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The IJC Menomonee River Watershed Study

Atmospheric Chemistry Of PCBs and PAHs

FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA, was established in Region V, Chicago to provide a specific focus on the water quality concerns of the Great Lakes. GLNPO also provides funding and personnel support to the International Joint Commission activities under the U.S.- Canada Great Lakes Water Quality Agreement.

Several land use water quality studies have been funded to support the pollution from Land Use Activities Reference Group (PLUARG) under the Agreement to address specific objectives related to land use pollution to the Great Lakes. This report describes some of the work supported by this Office to carry out PLUARG study objectives.

We hope that the information and data contained herein will help planners and managers of pollution control agencies make better decisions for carrying forward their pollution control responsibilities.

Madonna F. McGrath
Director
Great Lakes National Program Office

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Atmospheric Chemistry of PCBs and PAHs

Volume 9

by

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PREFACE

The significance of atmospheric input of PCBs and PAHs to Lake Michigan is assessed utilizing dry and wet deposition information obtained over the lake's surface. Possible cycling of these compounds over Lake Michigan is discussed.

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PART I

TRANSPORT OF AIRBORNE PCBs TO LAKE MICHIGAN

by

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ABSTRACT

The air over Lake Michigan was sampled during 1977 to develop a collection method for PCBs and obtain data about their atmospheric transport and dry deposition onto the lake. A resin, XAD-2, was the most efficient collection medium for PCB vapor and was incorporated into standard high volume air samples for the collection of particulate and vapor phase PCBs. PCB concentrations in air samples taken over Lake Michigan were lower than those taken from urban areas; i.e., Milwaukee. Aroclors 1242 and 1254 were the main components of vapor phase PCBs while in some instances the particulate phase PCBs contained Aroclor 1260. The particulate phase PCBs over Lake Michigan contained a larger percentage of the more volatile mixtures than those reported in urban areas such as Chicago and Milwaukee. PCBs tend to associate with particulates 0.002 to 0.1 μm in diameter. The amount and organic carbon content of the particulate phase appear to control vaporization and revolatilization of PCBs.

The net atmospheric input to Lake Michigan based upon the liquid and gas phase control models was 2848 and 8655 kg/yr, respectively. Bubble ejection was not found to be a probable water to air transport process over the lake. It is estimated that the atmopshere contributes >70% of the PCB load to Lake Michigan.

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I-1. INTRODUCTION

Polychlorinated biphenyls (PCBs) have become an environmental problem in Lake Michigan. Concentrations in lake trout, exceeding the 5 ppm standard set by the FDA, are frequently observed. High PCB concentrations in Lake Michigan fish have caused a closing of the commercial fishing industry on the lake.

Monsanto, the sole producer of PCBs in the United States, voluntarily banned the sale of PCBs for use in "open" systems in 1971. Even though Monsanto no longer produces PCBs, the ban on PCBs in the United States will not come into effect until July 1, 1979 (Toxic Substances Control Act of 1976, PL94-46). After the ban, PCBs will continue to escape into the environment from products in which they were formerly used.

The detection of PCBs in Antarctic snow samples (1) strongly suggests that the atmosphere is a major transport route. Proof of this hypothesis, in the Great Lakes region, has come from the determination of PCBs in precipitation over Lake Michigan (2) and its significant contribution to the present PCB loading of the lake (Table I-1).

Any study of the cycling of a trace contaminant in the environment must deal with its source, transport, and sink. This study was initiated to obtain a better understanding of the transport of PCBs in the atmosphere and their dry deposition onto Lake Michigan.

The main objectives of this study were:

1. To develop a method of collection for atmospheric PCBs which was both qualitative and quantitative.

2. To employ the method to obtain information about the concentrations of PCBs in air over Lake Michigan.

3. To utilize the data to estimate the dry flux of PCBs to Lake Michigan.

Table I-1. Inputs of PCBs (kg/yr) to Lake Michigan (2)

Source	Prior to 1975	1977
Industrial discharges	25,000	--
Precipitation	4,800	4,800
Streams and wastewater effluent	750	700
Others*	2,750	2,750
TOTAL	33,300	8,300

*Accounts for dry deposition and unknown industrial discharges.

I-2. CONCLUSIONS

Laboratory experiments performed with XAD-2, polyurethane foam, polyurethane foam coated with DC-200 and florisil, showed XAD-2 to be the most efficient collection medium for PCB vapor and well-suited for high volume air sampling. A standard high volume air sampler was modified to incorporate XAD-2 resin for the collection of particulate and vapor phase PCBs. The sampler is 90 to 100% efficient for collection of even the most volatile vapor phase PCB mixtures. Retention efficiencies depend upon the volatility of the isomers with Aroclor 1221 being retained at an average of 83%.

Air samples taken over Lake Michigan were less concentrated in PCB than those taken in urban areas such as Milwaukee. Vapor phase PCBs were mainly composed of Aroclors 1242 and 1254 while the particulate phase PCBs also contained Aroclor 1260 in some instances. The particulate phase PCBs over Lake Michigan contained a larger percentage of the more volatile mixtures than those reported in urban areas such as Chicago or Milwaukee. Adsorption theory based upon the volatility of PCBs and amount of particulate surface area fails to explain this finding. The higher proportion of PCBs in the particulate phase over Lake Michigan and Milwaukee as compared to the ocean is probably a result of the higher concentration of particulate matter near urban centers.

Vaporization of PCBs from PCB coated particulates placed on a glass fiber filter did not occur under conditions where the particulate matter contained large amounts of organic carbon. While the experiment did not give entirely conclusive evidence, the desorption kinetics under environmental conditions should be slow since particulates collected over Lake Michigan contained large percentages of the more volatile PCBs.

Calculations based on the revolatilization experiment produced air/water partition coefficients for Aroclors 1242 and 1254 which were orders of magnitude less than the theoretically determined Henry's Law constants. The coefficients were in the same range as those reported for saturated water solutions of Aroclors 1221 and 1016. Theoretical calculations of the vapor phase washout coefficients for 1242 and 1254 showed them to be the same order of magnitude as the air/water partition coefficients. The magnitude of the coefficients indicated gas phase control of PCBs. The revolatilization rate for PCBs was found to be slower under conditions where particulate matter was present, showing that if PCBs are liquid phase controlled, environmental revolatilization rates cannot be estimated in filtered-organic free aquatic environments.

Theoretical calculations based upon washout coefficients indicated that PCBs are associated with particulates between 0.002 and 0.1μ in diameter. The calculations could not conclusively predict the existence of vapor phase PCBs but the best estimates of wet fluxes from air concentrations can be made by employing both a particulate and vapor phase washout coefficient.

Due to the scarcity of experimental evidence for gas phase control of PCBs, atmospheric fluxes to Lake Michigan based upon both a liquid and gas phase control model were calculated. Bubble ejection of PCBs was not an important water to air transport process in Lake Michigan. More experimental evidence is needed to estimate the alteration of airborne PCBs by photolysis. The net atmospheric input based upon the liquid and gas phase control models was 2848 and 8655 kg/yr respectively.

At the present time the atmosphere is estimated to be contributing greater than 70% of the PCB load to Lake Michigan. These estimates show that futher investigations of the transport of PCBs must be made.

Futher studies should involve a determination of the vapor/particulate partitioning of airborne PCBs, determinations of Henry's Law constants under simulated environmental conditions, and estimations of the importance of photolytic processes on atmospheric PCBs. The effects of the atmospheric transport of PCBs on composition, vapor/particulate partitioning, and deposition rates should also be explored so accurate estimates of fluxes can be made.

I-3. BACKGROUND

General Information

PCBs have had a widespread application due to their general stability, inertness and dielectric properties. In the United States they were produced by the Monsanto Company under the trade name Aroclor. Aroclors are mixtures of PCB isomers which are designated by a four digit number. The first two digits give the molecule type, while the second two give the weight percentage of chlorine. For example, Aroclor 1242 is a mixture of biphenyl molecules with 42% chlorine by weight. A listing of the Monsanto Aroclor products along with their molecular weights and average chlorine numbers can be found in Table I-2.

Some of the products in which PCBs were used include: transformer fluids, hydraulic fluids, PCB-impregnated paper in capacitors, caulking compounds, carbonless duplicating paper, plasticizers, adhesives and wax extenders. Nisbet and Sarofim (3) and Hutzinger et al. (4) give a complete breakdown of their former uses. Versar (5) compiled a summary of the total amount of Aroclors used in different products from 1930-1974 and also, the environmental load by Aroclor type. The most widely used Aroclors were 1242, 1248, 1254 and 1260. Aroclor 1016 was used after 1970 but to a much lesser extent than the other four.

Polychlorinated biphenyls have been found in virtually every compartment of the environment. The atmosphere is one of the major compartments and is probably the most important transport route, at least on a global basis. This is exemplified by their discovery in Antarctic snow samples (1).

There are several possible routes into the atmospheric environment. One route is vaporization from PCB containing formulations. Also, due to their widespread use in many products, they can be volatilized during incineration in poorly operated commercial and municipal incinerators. Incineration at 2000+°F for 2 sec will destroy PCBs. They can also volatilize from products buried in sanitary landfills. Murphy and Rzeszutko (2) have determined the concentration of PCBs in a sanitary landfill's vent gases. The concentration was much higher than those normally found in ambient air, making landfills a definite PCB source. Other sources of polychlorinated biphenyls include small domestic and apartment incinerators and open burning dumps. Table I-3 contains Nisbet and Sarofim's (3) estimates of the rates of input of PCBs to the North American continent. They estimated the atmospheric emission rate of PCBs to be 1.5 to 2 x 10^3 Tonnes/yr, amounting to a vaporization of 30,000 Tonnes since 1930.

An examination of the physical properties of PCBs may give some insight as to why their mode of transport is important. PCBs can theoretically exist as 209 different isomers (4). Two important physical properties, from an environmental standpoint, are their vapor pressures and solubilities. The solubility of the isomers decreases with increasing chlorine content (6,7). Vapor pressures of some Aroclor mixtures can be found in Table I-4. Hutzinger et al. (4) give a complete listing of the physical and chemical properties of PCBs.

Table I-2. Average chlorine numbers and molecular weight of Aroclor mixtures (4)

Aroclor	Average Cl No/molecule	Molecular wt.
1221	1.15	192
1232	2.04	221
1016	2.96	256
1242	3.10	261
1248	3.90	288
1254	4.96	327
1260	6.30	372
1262	6.80	389
1268	8.70	453

Table I-3. Gross estimates of rates of input and accumulation of PCBs in 1970 (3)

Input	Rates, tonnes/yr	PCB
Vaporization of plasticizers	1 to 2 x 10^3	1248 to 1260
Vaporization during open burning	4 x 10^2	Mainly 1242
Leaks and disposal of industrial fluids	4 to 5 x 10^2	1242 to 1260
Destroyed by incineration	3 x 10^3	Mainly 1242
Disposal in dumps and landfills	18 x 10^3	1242 to 1260
Accumulation in service	7 x 10^3	1242 to 1254

Table I-4. Vapor pressures and saturation vapor densities of Aroclor mixtures

Aroclor	Temp, °C	Vapor pressure,* mm Hg	Sat. vapor density,** mg/mm^2
1242	25	4 x 10^{-4}	5.5
1248	25	5 x 10^{-4}	7.9
1254	25	8 x 10^{-4}	1.4
1260	25	4 x 10^{-5}	0.73

*Mackay and Wolkoff (Ref. 8)
**Calculated using the ideal gas law (PV = nRT).

A calculation of the saturation vapor densities of PCBs from their vapor pressures and the ideal gas law indicates that PCBs could be present in the atmosphere at extremely high concentrations (Table I-4). This is only a theoretical calculation and does not necessarily indicate the volatility of the PCB mixtures in nature. It would be expected that the more volatile mixtures would be present in the atmosphere. Mieure et al. (9) have shown that the vapors above a standard Aroclor 1016 mixture were enriched in the more volatile components. This points out that the atmospheric component of the mixture may bear no resemblance to the original Aroclor product. This fractionation makes interpretation of the data extremely difficult. The affinity of PCBs in aqueous solutions for surfaces (4) would seem to indicate that they would be adsorbed to particulates but the extent to which this occurs in the atmosphere is presently uncertain.

Collection Methods

Many methods have been employed to measure the concentrations of PCBs in air. Three important facts must be kept in mind when designing a collection method:

1. PCBs are a mixture of isomers having variable volatilities.

2. Atmospheric samples most likely contain fractionated PCBs which do not reflect the composition of the original Aroclor mixtures.

3. Air concentrations are usually in the sub-part per trillion range.

Keeping these factors in mind, certain criteria must be met by the collection method so both a qualitative and quantitative sample can be obtained:

1. The sampler must have a high collection efficiency for all the PCB isomers, even the most volatile species.

2. Since the concentrations in air are usually in the nanograms per cubic meter range, a substantial flow rate through the collection medium is essential to avoid extremely long sampling periods.

3. It must be relatively easy to recover the PCBs from the collection medium since only a small quantity is collected and lengthy procedures would allow more opportunity for loss of sample.

4. Interfering substances from the blank medium must be few to minimize difficulties in quantification and interpretation of gas chromatograms.

Many methods have been employed to collect PCBs from air but at the present time none is uniformly accepted. The methods can be grouped into two categories. One category is designed to measure air

concentrations. These methods employ pumps to force air through a collection medium. The other category contains methods to measure fluxes of PCBs. An adsorbent medium is coated on a surface, such as glass, onto which PCBs deposit.

One type of forced air method employs impingers containing ethylene glycol. These samplers have been found to be adequate in areas containing high levels of pesticides (10). Both their low collection efficiency and flow rates are inadequate for high volume air sampling (11). Two types of high volume air samplers have been tested. These employ a filter for collecting particulates and a chamber behind the filter holder assembly containing an organic vapor trap. Harvey and Steinhauer (12) used ceramic saddles coated with silicone oil to collect PCB vapor. They reported a collection efficiency of 70% for either tri- and hexachlorobiphenyl or Aroclor 1254. Bidelman and Olney (11) used polyurethane foam plugs as a vapor trap. Collection efficiencies of 96 to 99% were obtained in laboratory experiments using tri-, tetra-, and pentachlorobiphenyl isomers. In actual air sampling experiments collection efficiencies of 79 to 99% were reported. Environmental Science and Engineering, Inc. (13) also evaluated the polyurethane foam method and reported collection efficiencies of 85% or greater. Lewis et al. (14) reported polyurethane foam collection efficiencies of 70 to 85% using Aroclor 1242. These researchers found that the collection efficiency was not uniform for all the components of a 1242 mixture. The range was 41 to 95%, the more volatile components being retained less efficiently.

An examination of the polyurethane foam collection efficiencies shows that they are both inconsistent and not extremely quantitative. The polyurethane foam method has been used quite extensively but the reported collection efficiencies are rather low in some cases.

Collection methods have also been employed to measure PCB fluxes. Nylon screens coated with silicone oil have been used to collect PCBs and pesticides, but their collection efficiency is unknown (15,16,17,18). Glass plates coated with a 5:1 mixture of hexane:mineral oil were used in California to collect PCBs (19). A collection efficiency of 50% was obtained for Aroclor 1254 over a week long period. Aroclor 1242 was volatilized from the plates during this period. The ability of these types of collection methods to measure a "natural" PCB flux must come under question. If PCBs are present mainly in the vapor phase, as has been conjectured by Bidelman and Olney (20) and Harvey and Steinhauer (12), samplers using coatings of silicone oil cannot be used to measure deposition rates. Due to the organic coating's high partition coefficient, samplers of this design efficiently scavenge PCB vapor as well as particulates. These sampling surfaces cannot reflect a natural surface such as turf or water. This sampling method is still adequate for measuring and comparing source strengths.

From the preceding discussion it is evident that many methods have been employed but PCB sample collection methodologies can still be improved upon.

Air Concentrations and Composition

Atmospheric concentrations and airborne fallout have been reported for a number of areas. Concentrations are highest in urban areas and particularly near industrial users.

Concentrations in remote areas are usually in the sub-nanogram per cubic meter range. Sampling air in Bermuda, Bidelman and Olney (11) found concentrations of 0.30 to 0.65 ng/m^3 (as 1248) while Harvey and Steinhauer (12) found a concentration of 0.5 ng/m^3 (as 1254). Concentration ranges over the North Atlantic have also been determined. Bidelman and Olney (20) found concentrations ranging from 0.2 to 1.6 ng/m^3 (as 1242 or 1248). Harvey and Steinhauer (12) found an exponential increase in PCB concentrations in air as they proceeded toward the New York Metropolitan area. At 2000 km from the coast (Grand Banks) they found ranges of 0.05 to 0.16 ng/m^3 (as 1254). Off Bermuda, concentration ranges of 0.15 to 0.4 ng/m^3 (as 1254) were observed while PCB concentrations in air 500 km from New York City (Georges Banks) ranged from 0.58 to 1.60 ng/m^3 (as 1254).

