. Test by turning on the hi-vol and allow it to run for 2 minutes. Record the manometer reading if applicable. Turn off the hi-vol. If the manometer reading is zero or much lower than the previous reading, retighten the cartridge holder and test again.

6. Set the timer for the desired sampling period. Normally, the TSP sampler should start at midnight (0:00, EST) and run for 24 hours until the following midnight (24:00 EST) once every 6 days or as specified in the weekly site protocol. The cartridge samplers should run as directed by the meteorological program over a 14-day period.

7. Mail all filters and cartridges to the address below. Copies of the data forms should be sent along with the samples.

> Dr. Clyde W. Sweet
> Illinois State Water Survey
> 2204 Griffith Dr.
> Champaign, IL 61820   Phone: 217-333-7191

7. Sample Codes:

HIGH VOL FOR ORGANICS		TSP/TOC HIGH VOL	
FILTERS:	nH-#-YR MO DA-F	FILTERS:	nT-YR MO DA
CARTRIDGE:	nH-#-YR MO DA-C		

The "n" refers to the site identifier (G for Green Bay; P for Peninsula; F for Fayette). The date in the code is the date sampling ended; the position marked "#" should be used to indicate the wind direction code (W,N,S at Green Bay; N,E at Peninsula; N,S at Fayette) T (TSP/TOC) and H (HIVOL FOR ORGANICS) refer to sample type.

GLAD ORGANICS FIELD REPORT FORM
Form 880328

Copy __

1. Station Name PENINSULA   2. Operator DAVID ESTANO

3. Sample Start 89 /09 /05 0945 End 89 /09 /19
   Yr / Mo / Da   Time   Yr / Mo /Da   Time
                   (24 Hr)   (24 Hr)

4. Sample Type   5. Sample Codes

Biweekly | Cartridge PB-_____-C Filter PB-__-_____-F
Precipitation __ |
                   | Rinse   PB-_____-W Ppt.Vol. _____ mL

TSP/TOC   __ | Filter   PT-_____   Manometer _____ in.
                   | Meter Start _____   Meter End _____
                   | Volume   _____   Set Up Date __/__/ + ____ days

Cascade | Filter   PI-_____-F Cartridge PI-_____-C
Impactor   __ | Meter Start _____   Meter End _____
                   | Manometer Start _____   Manometer End _____

High-   __ | Filter   PH-NF 890919-F Cartridge PH-NC- 890919 -C
Volume | Meter Start 1944.42   Meter End 2016.35
                   | Manometer Start 1.9   Manometer End 1.9

9. Comments on sample condition or site operation:

FILTER # 5643/0

   4.3647
   3260
   387

FLOW CHECK/CALIBRATION		
DATE 9/5/89	PRE.ADJ	POST ADJ
ORIFICE MAN.RDG.	1.4	1.4
ORIFICE FLOW	20.8	20.8
INSTRUMENT MAN. RDG.	1.9	1.9

10. Date Shipped: 89 / 09 / 19 DE   Received: __ / __ / __
                  Yr   Mo   Da   Initials   Yr   Mo   Da   Initials

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