Bidelman (21) collected a number of samples over the North Atlantic during the period 1973 to 1977 (Table I-5). Examination of the results indicates that the concentrations have decreased. The restriction by Monsanto in 1970 on the sale of PCBs for use only in closed systems may have contributed to the decrease. A certain lag period may have taken place, the length of which depended upon the atmospheric residence time of the mixtures. The change in composition of the air samples from Aroclor 1248 to 1254 is more difficult to explain. The environmental loads of Aroclor 1248 and 1254 during the period 1930 to 1974 are very nearly equal (5). The change may be due to a different release rate of the two mixtures, dependent upon the type of products in which they were used. Another explanation may be that the deposition rate of Aroclor 1248 is much greater than that of 1254. A seasonal trend for Bidelman's samples was not apparent.

Concentrations of PCBs in urban air are usually an order of magnitude higher than those found in remote areas. On the University of Rhode Island campus and urban Providence, Rhode Island, Bidelman and Olney (20) found concentrations ranging from 2.1 to 9.4 ng/m^3. Harvey and Steinhauer (12) found concentrations of 3.9 to 5.3 ng/m^3 (as 1254) in Vineyard Sound located near the New York metropolitan area. Murphy and Rzeszutko (2) measured concentrations of 3.6 to 11.0 ng/m^3 in urban Chicago air. At least 85% of each sample was found to most closely resemble an Aroclor 1242 mixture. Air sampled in Jacksonville, Florida was found to contain 3 to 36 ng/m^3 (13). The samples most closely resembled Aroclors 1242 and 1254.

Atmospheric concentrations near industrial users of PCBs are higher than those normally found in urban areas. Concentrations near a General Electric facility in New York were found to be in the range of 20 to 4000 ng/m^3 (22). After ceasing to use PCBs at their facilities, average levels dropped below 300 ng/m^3. Average air concentrations around dump and contaminated dredge spoil areas were 3240, 2160 and 107 ng/m^3 (as 1016). Environmental Science and Engineering, Inc. (13) collected samples around a major industrial user and found concentrations to be in the range of 300 to 498 ng/m^3 (as 1016). Tables I-6,

Table I-5. Trends in concentration of PCBs (as Aroclor 1248) in N. Atlantic air (Bermuda)--seasonal and long term (21)

Time	In air, ng/m^3
April 73-Sept. 73	0.76 ± 0.55(5), 4 were <0.33
Oct. 73-March 74	0.51 ± 0.53(7), 5 were <0.24
April 74-Sept. 74	0.20 ± 0.09(19)
Oct. 74-March 75	No samples taken
April 75-Sept. 75	0.076 ± 0.063(6)
Oct. 74-March 76	No samples taken
April 76-Sept. 76	0.077 ± 0.035(11)*
Oct. 76-March 77	0.074 ± 0.099(11)*

*These samples matched Aroclor 1254 more closely.

Table I-6. PCB concentrations in marine air (23)

Location and date	In air, mg/m^3	Ref.
Bermuda, 1973	0.15 to 0.5	12
Bermuda, 1973	0.19 to 0.66	11,20
Bermuda, 1974	0.08 to 0.48	11,20
Cruises, Bermuda-U.S., 1973-74	<0.05 to 1.6	11,20
Chesapeake Bay, 1973	1.0 to 2.0	11,20
Grand Banks, 1973	0.05 to 0.16	12
Georges Banks, 1973	0.58 to 1.6	12

I-7, and I-8 contain a summary of the air concentrations cited in this section and also additional data from Bidelman et al. (23).

Attempts to measure PCB fallout have also been made. Measurements in Sweden showed a range of 620 to 10,510 ng/m^2-month (17). Fluxes determined by Bengston and Sodergren (18) in Iceland showed a range of 40 to 1050 ng/m^2-month. McClure and Lagrange (24) measured an average Aroclor 1254 flux at La Jolla, California of 3×10^{-7} g/m^2-day 9 $\mu g/m^2$. For reasons stated in the collection methods section, these numbers should not be used to represent natural PCB fluxes. A summary of the data can be found in Table I-9.

The reported data definitely shows that concentrations are lowest in remote areas and highest in urban areas, particularly near industrial users. Since there are many ways of collecting and quantifying air samples, extreme caution must be taken when comparing results. Differences in quantification methods will give variable results. The air composition data show that samples were reported predominantly as Aroclors 1242, 1248 and 1254. The determination of the composition of an air sample is very subjective unless a systematic method of chromatogram division such as the Webb and McCall (25) method is used. Samples can still be used to determine trends and comparisons can be made if methods of collection and quantification are similar.

Nature of Airborne PCBs

Determinations of PCB concentrations in air by different high volume collection methods have shown that greater than 90% of the airborne PCBs pass through a glass fiber filter and are collected on a PCB adsorbent material (2,11,12,20). Whether these PCBs are associated with particles too small to be collected by a glass fiber filter or are actually present in ambient air as vapor is uncertain. The problem is compounded by the hypothesis that PCBs initially associated with particulates can be vaporized during collection, become entrained in the flow and, subsequently, be collected as vapor (2,12,20). Operationally defined particulate and vapor concentrations have been determined, but the true nature of atmospheric PCBs has not been investigated extensively.

Theoretical calculations have been made to estimate the amount of PCBs present in the particulate phase. Murphy and Rzeszutko (2) used the composition of their rain and air samples to estimate the vapor/particulate partitioning. Two assumptions were made. The first was that all the Aroclor 1260 in air is associated with particulates. This is a logical assumption since the vapor pressure of Aroclor 1260 is approximately an order of magnitude lower than the vapor pressures of the lighter mixtures (1242, 1254). The second was that all PCBs in rain are due to particulate washout. This assumption is based upon the Henry's Law constant of Aroclor 1260. The previously reported Henry's Law constant (9) predicts that the concentration of scavenged vapor is negligible. Following from these two assumptions and using the average concentration of 1260 in the air samples (3%) and that in the rain samples (13%), the amount of PCBs on particulates is 3/13 or 27%. Whether or not the second assumption is correct is uncertain since the Henry's Law constants for Aroclor mixtures may be in error and PCBs could possibly be gas phase controlled (26). If PCBs are

Table I-7. PCB concentrations in continental air (23)

Location and date	In air, ng/m^3	Ref.
Kingston, R.I., 1973-75	1 to 15	23
Organ Pipe National Park, Ariz., 1974	<0.02 to 0.41	23
Hays, Kans., 1974	<0.03	23
Northwest Territories, Canada, 1974	<0.002 to <0.07	23
La Jolla, Cal., 1973	0.5 to 14	24
Vineyard Sound, Mass., 1973	4 to 5	12
University of R.I., 1973	2.1 to 5.8	20
Providence, R.I., 1973	9.4	20
Chicago, Ill., 1975-76	3.6 to 11.0	2
Jacksonville, Fla., 1976	3 to 36	13

Table I-8. PCB concentrations in continental air near sources

Location and date	In air, ng/m^3	Ref.
Washington County, N.Y., 1978	20 to 4000(300)*	22
Washington County, N.Y. dredge spoil sites, 1978	107 to 3240	22
Jacksonville, Fla., 1977	498	13

*Concentration after PCB use was stopped.

gas phase controlled, rain may be able to scavenge PCB vapor and an estimate of this type could not be made.

Junge (27) estimated the amount of vapor/particulate partitioning of chlorinated hydrocarbons (CHC) over the ocean using a different approach. He applied adsorption theory along with the number of particles per cubic centimeter, the surface area represented by the particles and the saturation vapor pressures of the chlorinated hydrocarbons. Ten percent of the CHC over the ocean was predicted to be in the particulate phase. Using Junge's approach less than 5% of the PCBs over the ocean would be associated with particulates. The situation in urban and rural air is more complex due to the increased number of particles. For Aroclor 1254 and 1260 approximately 10 to 45% would be associated with particulates while less than 5% of the 1242 would be found in the particulate phase. This can only be considered an estimate since adsorption not only depends upon the amount of surface area and the vapor pressure of the adsorbate but also the nature and subdivision of the adsorbent.

Table I-9. PCB fallout data

Location and date	PCB, ng/m^2-month	Ref.
Sweden, 1972	620 to 10,510	17
Iceland, 1974	40 to 1,050	18
La Jolla, Cal., 1977	9,000	24
Southern Cal., Bight, 1974	1,560 to 34,890	19
Bratislava, Czech., 1972 to 1973	120 to 3,440	28
Tsavo East, Kenya, 1973	20	28
Nakuru, Kenya, 1973	15 to 25	28
Gambia, 1973	184	28

I-4. SAMPLE CLEANUP AND QUANTIFICATION

XAD-2 Cleanup

Considerable difficulty was experienced in obtaining a low blank extract from XAD-2 resin. Air sampling required use of the resin on a dry basis; upon drying however, contaminants are released from inside the beads (29). These contaminants are formed during the manufacturing process. It was necessary to remove as many of the contaminants as possible so they would not affect the collection efficiency and complicate interpretation of chromatograms.

Several cleanup procedures were attempted in order to reduce the contamination level. A 24-hr soxhlet extraction with hexane as well as three successive 24-hr extractions, failed to produce a low blank. An extensive extraction scheme using warm water, methanol, acetone, ethyl acetate, dichloromethane and petroleum ether was tried. A 24-hr soxhlet extraction with each of these solvents of decreasing polarity failed to reduce the contaminant level. While the interfering organic constituents could not be identified as PCBs, they still obscured the early portion of the chromatograms where many of the more volatile PCB components elute.

A 24-hr soxhlet extraction with petroleum ether gave better results than either of the two previous methods. It was possible that the contaminants had a vapor pressure similar to that of the other solvents and instead of the compounds being removed during the extraction they were continually condensing on the XAD-2. A 72-hr extraction with petroleum ether, changing the solvent every 24 hr, was found to be satisfactory. Eluting the XAD-2 extract through an alumina column (6% H_2O w:w) showed no PCB interfering contaminants present (Fig. I-1). The XAD-2 cleanup procedure can be found in Appendix I-A.

Some difficulty was also experienced with reuse of the resin. Samples taken in the Milwaukee area over a 3 day period turned the usually white XAD-2 resin yellow. A 24-hr soxhlet extraction with petroleum ether failed to produce a clean blank. The resin was found to be permanently contaminated and could no longer be used. These problems were not experienced when collecting air samples over Lake Michigan. During the duration of the Lake Michigan sampling program the resin was continually reused for both sampling and lab experiments. Discoloration of the XAD-2 or unsatisfactory blanks were not observed. The discoloration of the resin may be due to the organic pollution load or the type of volatile organics present in the sampling area. A more extensive cleanup procedure may be necessary. This was not investigated.

In applications of XAD-2 for air sampling, the best cleanup method is soxhlet extraction with a low boiling solvent such as petroleum ether. Clean blanks are obtained which show no interfering components when eluted through an alumina column. Also reuse of XAD-2 may not be possible in heavily polluted areas unless a more extensive cleanup procedure is employed.

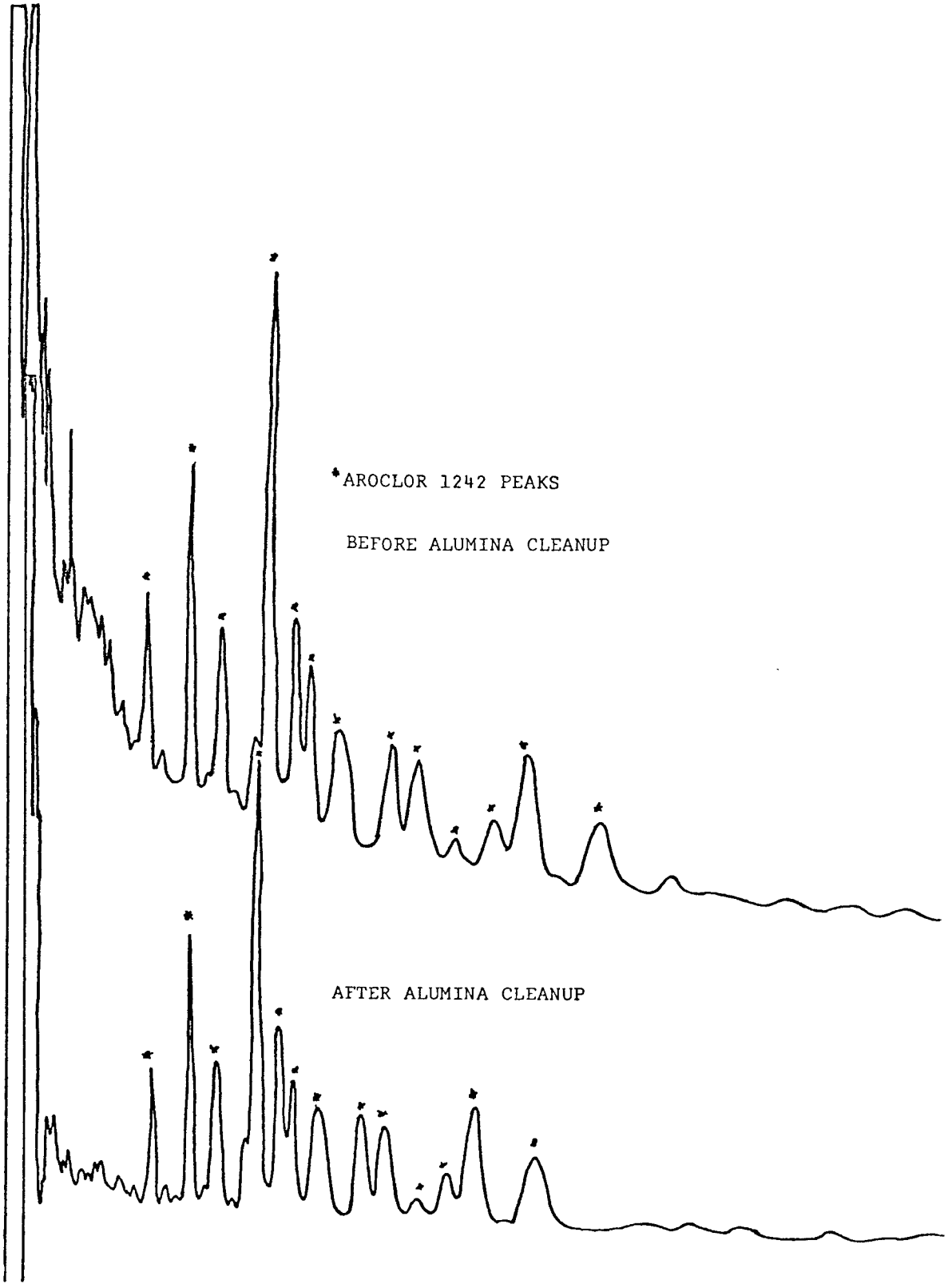


Fig. I-1. Aroclor 1242 in XAD-2 extract before and after alumina cleanup.

Sample Cleanup

In the process of deciding upon a quantitative, as well as qualitative, cleanup procedure, many methods were tried with limited success. Air samples were collected in Madison, Wisconsin and submitted to various techniques. The method of Ketseridis et al. (30) was modified somewhat by coupling it with column chromatography. The sample was extracted with concentrated sulfuric acid and KOH in methanol. It was then submitted to either florisil, alumina, or silicic acid chromatography. A very clean sample was obtained but the recovery was low. Using TCB, the acidic and basic extractions coupled with alumina chromatography produced an analytical recovery of 68%.

Junk et al. (29) used an acidic (1 N HCl) and basic (0.05 N NaOH) extraction to elute organic acids and bases from XAD-2 resin. The procedure was modified somewhat in this study. The resin was eluted with acid and base and then soxhlet extracted with a mixture of petroleum ether and acetone. The extract was then eluted through an alumina column. The PCBs were not clearly visible.

Sample extracts submitted to column chromatography using alumina (6% H_2O w:w), florisil (2% H_2O w:w) and silicic acid (3.3% H_2O w:w) gave similar results. Chromatograms of extracts seemed extremely complex, even more so than those obtained by researchers using similar cleanup techniques. From these results it was conjectured that XAD-2 was a more efficient collection medium for organic vapors than other media such as polyurethane.

It was decided that alumina chromatography would be used while trying to optimize GC conditions to resolve as many PCB components as possible. A listing of the analytical methodology of air sample analysis can be found in Appendix I-A. Analytical recoveries for direct spikes on the resin, with subsequent elution of the concentrated extract through alumina were: 85.5, 80.1 and 64.9% for TCB, Aroclor 1242 and Aroclor 1221 respectively.

The best cleanup procedure for air samples collected in this study was found to be alumina column chromatography. Satisfactory recoveries were obtained using both labelled and unlabelled PCBs. Recoveries were found to depend upon the volatility of the PCB mixture with Aroclor 1221 being the most difficult to recover.

Sample Quantification

The difficulties experienced with the quantification of air samples are the result of two factors: interfering volatile organics present in ambient air and nonconformance of samples to standards. Many of the volatile organics elute very early when chromatographed and totally obscure the components of an Aroclor 1221 mixture. Cleanup procedures, such as alumina, remove some of the interfering organics.

Air samples very rarely contain PCB components in the same proportion as those found in the original Aroclor mixture. Also,

mixtures of Aroclors sometimes occur in air, as was the case in this study (Figs. I-2 to I-5). It became apparent that the samples most closely resembled a mixture of Aroclors 1242 and 1254 rather than Aroclor 1248. The standard error can be used as a measure of the sample's conformance to the standard. The errors were rather sizeable in most cases (Table I-10). One reason for the large error is enrichment of the lighter components of the original mixture in the vapor phase.

The samples were quantified by electron capture gas chromatography on a Varian Aeorograph Series 1700 gas chromatograph equipped with two Sc (^{3}H) foils. A 3.35 m column (2 mm ID) packed with 1.5% OV-17:1.95% OF-1 on 80/100 mesh Gas Chrom W(AW) and a 3.05 m column (2 mm ID) packed with 4% SE-30:6% OV-210 on 80/100 mesh Gas Chrom W(AW) were used for identification purposes. Since the cleanup procedure did not remove all PCB interfering substances, it was necessary to use 2 different liquid phases for positive identification of PCB components. Coinjection of samples with Aroclor standards was also used for identification purposes.

The samples could not be temperature programmed due to severe baseline drift. They were alternatively chromatographed at three different temperatures to obtain the best resolution and sensitivity possible. The isothermal temperatures were 175, 205 and 230°C for Aroclors 1242, 1254 and 1260 respectively. Samples and standards were always in the linear range of the detector so peak heights were used for quantification. Three standards were run each day and the precision of the injections was always 5% or better. Duplicate injections of the sample always produced a precision within 5 to 10%.

The samples were quantified by dividing the peak heights of the sample peak by the sensitivity (deflection per amount injected) of the matching peak in the Aroclor standard. The amount of PCB represented by the peaks in the sample were then averaged to obtain the amount of Aroclor in the sample. The standard error can be obtained by finding the deviation of the peaks from the average.

To determine the Aroclor composition of the sample, chromatograms were divided according to the method of Webb and McCall (26), which is presently one of the best GC quantification methods. The total amount of PCBs is found by determining the actual amount of PCB under each peak. This is possible if the weight percentage of each component in an Aroclor mixture is known. To apply the weighting factors they obtained, the resolution of the gas chromatographic columns must be identical to theirs. The resolution of the gas chromatographic columns in this study was much better. Chromatographing the air samples under their conditions, in an attempt to reproduce their resolution, would have totally obscured peaks in the sample matching Aroclor 1242. This is a result of the many early eluting volatile organics. Since more than one Aroclor standard was used to quantitate a sample, duplication of results was avoided by using nonoverlapping peaks in each of the PCB mixtures. Five peaks from Aroclor 1242, seven from Aroclor 1254 and five from Aroclor 1260 were used to quantitate the samples.

There are other alternative methods which are better than the one

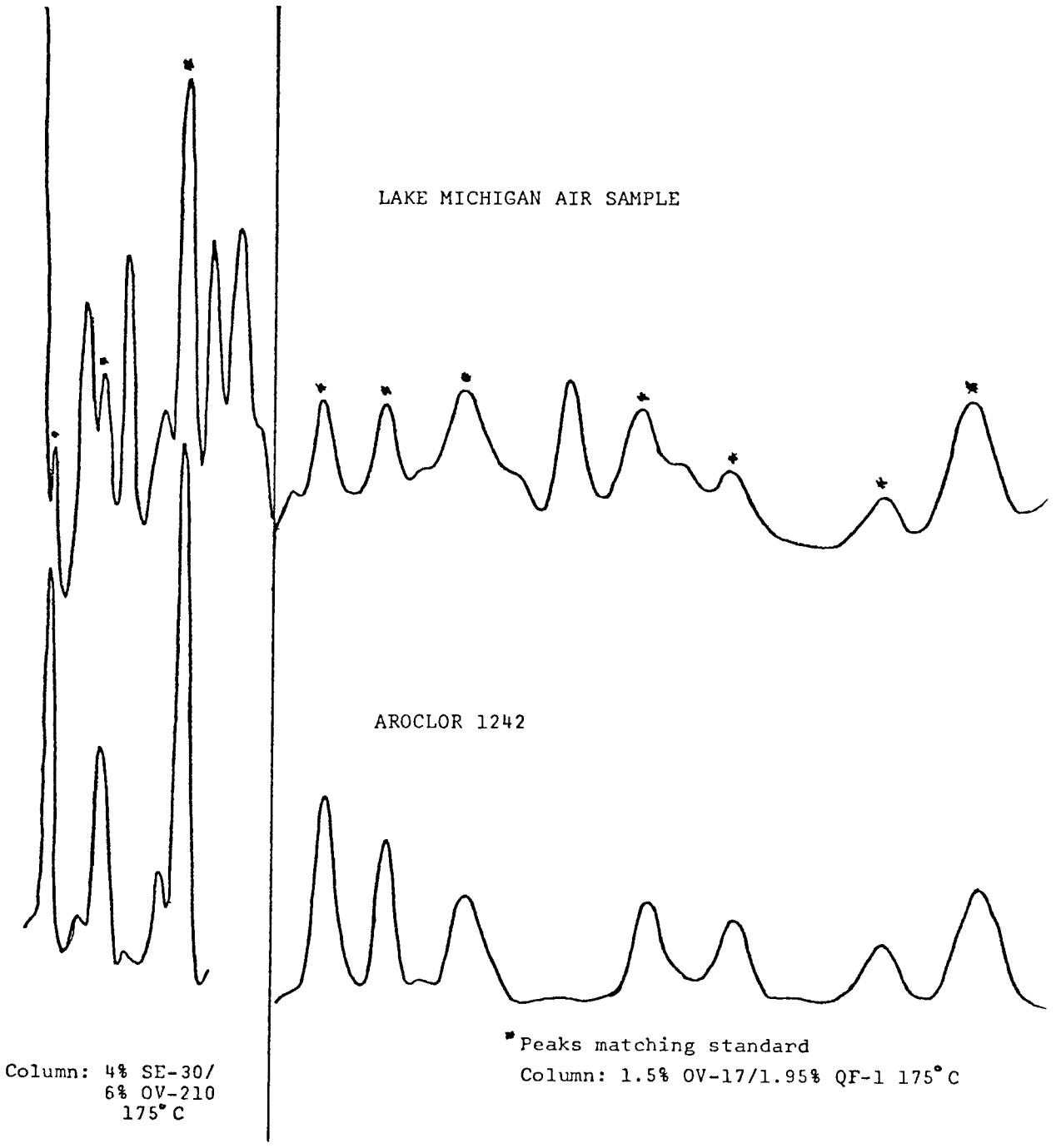
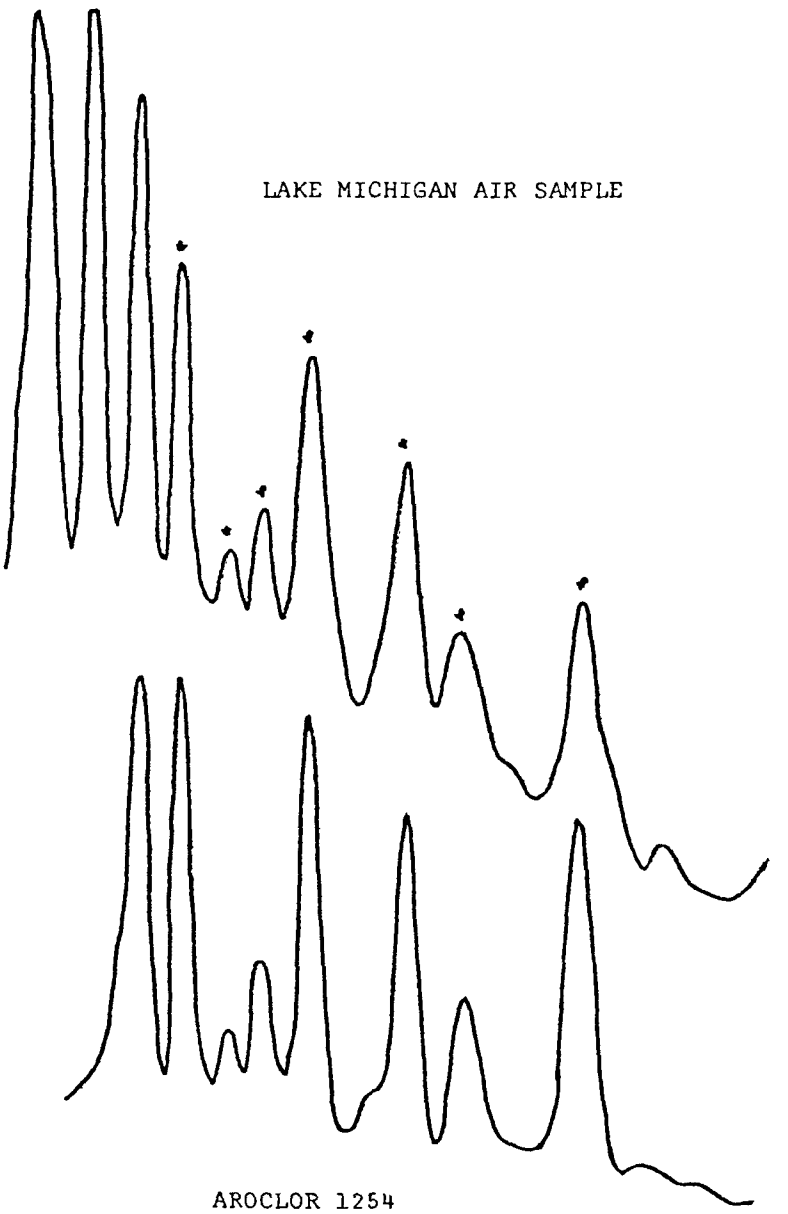


Fig. I-2. Lake Michigan air sample and Aroclor 1242 (175°C).



*Peaks matching standard

Column: 4% SE-30/6% OV-210 205°C

Fig. I-3. Lake Michigan air sample and Aroclor 1254 (205°C).

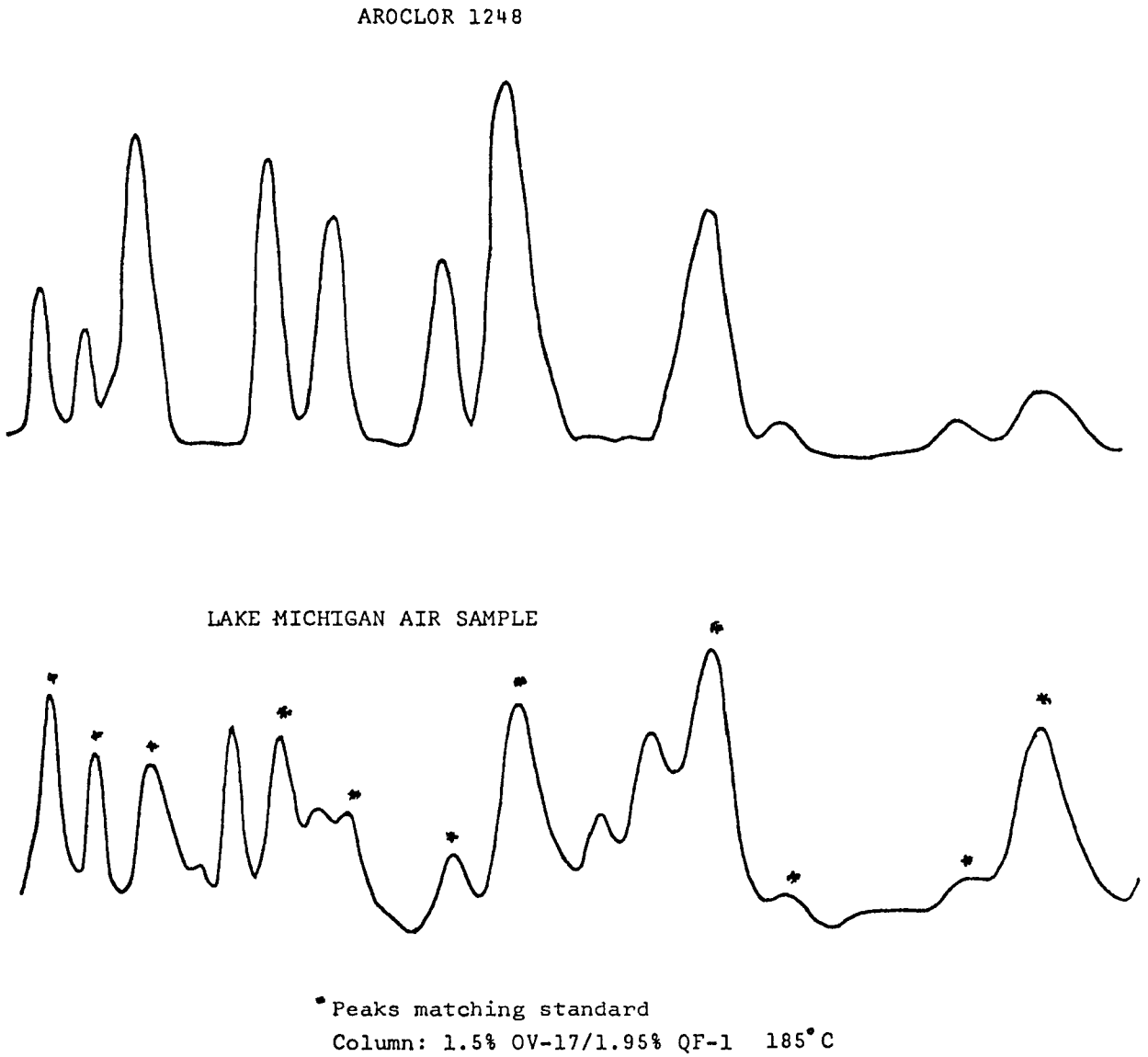


Fig. I-4. Lake Michigan air sample and Aroclor 1248 (185°C).

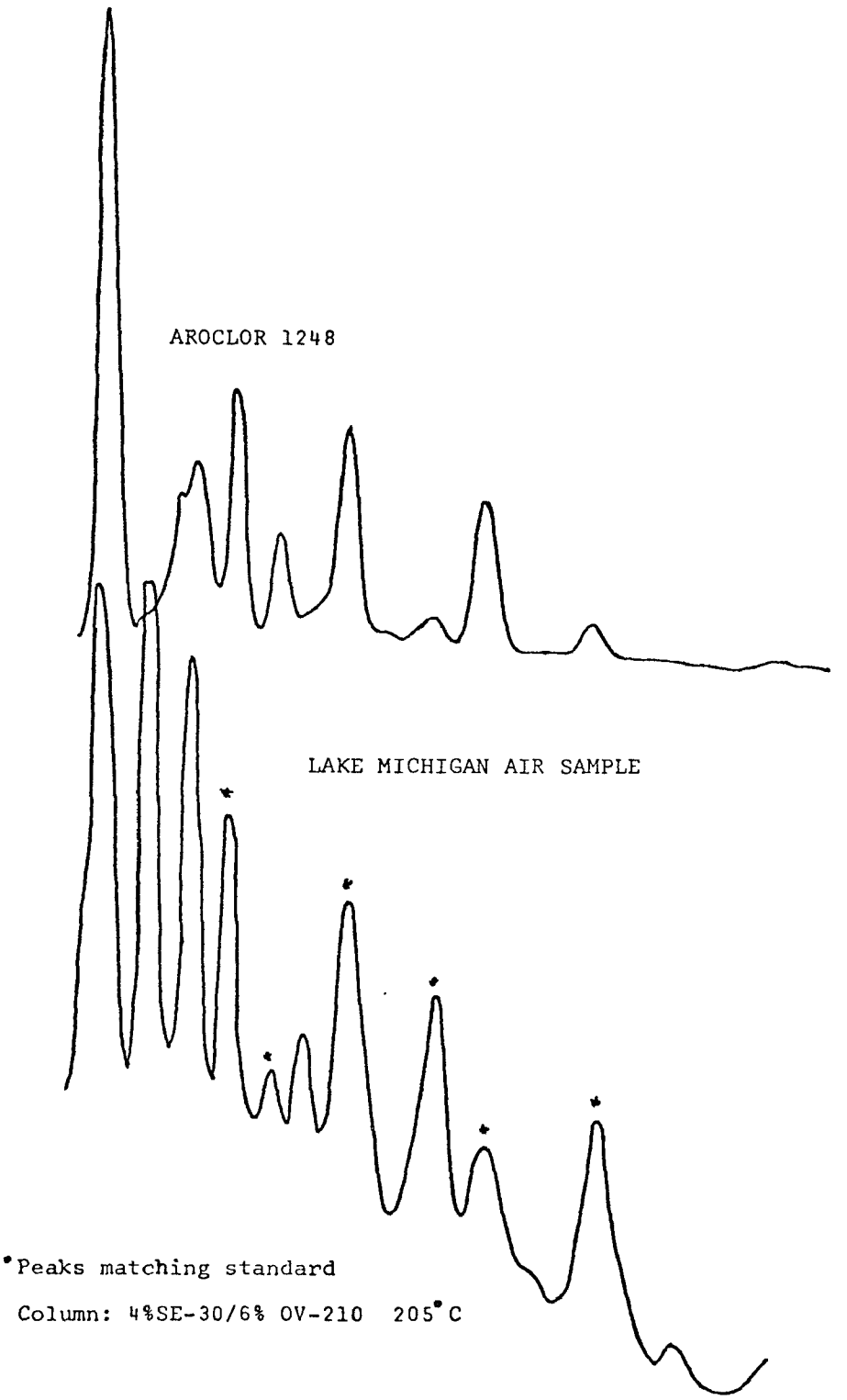


Fig. I-5. Lake Michigan air sample and Aroclor 1248 (205°C).

used in this study. The Webb and McCall (26) method is excellent for samples which do not exactly conform to the original Aroclor mixture. The only drawback is that weighting factors must be determined for the resolution of the instrument on which the analysis is being performed. To obtain an accurate number all the components that are resolved in the standard must also be resolved in the sample. Gas chromatography-mass spectrometry is an excellent tool to use for identification. The instrument is practically unisensitive to a family of compounds such as PCBs, so a much more concentrated sample than the ones collected in this study is necessary. Perchlorination of the PCBs to decachlorobiphenyl (31) would be an excellent way to quantitate samples but this method has not been perfected enough to give consistent and quantitative recoveries (32). Perchlorination also would destroy any qualitative information about the sample but GC analysis of the raw sample could still be used to obtain this information. In the future, PCB analysis must move towards quantification of separate PCB components to gain a better understanding of the partitioning of PCBs between air, land and water.

Table I-10. Standard errors of Lake Michigan and Milwaukee samples

	Standard error for Aroclors**			Standard error for Aroclors**		
Sample*	1242	1254	Sample*	1242	1254	1260
XLM2	21.4	10.1	LM2	3.7	20.7	
XLM4	26.4	20.3	LM3	13.1	20.3	
XLM5	19.5	36.5	LM4	10.6	37.0	
XLM6	26.2	27.1	LM5	14.0	20.0	18.7
XLM7	17.2	24.6	LM6	19.1	14.7	9.8
XLM8A	18.1	6.4	LM8A	13.5	17.3	17.0
XLM9A	20.4	34.9	LM9A	13.1	10.9	25.9
XMIL1	15.2	20.2	MIL1	5.5	21.6	17.0
			MIL3	11.4	15.9	26.0
			MIL5	10.2	17.2	19.8
			MIL7	10.6	22.4	43.8
			MIL8	6.9	19.1	
			MIL9	13.4	13.7	35.5
			MIL10	9.5	22.0	

*Samples with X are XAD-2 extracts, others are filter extracts.

**Standard error is $\frac{\text{(Amount under each peak - average amount)}}{\text{Average amount}}$

I-5. SAMPLING

Air was sampled over Lake Michigan and in Milwaukee, Wisconsin. The samples collected over Lake Michigan were taken aboard the EPA research vessel, Roger R. Simons, during the spring, summer and fall of 1977. Air sampling was performed in conjunction with the water sampling program being conducted by the EPA and air monitoring by Dr. Herman Sievering.

During the EPA cruises, transects of the southern lake basin were made (Fig. I-6 and Table I-11). The ship's running time averaged approximately 8 hr a day. In order to collect a detectable quantity of PCBs, a single sampling period usually extended over a period of 3 days. Samples were collected over large areas (Table I-12) and under variable weather conditions.

The samplers were located on the focsle deck of the ship, as far away from the stack as possible, to eliminate contamination from ship fuel. Contamination was easily avoided when the ship was underway but problems occurred when the wind was blowing over the stern of the ship. The samplers were turned off under these conditions. Under heavy sea conditions the focsle deck takes on a large quantity of sea spray. The samplers were turned off and covered under these conditions. Precipitation events and fog also required that the samplers be covered in order to eliminate contamination from wet fallout. To avoid sample collection of on shore point sources, the samplers were operated only when the ship was at least 3.2 km off shore.

Meteorological data were taken at hourly intervals during the sampling periods. The data included relative humidity, air temperature, wind speed and wind direction.

Samples were also taken during the winter of 1977 to 1978 in the Milwaukee area within the Menomonee River Watershed. A stationary sampling network had been previously established for the IJC Menomonee Watershed study (33). Two of the seven locations were chosen for PCB sampling: the Falk Corporation and River Lane (Fig. I-7). The Falk Corporation is located in the industrial section of the city while the River Lane station is located in a rural area. These locations were chosen so a comparison could be made between the environmentally different areas. Daily access to the samplers was not possible, which resulted in continuous operation of the samplers for extended lengths of time. Weather data were not available for these sampling locations.

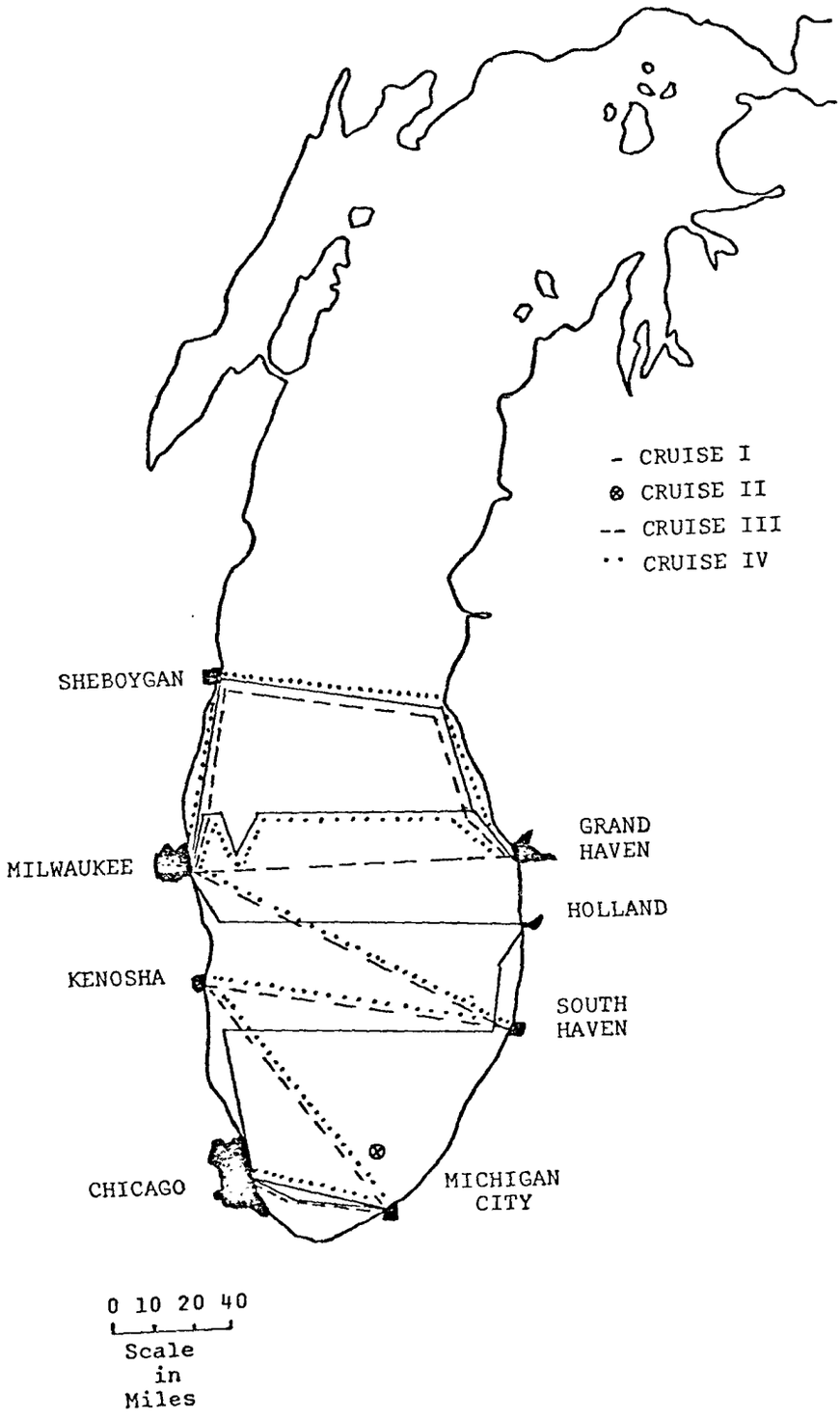


Fig. I-6. Lake Michigan cruise tracks.

Table I-11. Lake Michigan cruise tracks

Cruise	Date	Decription
I	11 to 17 June, 1977	Transects from Chicago to Michigan City, Michigan City to Chicago, Chicago to Holland, Holland to Milwaukee, Milwaukee to Grand Haven, Grand Haven to Sheboygan, Sheboygan to Milwaukee
II	14 to 19 Aug., 1977	Stationary sampling northwest to Michigan City
III	20 to 26 Aug., 1977	Transects from Chicago to Michigan City, Michigan City to Kenosha, Kenosha to South Haven, South Haven to Milwaukee, Milwaukee to Grand Haven, Grand Haven to Sheboygan, Sheboygan to Milwaukee
IV	17 to 24 Aug., 1977	Sheboygan to Grand Haven, Grand Haven to Holland to Grand Haven, Grand Haven to Milwaukee, Milwaukee to South Haven, South Haven to Kenosha, Kenosha to Michigan City, Michigan City to Chicago

Table I-12. Lake Michigan sample locations

Sample	Date	Location
2	15 to 17 June, 1977	Milwaukee to Grand Haven, Grand Haven to Sheboygan, Sheboygan to Milwaukee
3	14 to 17 Aug., 1977	Stationary sampling northwest to Michigan City
4	18 to 19 Aug., 1977	Stationary sampling northwest to Michigan City
5	20 to 21 Aug., 1977	Chicago to Michigan City, Michigan City ot Kenosha
6	22 to 24 Aug., 1977	Kenosha to South Haven, South Haven to Milwaukee, Milwaukee to Grand Haven
	25 Aug., 1977	Grand Haven to Sheboygan
8A	17 to 21 Sept., 1977	Sheboygan to Grand Haven, Grand Haven to Holland to Grand Haven, Grand Haven to Milwaukee, Milwaukee to South Haven
9A	22 to 24 Sept., 1977	South Haven to Kenosha, Kenosha to Michigan City, Michigan City to Chicago

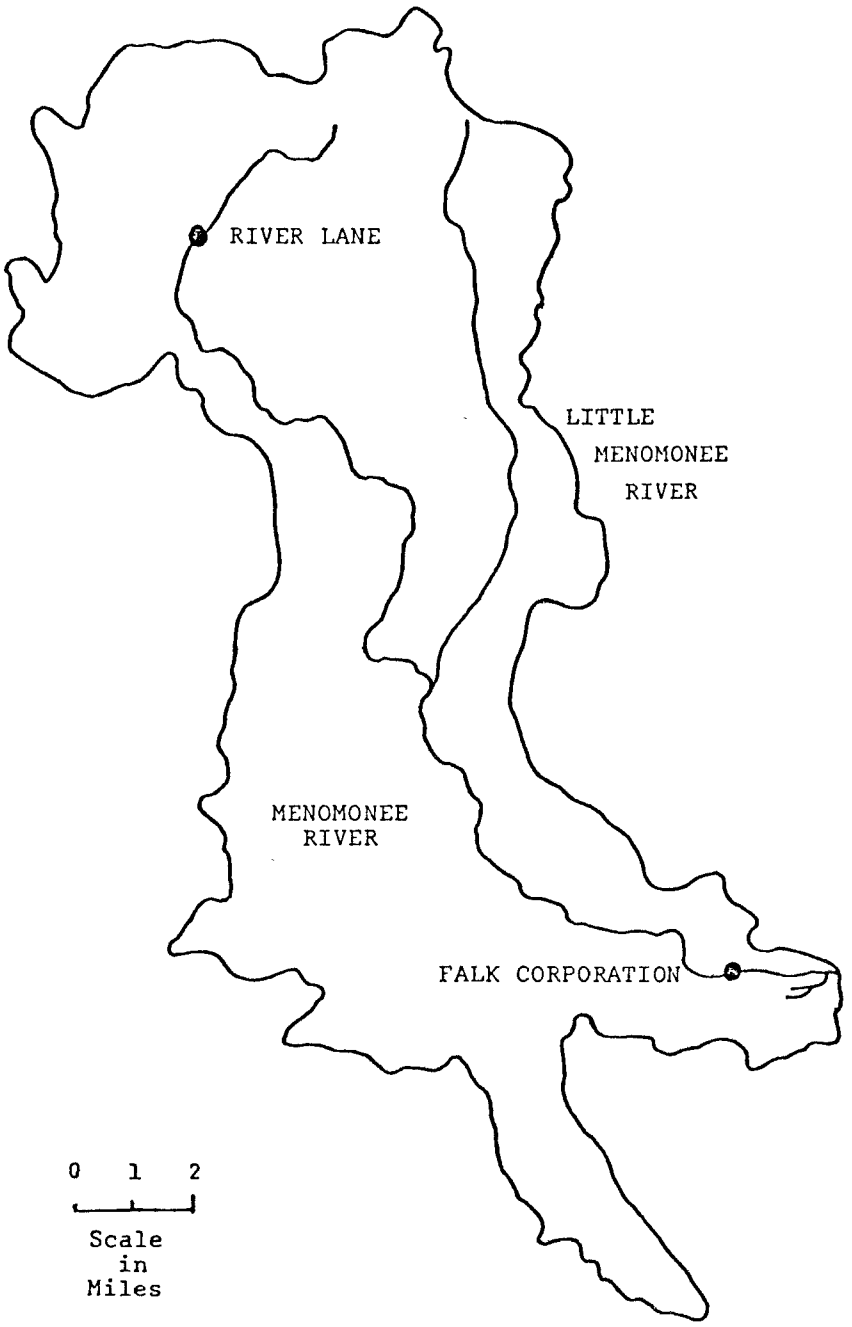


Fig. I-7. Milwaukee sampling locations.

I-6. SAMPLE RESULTS AND DISCUSSION

Comparison and Interpretation of Air Concentrations and Composition

A total of 15 air samples were collected for PCB analysis, eight from Lake Michigan and seven from the Milwaukee area. To simplify the discussion of results, PCB passing through a glass fiber filter is assumed to be vapor. What is operationally defined as vapor may actually be particles too small to be collected by a glass fiber filter.

PCB vapor over Lake Michigan was composed mainly of Aroclor 1242 (Table I-13). The XAD-2 extracts had an average composition of 75% of Aroclor 1242 and 25% of Aroclor 1254. The average vapor concentration was 0.87 ng/m^3 (0.44 to 1.33 ng/m^3). The particulate phase composition was similar to that of the vapor in almost all cases (Table I-14). Four of the seven filter samples contained a small percentage of Aroclor 1260. The average composition of the vapor phase was 86% of Aroclor 1242, 13% of 1254 and 1% of 1260; whereas the particulate phase was 33% of Aroclor 1242, 39% of 1254 and 30% of 1260. The average composition of the particulate PCBs was 69% of Aroclor 1242, 23% of 1254 and 8% of 1260.

Table I-13. PCB content of Lake Michigan XAD-2 extracts

Sample	Amount of air, m^3	PCBs, ng	Percent 1242	Percent 1254	PCBs, ng/m^3
XLM2	813	905	69.1	30.9	1.11
XLM4	900	597	83.6	16.4	0.66
XLM5	929	550	80.0	20.0	0.59
XLM6	1102	487	80.1	19.9	0.44
XLM7	422	303	815	18.5	0.72
XLM8A	897	1192	66.4	33.6	1.33
XLM9A	716	891	65.2	34.8	1.24
Average			75.1	24.9	0.87

Table I-14. PCB content of Lake Michigan filter extracts

Sample	Amount of air, m^3	PCBs, ng	Percent 1242	Percent 1254	Percent 1260	PCBs, ng/m^3	Particulate PCB, ppm
LM2	813	98	74.5	25.5	0	0.12	1.7
LM3	2428	231	72.7	27.3	0	0.10	3.7
LM4	900	119	79.0	21.0	0	0.13	7.5
LM5	929	172	59.3	22.6	18.1	0.19	2.4
LM6	1102	114	70.2	18.4	11.4	0.10	5.6
LM8A	897	109	58.7	24.8	16.5	0.12	4.2
LM9A	716	106	67.9	23.6	8.5	0.15	2.8
Average			68.9	23.3	7.8	0.13	4.0

Table I-15. Lake Michigan samples, PCBs in total sample

Sample	Amount of air, m^3	PCBs, ng	Percent 1242	Percent 1254	Percent 1260	PCBs, ng/m^3	TSP,* $\mu g/m^3$
2	813	1003	69.6	30.4	0	1.23	69.9
4	900	716	82.8	17.2	0	0.80	17.3
5	929	722	75.1	20.6	4.3	0.78	17.9
6	1102	601	78.2	19.6	2.2	0.55	31.0
8A	897	1301	65.8	32.8	1.4	1.45	28.4
9A	716	997	65.5	33.6	0.9	1.39	54.5
Average			72.8	25.7	1.5	1.03	36.5

*Total suspended particulates.

The results from the Lake Michigan samples are similar in concentration to samples taken by Bidelman and Olney (20) in the North Atlantic in 1973. These researchers found a concentration range of 0.21 to 1.6 ng/m^3 in marine areas. Additional results from their study (Table I-5) showed that from 1973 to 1975, samples matched Aroclors 1248 and 1242 but the composition changed to Aroclor 1254 in 1976. The Lake Michigan samples were different in that they were composed of a mixture of Aroclors 1242 and 1254 rather than single Aroclors. Bidelman and Olney (20) found that 2% of the total PCBs was associated with particulate matter. A larger percentage (13%) of the PCBs over Lake Michigan are associated with particulate matter. The Lake Michigan samples are also similar in concentration, but not composition, to those taken by Harvey and Steinhauer (12). PCB concentrations in the North Atlantic, 500 km off the New York Metropolitan area, ranged from 0.58 to 1.60 ng Aroclor 1254/m^3 and <1% of the PCBs were associated with particulate matter.

The concentrations of the Lake Michigan samples are lower than those reported for urban areas within the continental U.S. Data for urban studies were discussed in Section I-3 (Table I-7). Concentrations in urban areas are usually greater than 1.0 ng/m^3. An average concentration for urban Chicago air, reported by Murphy and Rzeszutko (2), was 7.7 ng/m^3 (Table I-16). The average composition of the vapor phase was 86% of Aroclor 1242, 13% of 1254 and 1% of 1260; whereas the particulate phase was 33% of Aroclor 1242, 39% of 1254 and 30% of 1260. The average concentration of PCBs in the particulate matter was 3 ppm, similar in concentration to the Lake Michigan samples. Four percent of the PCBs were associated with particulate matter which was a lower percentage than the partitioning over Lake Michigan.

The Milwaukee filter extracts (Table I-17) were quite different from those of Lake Michigan. Unlike the Lake Michigan samples and similar to urban Chicago air, the Milwaukee particulate matter composition was weighted more towards heavily chlorinated PCB mixtures. At the Falk Corporation the average composition was 14% of Aroclor 1242, 59% of 1254 and 27% of 1260; whereas the River Lane samples had an average composition of 56% of 1242 and 44% of 1254. The average PCB concentration in particulates was higher at the Falk Corporation (7.0 ppm) than either Lake Michigan (4.0 ppm) or Chicago (3.0 ppm). The River Lane station concentration (2.5 ppm) was similar to average values over Lake Michigan and Chicago. The two sample pairs, namely MIL7 and MIL8 and MIL9 and MIL10, were taken concurrently at the two Watershed stations. The Falk Corporation showed higher concentrations in both cases. The vapor concentration and composition reported for one Milwaukee sample taken at Falk was 73% of Aroclor 1242 and 27% of 1254. The composition was comparable to that of the Lake Michigan samples. Of the PCBs, 16% were found to be associated with particulate matter, a number comparable to the 13% obtained from the Lake Michigan samples. The vapor phase concentration (2.25 ng/m^3) was three times higher than the average found over Lake Michigan but lower than that reported for Chicago.

The wind roses and other meteorological data for the Lake Michigan samples are given in Fig. I-8 and Table I-18. The samples, with the exception of number 7, were usually collected over a 3 day period during which time the meteorological conditions were subject to

Table I-16. Chicago air samples (2)

Date	Amount of air, m^3	PCBs, ng	Percent 1242	Percent 1254	Percent 1260	PCBs, ng/m^3
		TOTAL SAMPLE				
27 Nov. 1975	1,788	12,017	78.7	20.7	0.6	6.7
5 Dec. 1975	1,106	8,288	84.6	6.8	8.5	7.4
20 Feb. 1976	1,072	3,912	81.5	12.0	6.3	3.6
29 Mar. 1976	1,138	11,337	75.3	24.5	0.2	9.9
19 Apr. 1976	954	10,528	93.8	5.3	0.7	11.0
Average			82.8	13.9	3.3	7.7
		POLYURETHANE FOAM EXTRACTS				
27 Nov. 1975	1,788	11,469	80.3	19.1	0.5	6.41
5 Dec. 1975	1,106	7,517	93.2	6.2	0.6	6.80
20 Feb. 1976	1,072	3,646	86.4	10.2	3.4	3.40
29 Mar. 1976	1,138	11,275	75.3	24.4	0.2	9.91
19 Apr. 1976	954	10,385	94.7	4.7	0.5	10.88
Average			86.0	12.9	1.0	7.5
		FILTER EXTRACTS				
27 Nov. 1975	1,788	547	45.2	54.2	2.6	0.31
5 Dec. 1975	1,106	771	0.7	12.6	85.5	0.70
20 Feb. 1976	1,072	266	14.3	36.6	46.0	0.25
29 Mar. 1976	1,138	62	75.3	42.6	0.2	0.05
19 Apr. 1976	954	143	28.4	48.8	15.2	0.15
Average			32.8	39.0	29.9	0.29

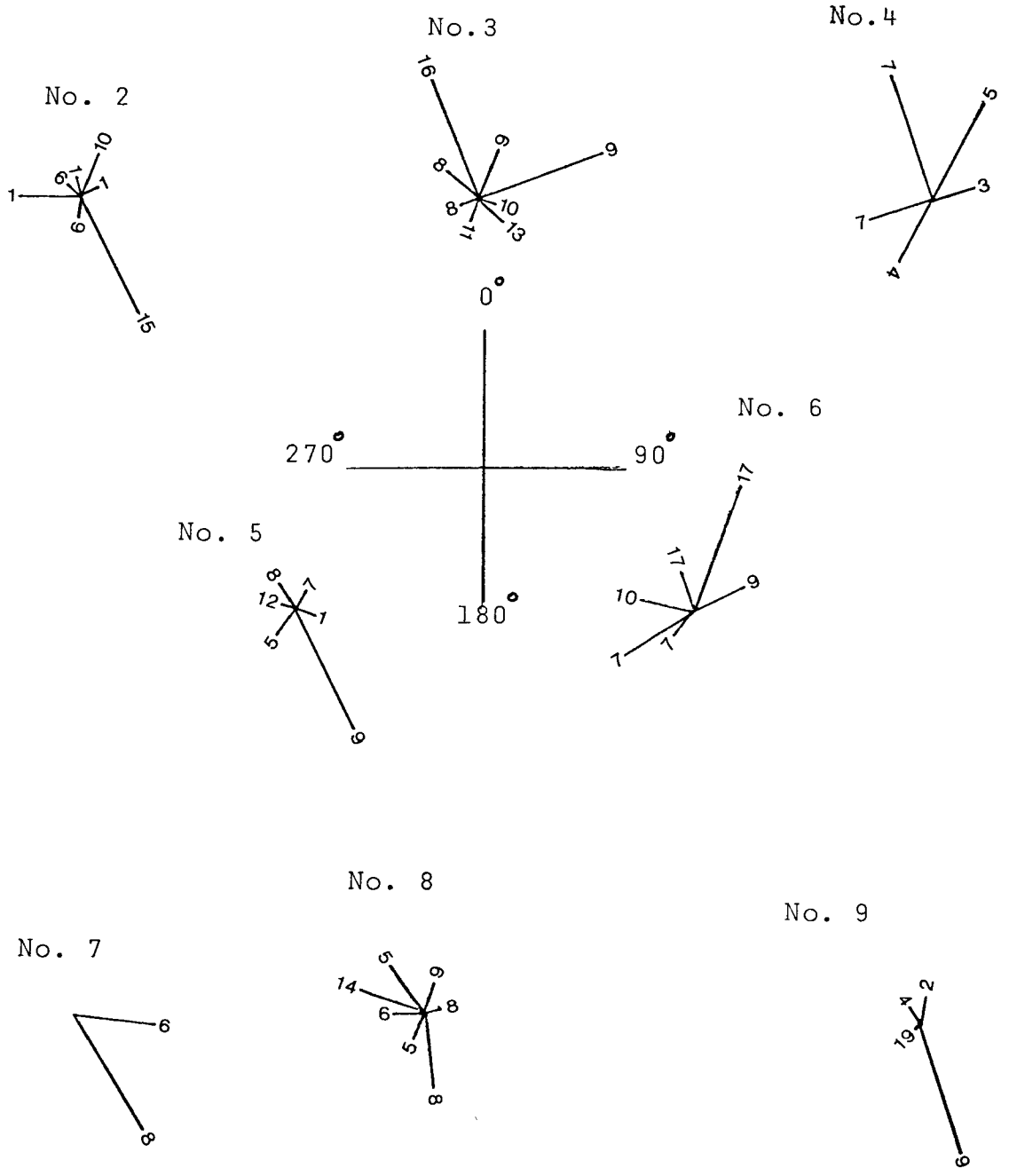
Table I-18. Average meteorological data for Lake Michigan air samples

Sample	Temp., °C	Rel. humidity, %	Bar. pressure, cm Hg
2	17.0	74	76.50
3	24.2	61	76.48
4	21.2	39	76.61
5	18.6	66	76.27
6	15.7	63	76.53
7	15.7	62	76.71
8A	14.2	--	76.33
9A	14.0	--	76.33

Table I-17. PCBs in Milwaukee samples

Sample*	Date	Amount of air, m^3	PCBs, ng	Percent 1242	Percent 1254	Percent 1260	PCBs, ng/m^3	TSP $\mu g/m^3$	Particulate PCBs, ppm
MIL1	Nov. 30 to Dec. 2, 1977	1821	650	9.1	54.9	36.0	0.36	51.0	7.1
MIL3	Dec. 5 to Dec. 9, 1977	3667	1120	11.6	57.7	30.7	0.31	50.1	6.2
MIL5	Dec. 12 to Dec. 16, 1977	3632	1184	15.1	61.7	23.2	0.33	54.0	6.1
MIL7	Jan. 31 to Feb. 3, 1978	2817	1176	26.7	50.9	22.4	0.42	63.9	6.6
MIL8	Jan. 31 to Feb. 3, 1978	3262	345	69.3	30.7	0	0.11	37.6	2.9
MIL9	Feb. 7 to Feb. 10, 1978	2822	1271	7.5	69.2	22.3	0.44	49.3	8.9
MIL10	Feb. 7 to Feb. 10, 1978	2662	193	42.0	5.0	0	0.07	35.3	2.0
Averages	Falk Corp.			14	59	27	0.37	53.7	7.0
	River Lane			56	44		0.09	36.5	2.5
XMILI**		1821	4102	73	27		2.25		

*Even numbered samples taken at River Lane, odd numbered samples taken at Falk Corp.
**XAD-2 extract corresponding to MIL1.



Numbers denote average wind speed in knots

Fig. I-8. Wind roses for Lake Michigan sampling stations.

considerable change. Due to these factors, it was not possible to correlate PCB concentrations with meteorological conditions. Since PCBs are more concentrated in urban air, it would be expected that southwest winds would bring elevated concentrations of PCBs over the lake from the Chicago and Milwaukee areas or metropolitan-industrial areas in general. The complex wind roses do not permit interpretation of the data to indicate this. PCB concentrations were highest on the June and September cruises but a seasonal trend can presently not be discerned due to the limited amount of data. Meteorological data were not available for the Milwaukee samples.

One result that was clearly evident from the preceding discussion was that urban particulates contained a higher percentage of the heavily chlorinated mixtures (Aroclors 1254, 1260) while the particulates over Lake Michigan contained higher percentages of the more volatile mixtures (Aroclor 1242). Adsorption theory, as applied by Junge (28), would predict that the less volatile PCB constituents would be associated with particulate matter. The Lake Michigan samples showed just the opposite trend indicating that other factors may be influencing the PCB composition of air particulates over the lake.

One possible approach to interpret the results in this study might be to consider the extent of particulate/vapor partitioning and composition as being a function of five factors:

1. The source of PCB emission

2. The amount of total suspended particulates (TSP)

3. The type of particulate matter present

4. The atmospheric residence time

   and possibly

5. Photolysis.

The number of conclusions drawn is limited by the scarcity of data. The following interpretation is largely speculation but it can be used to design better sampling schemes for future investigations of aerial PCB transport.

The source of PCB emission will influence the composition of airborne PCBs in close proximity to that source. If the source is a major industrial user of a particular Aroclor, the same mixture would be reflected in the atmosphere with possible enrichment of the more volatile components. Sources such as poorly operated incinerators or sanitary landfill gas vents might emit mixtures of Aroclors in variable proportions due to the many former uses. The composition of Aroclors emitted from landfills would depend upon the volatility of the mixtures. Murphy and Rzeszutko (2) found that PCB in the vent gases of a sanitary landfill consisted of 98% of Aroclor 1242, the most volatile mixture of the more widely used Aroclors. The temperatures in a poorly operated incinerator, while not high enough to destroy PCBs (2000+°C), would be high enough to vaporize all the Aroclor mixtures. The amounts and composition present in the atmosphere

would thus depend upon the amounts and composition of the incinerated PCB containing products.

The amount of total suspended particulates present in the atmosphere may also determine the extent of vapor/particulate partitioning. Thomas et al. (34) found that the vapor concentration of polyaromatic hydrocarbons (PAHs), at a generation source having temperatures ranging from 80 to 90°C, equalled the saturation vapor density of the pure state and exceeded that of the adsorbed state. Even in the presence of excess soot the vapor phase PAHs were in excess. Attainment of adsorption equilibrium was slower than condensation (homogeneous nucleation) of the vapor. Since PCBs are more volatile than PAHs it seems logical that vapor phase PCBs close to a source, such as an incinerator stack, will be in greater concentrations than the adsorbed species. Distant from the source of generation, the PCBs will become diluted, the total amount of particulates will become greater than the amount of volatile PCBs, and adsorption will become a factor. If this theory applies to PCB adsorption, higher TSP loads will result in higher concentrations of PCBs in the particulate phase.

This correlation was not evident in the sets of samples taken on Lake Michigan or at the Falk sampling site. The Falk samples did show high particulate PCB and TSP concentrations while the River Lane samples, which were taken concurrently, showed an opposite trend. Table I-19 contains a comparison of the average particulate PCB concentration, PCB vapor concentration, and TSP for four locations. A coincident correlation exists between particulate PCB concentration and the TSP, with high TSP values producing high particulate PCB concentrations. A correlation did not exist between the percentage of the total PCBs in the particulate phase and TSP. Chicago, which had a TSP concentration intermediate between that of Lake Michigan and the Falk Corporation, had the lowest percentage (2). Over the ocean however, where TSP values would probably be lower than those reported for Lake Michigan and urban areas, particulate PCBs comprised only 2% of the total amount (11).

The type of particulate matter present in the atmosphere may also influence the extent of adsorption. Murphy and Rzeszutko (2) reported that the concentration of PCBs in non-polar organic extractable solids (18 ppm) was greater than that in the total particulate matter (3 ppm). This may indicate that PCBs have a tendency to associate predominantly with aerosols containing non-polar organic matter. If the organic composition of aerosols has a spatial dependence the PCB composition may also show the same trend. Strand (35) showed that TOC in aerosols varies considerably. If PCBs are closely associated with TOC in aerosols a better correlation might exist between PCBs and TOC than PCBs and TSP.

The residence time of PCBs and particulates may also influence the vapor/particulate partitioning as well as the composition. If it is assumed that the particulate matter from Milwaukee and Chicago is moving out over the lake, the particles will have aged somewhat when they reach the lake. In urban areas, where PCB concentrations are usually high, the more highly chlorinated mixtures may associate with particulates more readily due to their low volatility, while the lower chlorinated mixtures remain predominantly in the vapor phase due to slow adsorption kinetics. As the particulates move out

Table 19. Average TSP and particulate PCB and vapor phase PCB concentrations

Location	TSP, $\mu g/m^3$	Particulate PCBs, ppm	Vapor phase PCB, mg/m^3
Falk Corp., Milwaukee	53.7	7.0	2.25
Chicago	48	3	7.5
Lake Michigan	40.6	4.0	0.87
River Lane, Milwaukee	36.5	2.5	

*(Ref. 2).

over the lake, the more volatile mixtures associate with particulate matter making vapor and particulate more homogeneous in composition. The size of the particulate associated PCBs, which will determine their residence time, may also determine their composition. Sampling air over the North Atlantic from 1973 to 1976, Bidelman (21) has found a change in PCB composition from Aroclor 1248 to 1254. The sale of PCBs in the U.S. was discontinued after 1974 so the change in composition cannot be due to a new source. Aroclor 1248 may be associated with particles which are depositing more rapidly.

The effect of photolysis on the PCB composition of air has not been investigated. The main reaction of the photolysis of PCBs in water or solvents is stepwise dechlorination (36,37,38). Stepwise dechlorination of PCBs in air would result in a predominance of the lower chlorinated mixtures. The process must be investigated more thoroughly before any conclusions can be made.

The vapor/particulate partitioning and composition of airborne PCBs is probably a complex combination of the five factors presented. This makes interpretation of results extremely difficult. In the discussion of results, seasonal trends were not investigated. The Lake Michigan samples were taken during the spring, summer and fall while those reported for Milwaukee and Chicago were taken predominantly during the winter. A correlation between particulate composition and season is not presently discernable. The limited number of samples used in the interpretation and the absence of meteorological correlations also present difficulties. The collection and quantification method may also influence the particulate/vapor partitioning and the reported composition of an air sample. Nevertheless, the above speculations can be used as a tool in designing future sampling schemes and laboratory experiments.

Vaporization

The degree of alteration of the vapor/particulate partitioning of airborne PCBs by a high volume air sampler is unknown. Vaporization of PCBs from collected particulate matter has been hypothesized (2,12,20). The vaporization of certain PAHs from collected particulates under ambient conditions has already been reported (39). Vaporization was greatest for the more volatile PAHs, such as fluoranthene and pyrene but losses were also observed with benzo(a)pyrene. PAHs are much less volatile than PCBs. This can be exemplified by comparing their calculated saturation vapor densities (Table I-20).

In the sampling system employed in this study, volatilized PCBs would be collected as vapor. This process would lead to an underestimation of the particulate PCB concentration. The degree of particulate/vapor partitioning is very important when estimating wet and dry fluxes.

Another problem associated with high volume air sampling is the performance characteristics of the filter media. The particulate/vapor partitioning of PCBs is operationally defined by the sampling system. The possibility exists that all airborne PCBs are associated

Table I-20. Saturation vapor densities of PAHS (ng/m^3) and PCBs (mg/m^3) (41)

Compound	Vapor density, ng/m^3
PAHs	
Pyrene	74,000
Benz-(a)-anthracene	1,050
Benz-(a)-pyrene	85
Benz-(e)-pyrene	85
Benz-(k)-fluorene	16
Benz-(ghi)-perylene	1.6
PCBs	
Aroclor 1242	5.5
Aroclor 1248	7.9
Aroclor 1254	1.4
Aroclor 1260	0.73

with particulate matter, but some of the particles are too small to be captured by a glass fiber filter. At the normal flow rate of the PCB sampler (0.566 to 0.708 m^3/min) the collection efficiency is 100% for particles greater than 0.3μ in diameter (40). Glass fiber filters may collect particles less than 0.3μ in diameter but the collection efficiency is unknown.

An attempt was made to determine the extent to which the sampler employed in this study altered the vapor/particulate partitioning of PCBs.

Experimental

An experiment was designed in which PCB coated particulate matter was dispersed on a glass fiber filter and subjected to normal sampling conditions. Fly ash and soil were used instead of atmospheric particulate matter. Both substances were dried before use. The soil sample was pulverized using a mortar and pestle. The fly ash and soil were then sieved in order to remove particles greater than 44μ (sand fraction).

The Lake Michigan air samples were used as the basis for estimating the amount of PCB that was coated on the particulate matter. A mixture of 75% Aroclor 1242 and 25% Aroclor 1254 was used. Assuming that all the airborne PCBs were originally associated with particulate matter, the average particulate PCB concentration would be 20 ppm. This number is half an order of magnitude less (4 ppm) if it is assumed that all the particulate PCBs are captured by the glass fiber filter.

The PCB coated particulate matter was prepared by immersing soil and fly ash in petroleum ether containing Aroclors 1242 and 1254 and allowing the slurry to equilibrate for a period of two days. The petroleum ether was evaporated slowly using a gentle vacuum and taken to dryness with a slow stream of nitrogen. The dried substances were transferred to bottles and put on a wrist action shaker for 30 min to insure homogeneity of subsamples. A portion of the coated particulate matter was submitted for analysis to determine its PCB content. The composition was never the same as the sought composition due to adsorption of PCB on container walls and losses during evaporation. The total organic carbon content of the fly ash and soil was also determined.

Two different experiments were performed. The first consisted of using prefiltered laboratory air. Two samplers were interconnected, one being used as a prefilter. A glass fiber filter was cut to fit on the top of one of the XAD-2 capsules. Coated fly ash was dispersed on the filter as evenly as possible. The sampler was operated for 48 hr during which time 1152 m^3 of air flowed over the particulate matter at 0.4 m^3/min. The total amount of air was approximately the same as the amount sampled during a normal collection period.

Analysis of the filter and XAD-2 showed that all the PCB was vaporized from the particulate matter. There were two unforeseen

problems associated with this type of experiment. A partial vacuum greater than the pressure drop experienced during a normal sampling situation, may have been created between the two XAD-2 capsules which increased the tendency for vaporization. The use of a prefilter insured that organic free air was continuously being drawn over the particles. The PCBs may have vaporized to attain equilibrium with the flowing air, which was completely devoid of vapor phase PCBs.

A second set of experiments was designed to avoid these problems. Two samplers were run concurrently and outdoors to model a normal sampling situation as closely as possible. One sampler was used as a blank. Using this experimental design insured that the particulates would be in quasi-equilibrium with the air being drawn over them. Also, the pressure drop across the filter would be the same as it is when a normal sample is taken (5 mm Hg).

Fifty to one hundred milligrams of coated particulate matter was dispersed on the filter surface as evenly as possible. The sampler was run for 12 hr during which time 504 m^3 of air flowed over the particles at 0.7 m^3/min. Difficulties with interpretation of results were avoided by sampling for a shortened length of time. This time reduction should have no serious effects on the results. During longer sampling periods the collection of a large quantity of organic vapors interferes with quantification of the most volatile PCB isomers. Since these would be the most important components in an experiment of this type, a 12 hr sampling period was chosen.

Results and discussion

The results show that more PCB was vaporized from fly ash than soil (Table I-21). The sampler used to collect the air blank collected a larger amount of particulate matter in both experiments. Correcting the loss of total PCB for the lack of reproducibility between the samplers showed that 19.8 and 90.1% of the PCB was lost from the soil and fly ash, respectively. It is also apparent that the more volatile Aroclor 1242 is lost to a greater extent. The chromatograms of the filter extracts showed that the heavily chlorinated components of Aroclors 1242 and 1254 were vaporized to a lesser extent.

Desorption from the particulate matter could be controlled by two factors. Kinetic effects determine the rate of vaporization. If the desorption kinetics are rapid all the PCBs may be lost from the particulate matter during a normal sampling period. The type of particulate matter onto which PCBs are adsorbed may also be a factor. The experiments may indicate that PCBs adsorbed to particles containing a high organic carbon content are unavailable for vaporization. The fly ash contained 4.9×10^{-4}% organic carbon while the soil contained 57%.

There is one major difference between the particulate matter used in this experiment and the particulate matter present in air. Airborne particulates should be in equilibrium with the surrounding air. It seems unlikely that equilibrated particulates would be stripped of their PCB content by a flow of air in which they had

Table I-21. PCB vaporization

Sample	PCBs, ng	Percent 1242	Percent 1254	Particulate PCBs, ppm	Total organic C, %
		BEFORE SAMPLING			
Soil	692	64.3	35.7	10.4	57
Fly Ash	1310	66.0	34.0	18.1	4.9×10^{-4}
		AFTER SAMPLING			
Soil	510	56.5	43.5	7.7	
Air blank					
Particulate	142	51.4	48.6	6.4	
Vapor	3542	85.7	14.6		
Percent loss	26.3	35.3	10.1		
Fly ash	123	39.0	62.0	1.7	
Air blank					
Particulate	61	0	100	5.5	
Vapor	4008	86.5	13.5		
Percent loss	90.6	94.4	83.2		

resided for a long period of time. Vaporization could take place if PCBs were weakly adsorbed onto inorganic particulates such as fly ash. Aerosols collected over Lake Michigan have been found to contain 20 to 70% organic carbon (35). As was the case with the soil, PCBs may not vaporize from particles containing organic carbon. The high percentage of Aroclor 1242 reported on Lake Michigan particulate matter may suggest that if vaporization does occur, the kinetics of desorption are rather slow.

Caution must be taken when extrapolating these results to the collection of an air sample. Soil and fly ash are not the same as airborne particulate matter. Also, the PCB was coated on the particulate matter by immersing it in an organic solvent, a process which may have altered the particle matrix.

The experiments indicate that vaporization may be a function of the organic carbon content of particulates. PCBs adsorbed onto particulates containing a high organic carbon content may not vaporize. PCBs weakly adsorbed to inorganic particulates will be vaporized during the collection process. Since Lake Michigan aerosols contain 20 to 70% organic carbon, vaporization of PCBs from these aerosols may not occur.

Volatilization

Volatilization of certain low solubility organic compounds from water bodies to the atmosphere has been proposed as an important environmental pathway (9). PCBs are sparingly soluble in water and have been included in this category (9,42). Versar (5), prepared a first order PCB mass balance model for Lake Michigan and estimated a PCB evaporation rate of 1160 kg/yr. A combination of an estimate for dry fallout of 2908 kg/yr (5) with a wet deposition rate of 4800 kg/yr (2) suggests that approximately 14% of the atmospheric input may be evaporating from the lake's surface. These estimates show that the revolatilization process is a potentially important environmental pathway and thus worthy of further investigation.

Recently the revolatilization process has been questioned. The phase (gas or liquid) which controls the transfer of PCBs across the air/water interface is now uncertain (27). The Henry's Law constant (H), which is a measure of the partitioning of a gas between air and water, has been calculated for Aroclor mixtures using solubility and vapor pressure data (42). In order to calculate H, the vapor pressure and aqueous solubility must refer to the same state of matter. Individual PCB isomers are solids at room temperature while Aroclors, which are complex mixtures of PCB isomers, are viscous liquids. This fact was not taken into consideration when the Henry's Law constants were calculated. Since Aroclors are non-ideal mixtures, the individual isomers, when present in air or water, will be partitioned individually and therefore must be treated accordingly. The published values of H may be in error by a factor of a thousand (27). PCBs may in fact be gas phase controlled, resulting in a flux of vapor phase PCBs to the water surface rather than from it.

The Whitman (43) two layer model, as applied by Liss and Slater (44), may be used as a first approximation to estimate the flux of gases across the air/sea interface. The liquid (k_L) and gas (k_G) phase mass transfer coefficients for PCBs can be estimated using the mass transfer coefficients for CO_2 and H_2O. The values for PCBs can be found in Table I-22. The overall liquid phase mass transfer coefficient (K_{OL}) can be obtained experimentally (42). K_{OL} can be calculated using the following equation:

$$C = C_0 \exp(-K_{OL}\ t/L) \qquad \text{Eq. (1)}$$

where

K_{OL} is the overall liquid phase mass transfer coefficient
t is time
L is the depth of water
C_0 is the original soluble concentration
C is the soluble concentration at time t

Examining the equation which is used to calculate an overall mass transfer coefficient (44):

$$1/K_{OL} = 1/k_L + 1/(Hk_G/RT) \qquad \text{Eq. (2)}$$

where

RT is 2.45×10^{-2} atm-m^3/mol at 25°C

it can be observed that with a knowledge of K_{OL} an experimental H can be obtained.

PCBs are rather insoluble in water and have a large affinity for surfaces (4). PCBs in Lake Michigan may be associated with particulate matter and therefore unavailable for revolatilization unless desorption is rapid. Analysis of Lake Michigan water indicates that 67% of the PCBs are present in the particulate phase (2). This number is operationally defined since PCBs may be adsorbed to particles too small to be collected by a glass fiber filter.

Hetling et al. (22) performed a revolatilization experiment using PCB saturated water solutions. They found almost total revolatilization of Aroclors 1221 and 1016 within a matter of days. They also stated that the introduction of organic particulate matter slowed the rate of evaporation. Data was presented only for the results of the saturated water solution experiments.

Experimental

Assuming that the partitioning of PCB between the particulate and soluble phase was important, an experiment was designed to examine the revolatilization rate under conditions similar to those found in the environment. A water sample was taken from Lake Emrick, a lake

Table I-22. Liquid and gas phase mass transfer coefficients for PCBs

Aroclor	Mol. Wt.	k_G, m/hr	k_L, m/hr
1221	192	9.19	0.10
1016	256	7.96	0.08
1242	261	7.88	0.08
1254	327	7.04	0.07

Table I-23. Liquid phase mass transfer coefficients (m/hr) for Aroclors 1221 and 1016 (22) and Aroclor 1242 and 1254 (this study)

Sample	Time,* hr	K_{OL} (1242)	K_{OL} (1254)
		FLY ASH EXPERIMENT (This Study)	
IRV1	112	2.10×10^{-4}	7.88×10^{-5}
IRV2	306	1.19×10^{-4}	5.26×10^{-5}
IRV3	493	8.96×10^{-5}	3.56×10^{-5}
IRV4	877	6.23×10^{-5}	2.33×10^{-5}
		ACETONE SPIKE EXPERIMENT (This Study)	
2RV1	112	1.14×10^{-4}	5.59×10^{-5}
2RV2	306	5.82×10^{-5}	3.86×10^{-5}
2RV3	493	4.06×10^{-5}	2.60×10^{-5}
2RV4	877	2.57×10^{-5}	1.62×10^{-5}
		(REF. 22)	
		K_{OL} (1016)	K_{OL} (1221)
1	24	1.04×10^{-3}	9.37×10^{-4}
2	48	8.40×10^{-4}	9.01×10^{-4}
3	72	7.31×10^{-4}	9.15×10^{-4}
4	96		8.04×10^{-4}

*Time sample taken after start.

in southern Wisconsin. Unfiltered lake water (1 L) was used in the experiment. Compressed air was fed into a 4 L flask through a glass frit at 50 ml/min. The air was purified by two XAD-2 columns. The outlet consisted of two glass columns filled with XAD-2 resin to capture any revolatilized PCB. The water was stirred with a magnetic stirrer to keep the particulate matter in suspension.

Two concurrent experiments were performed. It was not practical to use a concentration as low as the 13 ng/L found in Lake Michigan (45). Any amount of revolatilized PCB would have been less than the detection limit of an electron capture detector. If the experiment was done on an extremely large scale this may have been possible. The experiment was designed so the solubilities of Aroclors 1242 and 1254 which are 0.240 mg/L and 0.012 mg/L, respectively (9), were not exceeded. In one experiment 10 mg of PCB coated fly ash (1050 ng of Aroclor 1242, 1530 ng of 1254) was added to the lake water. In the other flask, a PCB spike (2087 ng of Aroclor 1242, 2339 ng of 1254) was introduced in 10μl of acetone. Acetone is water soluble. It was used with the assumption that PCB introduced into the lake water in this manner would initially be in solution. Ten milligrams of fly ash were also added to keep the suspended solids load in each flask identical. Analysis of the XAD-2 vapor traps was performed over regular intervals. The duration of the experiment was one month after which time the water was filtered with a glass fiber filter and batch extracted with hexane. The non-filterable material was soxhlet extracted with petroleum ether.

Results and discussion

The results from the experiments performed in this study as well as those of Hetling et al. (22) will be used to discuss the revolatilization of PCBs. By transforming Eq. (1) into the following form,

$$\ln(C/C_0) = -(K_{OL})t/L \qquad \text{Eq. (3)}$$

it can be observed that K_{OL} should be a constant. In the experiments performed in this study the actual amount of PCBs in solution (C) was found by subtracting the vapor concentration at time t from the total amount of PCB spiked into the lakewater (C_0); therefore, (C) may include both adsorbed and soluble PCBs. This calculation was also necessary to interpret the experiment of Hetling et al. (22) since only the amount revolatilized was determined. The values of K_{OL} for each of the evaporation studies can be found in Table I-23. Plotting the values of K_{OL} versus time, it became apparent that the overall mass transfer coefficient changed with time (Figs. 9-11).

The change in the overall mass transfer coefficient may be the result of two factors, adsorption of PCBs to particulate matter and different revolatilization rates for different PCB components. In the fly ash and acetone spike experiments, particulate matter was present in the system. Adsorption of PCBs to particulate surfaces will retard the evaporation process (22). The change in concentration of the PCBs in solution is due to both evaporative loss and desorption from particulate matter. The experimentally derived K_{OL} is actually a

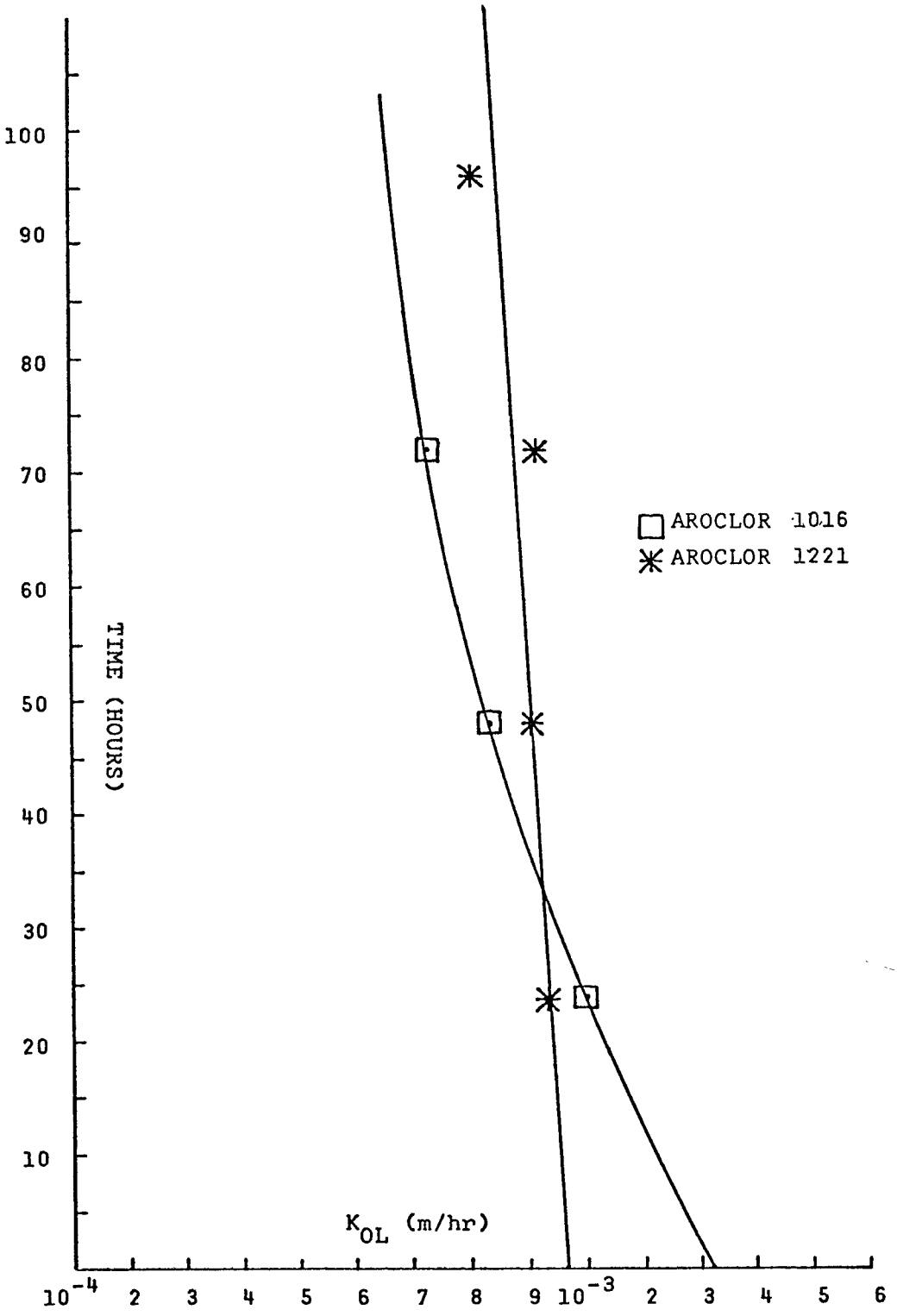


Fig. I-9. K_{OL} against time for Aroclors 1016 and 1221.

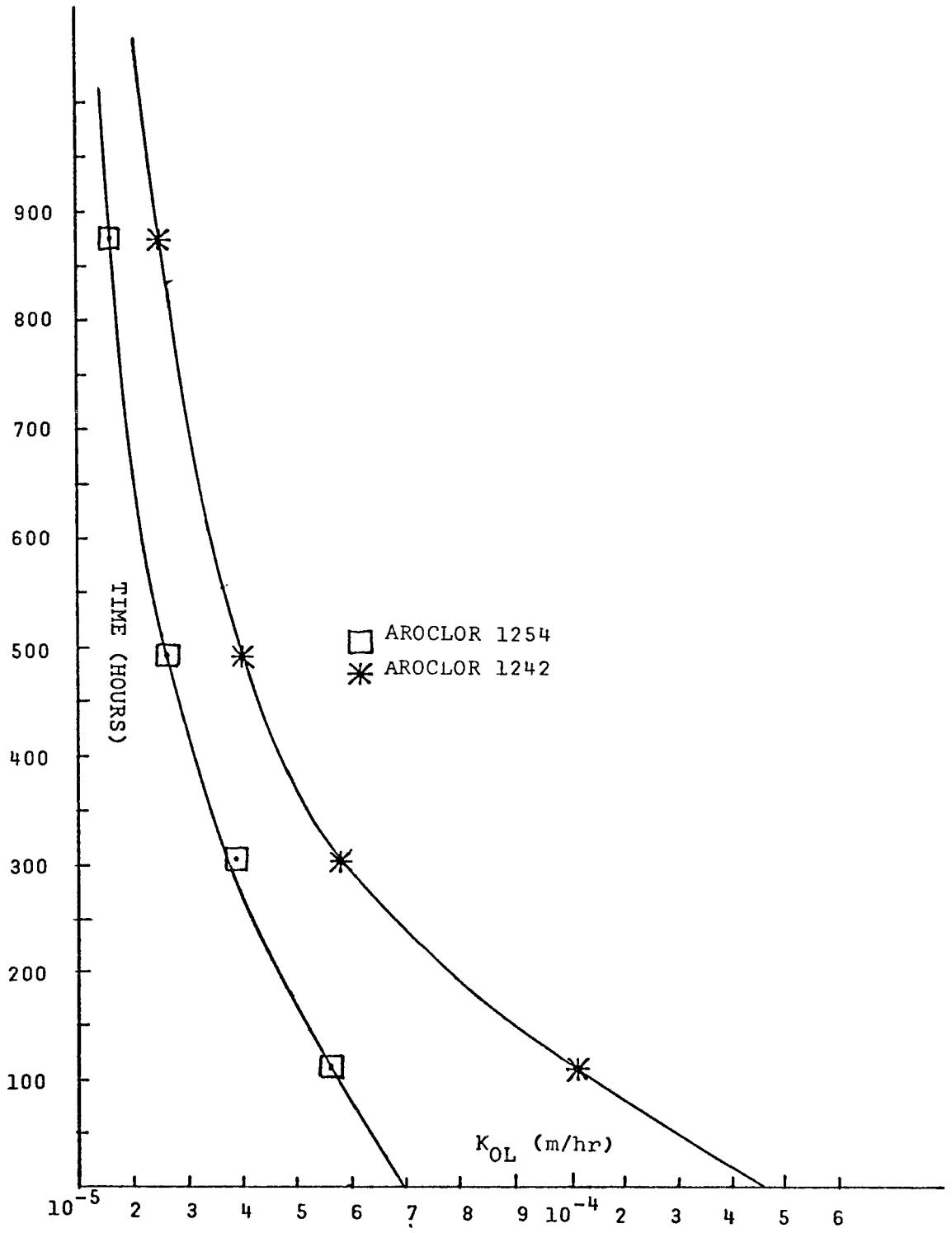


Fig. I-10. K_{OL} against time for Aroclors 1242 and 1254 for acetone spike experiment.

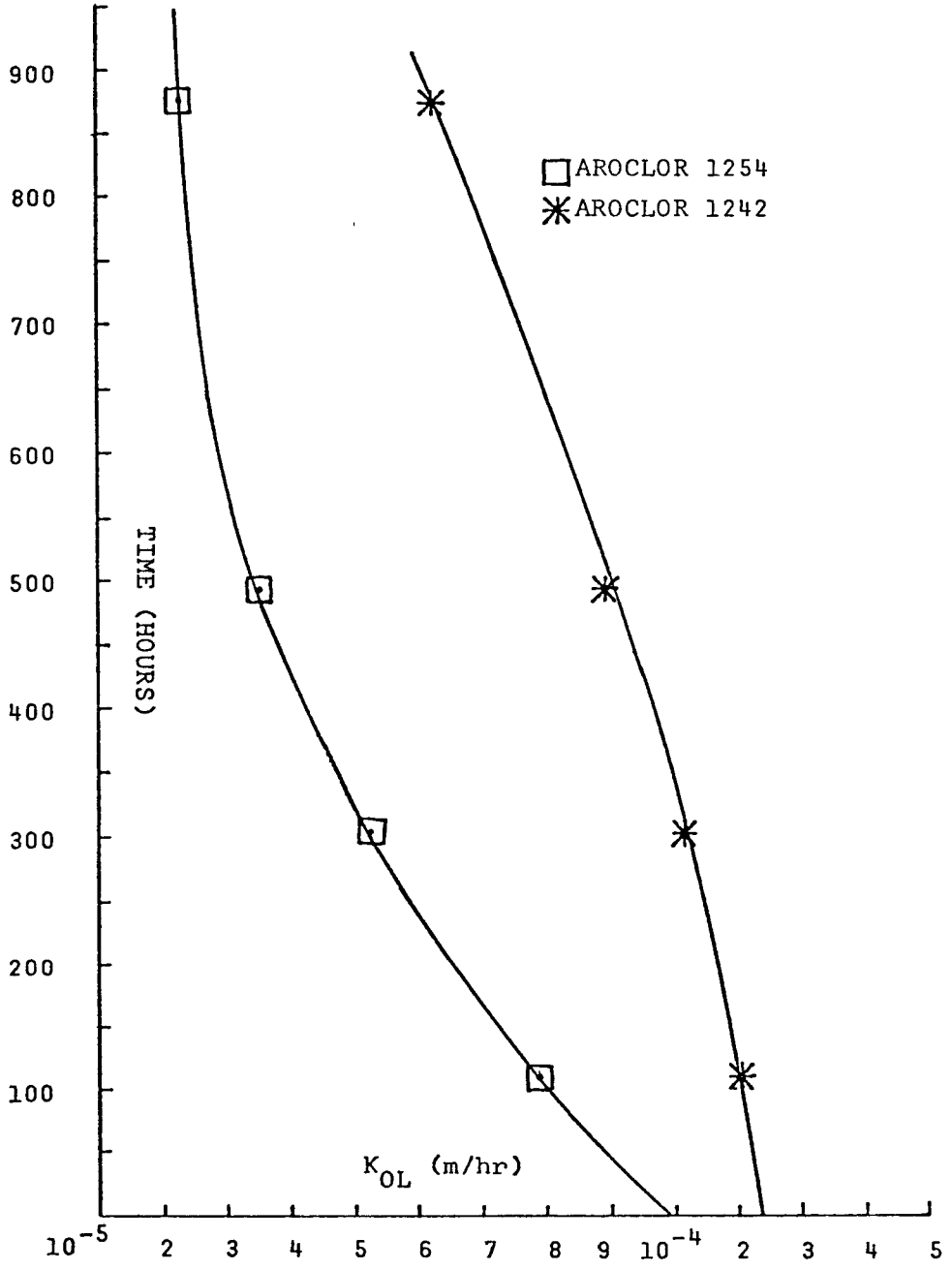


Fig. I-11. K_{OL} against time for Aroclors 1242 and 1254 in fly ash experiment.

combined revolatilization and desorption rate. The nonlinearity of the K_{OL} versus time curve was the result of applying Eq. (1) to a system it could not describe. A desorption term would have to be added to linearize the results.

The processes of adsorption, desorption and revolatilization are related in a complex fashion. Figures I-12 and I-13 show that the loss curves for the fly ash and acetone spike experiments are identical in shape, although the loss of Aroclor 1242 in the fly ash experiment is much greater. Desorption from the fly ash had to occur before the PCBs were revolatilized. The process must have been rapid since the results are similar to those of the acetone spike experiment. The solubilized PCBs must have subsequently adsorbed to the particulate matter originally present in the lakewater. The K_{OL} versus time curves (Figs. I-10 and I-11) for Aroclor 1242 in both experiments are not identical which suggests that adsorption, desorption and revolatilization are related in a complex fashion. The Aroclors 1242 and 1254 in the acetone spike experiment might have associated with the fly ash in that system, however this is unlikely since the fly ash is inorganic in nature. A more logical explanation might be that the PCBs were adsorbed to the particulates originally present in the lakewater.

The change in total mass transfer coefficient may also be the result of different revolatilization rates for the individual components of the two Aroclor mixtures. The explanation can be found by examining Henry's Law:

$$P_j = K_j \, xj \qquad \text{Eq. (4)}$$

where

p is the partial pressure
K is the mass transfer coefficient
x is the mole fraction
j is any solute in the system (in this case the individual PCB isomers)

Henry's Law states that all real solutions should approach the behavior described by this equation provided the solution is sufficiently dilute. If several solutes are present, which is the case described by these experiments, the solution must be dilute in all solutes. Each of the different solutes has a different value of K (46).

The deviations of Aroclor mixtures from the behavior described by Henry's Law are readily apparent. In the experiments performed in this study, the PCB concentrations, while not exceeding the published solubilities, definitely exceeded those in Lake Michigan. Uncertainties may arise when extrapolating Henry's Law data from high to low concentrations. Different revolatilization rates for individual PCB components were observed. The standard error can be used as a measure of the deviation from a standard Aroclor mixture. The standard errors for each of the vapor samples can be found in Table I-24. The deviations were rather sizable indicating that the components did in fact have different revolatilization rates. Figure I-9 is a graph of the data from Hetling et al. (22) for the revolatilization of

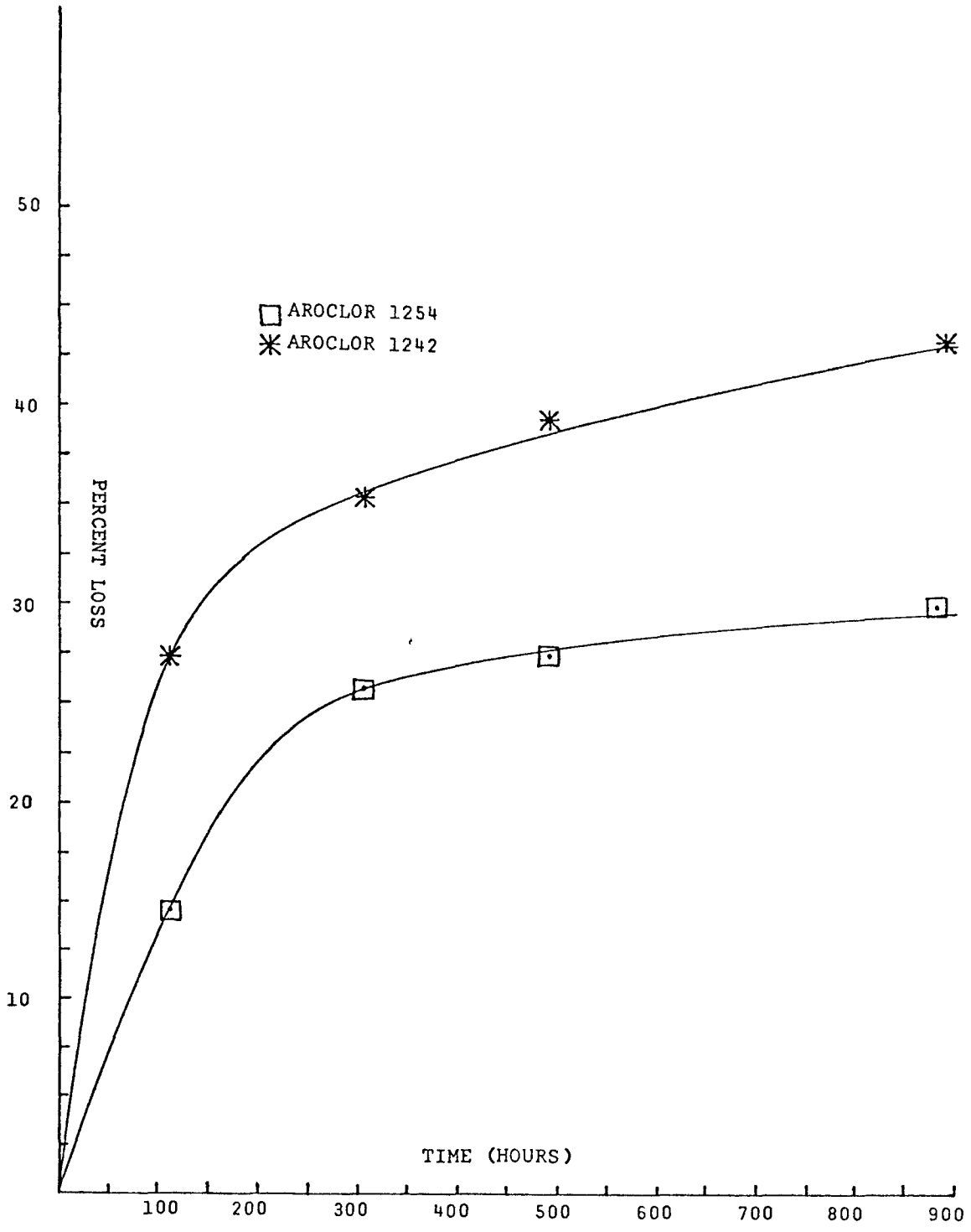


Fig. I-12. Loss of PCBs (%) with time for acetone spike experiment.

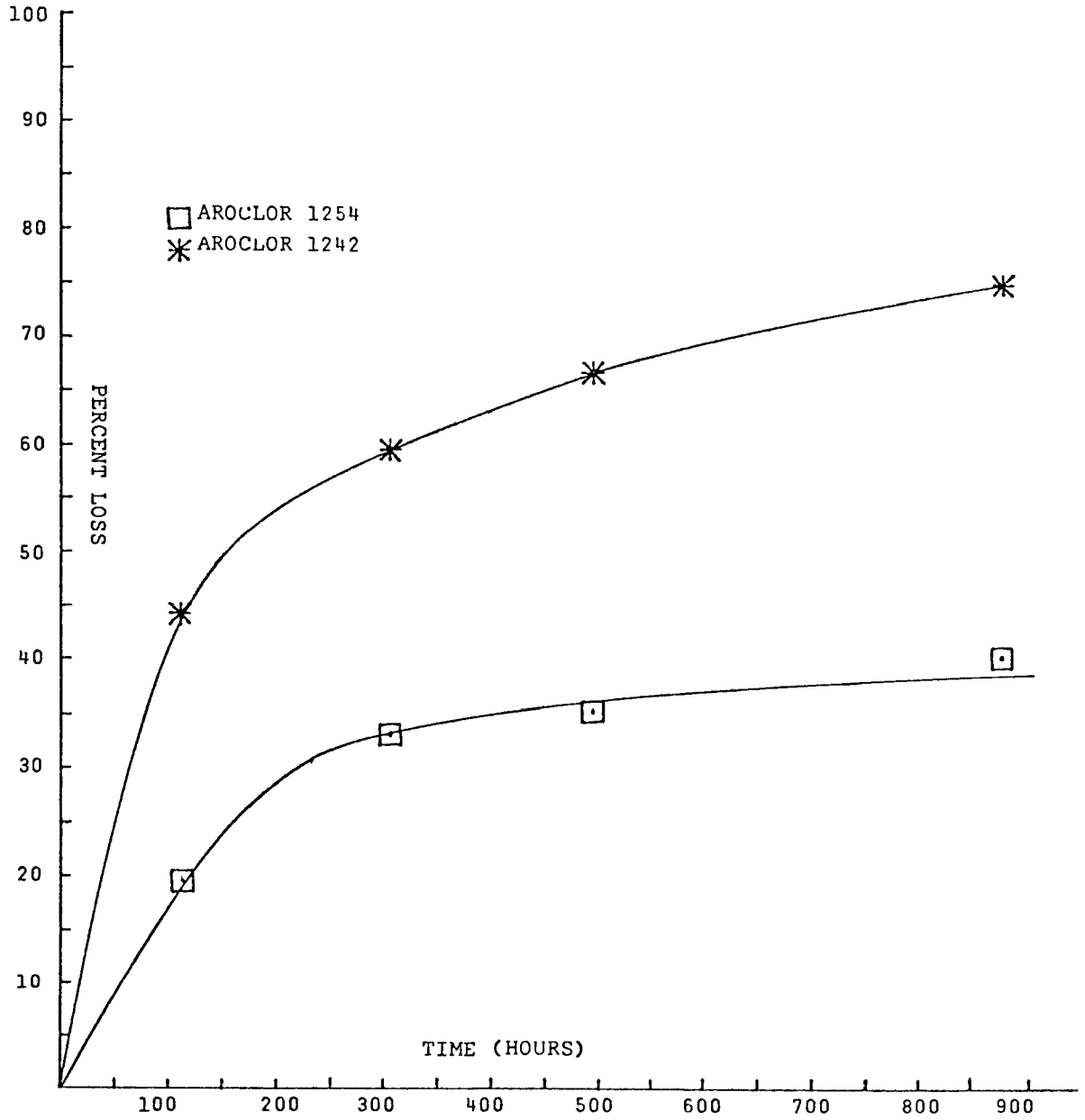


Fig. I-13. Loss of PCBs (%) with time for fly ash experiment.

Table I-24. Standard errors for revolatized PCB vapor

Sample*	Time,** hr	Standard error, *** %	
		Aroclor 1242	Arochlor 1254
IRV1	112	11.2	19.9
2RV1	112	7.7	19.8
1RV2	306	25.0	5.2
2RV2	306	19.3	6.9
1RV3	493	27.2	13.7
2RV3	493	28.1	15.5
1RV4	877	40.4	37.4
2RV4	877	27.5	32.2

*If first number is 1 it is fly ash if 2 it is acetone spile experiments.
**Time sample taken.
***$\frac{\text{(Amount under each peak - Average amount)}}{\text{Average amount}}$

Table I-25. Composition of Aroclor mixtures (9)

Chlorines per biphenyl	Composition, %			
	1221	1016	1242	1254
0	11	0.1	0.1	0.1
1	51	1	1	0.1
2	32	20	16	0.5
3	4	57	49	1
4	2	21	25	21
5	0.5	1	8	48
6	ND	0.1	1	23
7	ND	ND	0.1	6
8	ND	ND	ND	ND

ND is not detectable.

Aroclor 1221 from a saturated water solution. It is apparent that the change in K_{OL} with time is very slight, in fact, K_{OL} is almost a constant. Eighty-three percent of Aroclor 1221 is either mono- or di-chlorobiphenyl (Table I-25). The mass transfer coefficients of these components are probably similar in magnitude. For Aroclors 1016, 1242 and 1254 the percentage compositions are more widely scattered among the isomeric components. The mass transfer coefficients would therefore be different.

A problem associated with the experiments described above is PCB adsorption to container walls. A final extraction of the water and particulate matter failed to account for all the PCBs. Either insufficient extraction or adsorption of PCBs to the glass occurred. A rinse of the glassware with hexane-acetone would have failed to show if the adsorption of PCBs was above or below the water's surface. A steady inflow and outflow of compressed air was used to minimize adsorption above the water's surface. Irreversible adsorption was not a problem in the experiment of Hetling et al. (22) since greater than 90% of the revolatilized PCBs were recovered by the vapor trap.

K_{OL} values were determined for each of the experiments. Since the K_{OL} versus time curves were not linear, both minimum and maximum values of K_{OL} were reported. The maximum value of K_{OL} was determined by extrapolating the curve to time zero while the minimum transfer coefficient was reported as the lowest observed value. Henry's Law constants were then calculated by employing Eq. (2). Table I-26 contains the experimentally determined values of K_{OL} and H for the Aroclor mixtures as well as the theoretical values. It is impossible to use the theoretically determined values as a comparison since the vapor pressures used to calculate H are for liquids. The experimental H values are similar to those of DDT (3.89×10^{-5} atm-m^3/mol) and lindane (4.93×10^{-7} atm-m^3/mol) (42) which are solids at room temperature. The vapor pressures of DDT and lindane would not be expected to be the same as those of PCBs. The experiments reported in this study show that a discrepancy exists between values of H determined experimentally and previously reported theoretical values.

Conclusions

The Mackay and Leinonen (42) model of revolatilization, which can be used to calculate H, cannot be purely applied to the experiments performed in this study for reasons which have already been elaborated upon. An estimate of a value of H for this experimental system can still be made.

The method of quantification prevents an accurate application of Henry's Law to the system. Each PCB isomer would have to be quantified separately. Isolating each individual isomer in an Aroclor mixture by present gas chromatographic methods is impossible. If Aroclors were quantified by chlorine numbers, more accurate information could be obtained. One assumption would still have to be made, i.e., positional isomers of the same chlorine number have the same mass transfer coefficient. This remains to be shown but it may simplify measurements and make the approach more environmentally realistic. In the environment PCBs are a complex mixture, not single isomers.

Experiments should be designed which model the environment as closely as possible.

The Henry's Law constants determined in this study should actually be termed air/water partition coefficients. Aroclors are mixtures and in actuality cannot have a Henry's Law constant.

Table I-26. Experimentally and theoretically derived Henry's Law constants (H) and liquid phase mass transfer coefficients (K_{OL})

Aroclor	Theoretical*	Maximum	Minimum
		K_{OL}, m/hr	
1221**		9.63×10^{-4}	8.04×10^{-4}
1016**		3.18×10^{-3}	7.31×10^{-4}
1242***	5.7×10^{-2}	3.47×10^{-4}	4.40×10^{-5}
1254***	6.7×10^{-2}	8.44×10^{-5}	1.98×10^{-5}
		H, atm-m^3/mol	
1221**		2.59×10^{-6}	2.16×10^{-6}
1016**		1.02×10^{-5}	2.27×10^{-6}
1242***	5.73×10^{-4}	1.08×10^{-6}	1.37×10^{-7}
1254***	2.76×10^{-3}	2.94×10^{-7}	6.89×10^{-8}

*(Ref. 42).
**(Ref. 22).
***This study.

I-7. FLUX CALCULATIONS

There are several processes that have to be considered when estimating an atmospheric flux of PCBs to Lake Michigan. Fluxes both to and from the lake must be investigated to obtain a net atmospheric input. Wet and dry deposition represent fluxes of airborne PCBs to the lake's surface. Dry deposition includes particulates and possibly vapor. Revolatilization and bubble ejection of particulate matter must be included as potential fluxes out of the lake. Bubble ejection is a major natural source of atmospheric particulate matter over the ocean (47,48); however, its significance for Lake Michigan has not been investigated. Revolatilization of PCBs has been theoretically investigated (5,42) but experimental evidence for the direction of the PCB vapor flux is lacking. An experiment was described in the results and discussion section which investigated the controlling phase of the PCB vapor flux. The following sections deal with each of these aspects for the purpose of estimating a net flux of PCBs to Lake Michigan.

Washout Coefficients and the Wet Flux

Washout coefficients can be utilized to determine both the wet flux of PCBs (using air concentration data) and the size of the particulates that PCBs are associated with. The washout coefficient for vapor depends upon the partitioning of the constituent between vapor and water, essentially H, while that for a particulate depends upon the collision efficiency of the raindrop and particle, which is a function of diffusion, interception and impaction processes (49). Since precipitation capture processes for the two phases are different, the vapor/particulate partitioning is of extreme importance. The extent of this partitioning is uncertain since it is not known if the PCBs that pass through a glass fiber filter are small particulates or vapor. Until further experimental evidence is obtained, it will be assumed in some of the following arguments that the vapor/particulate partitioning is operationally defined by the collection method.

If washout coefficients are to be employed to indirectly determine particle size, the scavenged vapor component of precipitation must be determined. Stracha et al. (50) monitored the PCB concentration throughout a single precipitation event. They found most of the deposition occurring in the early portion of the rain, which could possibly indicate particulate washout. If a gas forms a simple solution, molecular diffusion to the drop is fast enough for equilibrium to occur within the atmosphere (49). Using this argument, if PCBs exist partially as vapor in the atmosphere and are gas phase controlled, the washout of PCB vapor could possibly show the same scavenging profile as that of particulate PCB.

The following relation can be used to calculate gas scavenging by rain (49):

$$W = \alpha p_0 \bar{C}_b \qquad \text{Eq. (5)}$$

where

W is the wet flux of the contaminant
α is the washout coefficient which is RT/H
p_0 is the annual amount of rainfall
$\bar{C}_b$ is the average contaminant concentration in air

A Henry's Law constant for Aroclor 1242 of 1.08×10^{-6} atm-m^3/mol was found in this study (Table I-26). H can be converted to dimensionless form by dividing by RT (2.45×10^{-2} atm-m^3/mol at 25°C). Substituting $\alpha = 2.27 \times 10^4$, $p_0 = 74$ mm/yr (51), and $\bar{C}_b = 0.65$ ng/m^3 (this study) into Eq. (5), the amount of Aroclor 1242 vapor scavenged annually over Lake Michigan was calculated to be 635 kg/yr. Murphy and Rzeszutko (2) reported that an average of 66% of the total PCBs in rain collected in Chicago passed through a glass fiber filter. Stracha et al. (50) also found that a majority of PCBs in rain collected around Lake Superior was in "soluble" form.

A vapor phase washout coefficient can be calculated from the precipitation data of Murphy and Rzeszutko (2). It will be assumed that the filtered portion of the rain samples contained only scavenged PCB vapor. They found that an average of 66% of the PCBs in their Chicago area samples was in soluble form, 54% of that fraction was Aroclor 1242. Applying these averages to the total wet flux (4800 kg/yr), a scavenged Aroclor 1242 vapor flux of 1711 kg/yr can be calculated. The following equation can be used to calculate the washout coefficient (r) for Aroclor 1242 vapor (49):

$$r = W/p_0 \bar{C}_b \qquad \text{Eq. (6)}$$

where

$$r = \alpha = RT/H \qquad \text{Eq. (7)}$$

Using Murphy and Rzeszutko's (2) value for the average Aroclor 1242 vapor concentration in Chicago air ($\bar{C}_b = 6.44$ ng/m^3), a washout coefficient of 6.18×10^3 was obtained. Applying Eq. (7), H_{1242} was found to be 3.96×10^{-6} atm-m^3/mol, a remarkable similarity to the value experimentally determined in this study. Table I-27 contains the atmospheric H values for Aroclors 1242 and 1254 along with the laboratory values.

Atkins and Eggleton (52) reported values for atmospheric and laboratory values of pesticide washout ratios (Table I-28). The laboratory washout coefficients they obtained for γ-BHC, p, p'-DDT and Dieldrin, which they termed partition coefficients, were actually the reciprocal of the Henry's Law constant. The atmospheric values were calculated from air and rain concentrations but unfortunately the samples were not taken concurrently. They found good agreement between the laboratory and atmospheric values for γ-BHC and Dieldrin but somewhat poorer agreement for p, p'-DDT. They attributed the disagreement to a larger proportion of airborne DDT being present in the particulate phase. Their study, while not giving entirely conclusive evidence, may indicate that utilizing the reciprocal of H

Table I-27. Vapor phase washout coefficients and Henry's constants for Aroclors 1242 and 1254. Samples taken by (2)

Aroclor	Scavenged vapor flux, kg/yr	Vapor concentration, ng/m^3	Washout coefficient	Henry's constant, $atm\text{-}m^3/mol$	
				Atmos.	Lab.
1242	1711	6.44	6.18×10^3	3.96×10^{-6}	1.08×10^{-6}
1254	1045	0.97	2.50×10^4	9.80×10^{-7}	2.94×10^{-7}

Table I-28. Atmospheric and laboratory determined washout ratios for pesticides (52)

Pesticide	Concentration,* parts per 10^{12}		Washout ratio, rain:air	
	Air	Rain	Atmospheric	Laboratory
γ-BHC	5 to 11	66	6 to 13	14
p,p'-DDT	3	194	65	2.3
Dieldrin	20	48	2.4	0.65

for vapor phase washout coefficients of pesticides and PCBs may be valid.

Using three different assumptions, more than one washout coefficient can be calculated from the air and rain data reported by Murphy and Rzeszutko (2). Assumption 1 is that all the PCBs in air are associated with particulate matter. Assumption 2 is that all the PCBs in rain are due to scavenged particulates but only the non-filterable fraction of an air sample is composed of particulate associated PCBs. Assumption 3 is that air and rain samples contain both a particulate and vapor phase component which are operationally defined by filtration through a glass fiber filter. Using the latter assumption, both a particulate and vapor phase washout coefficient can be determined. Murphy and Rzeszutko also measured washout coefficients by concurrently sampling air and rain during 2 precipitation events. These coefficients were based on total PCB concentrations in air and rain. Equation (6) can be used to calculate washout coefficients.

By using assumption 1, the total PCB wet flux to Lake Michigan (4800 kg/yr) and the average total PCB concentration in Chicago air (7.7 ng/m^3) a washout coefficient of 1.45×10^4 was calculated. A washout coefficient of 3.84×10^5 was obtained by employing assumption 2, the average concentration of particulate associated PCBs in Chicago air (0.29 ng/m^3) and the total PCB wet flux. A particulate phase washout coefficient of 1.31×10^5 was calculated by using assumption 3, the non-filterable fraction of the wet flux (0.34 x 4800 kg/yr) and an average air concentration of particulate associated PCBs of 0.29 ng/m^3. By using assumption 3, the filtered fraction of the wet flux (0.66 x 4800 kg/yr) and an average vapor concentration in air of 7.48 ng/m^3, a vapor phase washout coefficient of 9.86×10^3 was obtained. Murphy and Rzeszutko (2) also determined PCB washout coefficients (g PCB/L of rain per g PCB/L of air) of 13 and 37 for two separate rain events. An average value of 2.08×10^4 was obtained by converting the average coefficient to a dimensionless constant using a conversion factor (10^6 cm^3/m^3 per 1.2×10^3 g/cm^3) to correct for the density of moist air. The calculated particulate PCB washout coefficients are in the same range as certain trace metals, such as lead, which has a washout coefficient of 2.4×10^5 (53).

Using the data presented by Slinn et al. (49) and the calculated washout coefficients, the size of the particles the PCBs are associated with can be estimated. From their graph of particle size versus collision efficiency of rain droplets (Fig. I-14), a washout coefficient (r) can be determined for each particle size (Table I-29) by using the following relation:

$$r = ch_w E_0 / R_{mo} \qquad \text{Eq. (8)}$$

where

- c is an empirical constant which equals 0.5
- h_w is the effective height from which the pollutant is removed by wet processes (500 m)
- E_0 is the collision efficiency
- R_{mo} is the drop radius (0.1 mm).

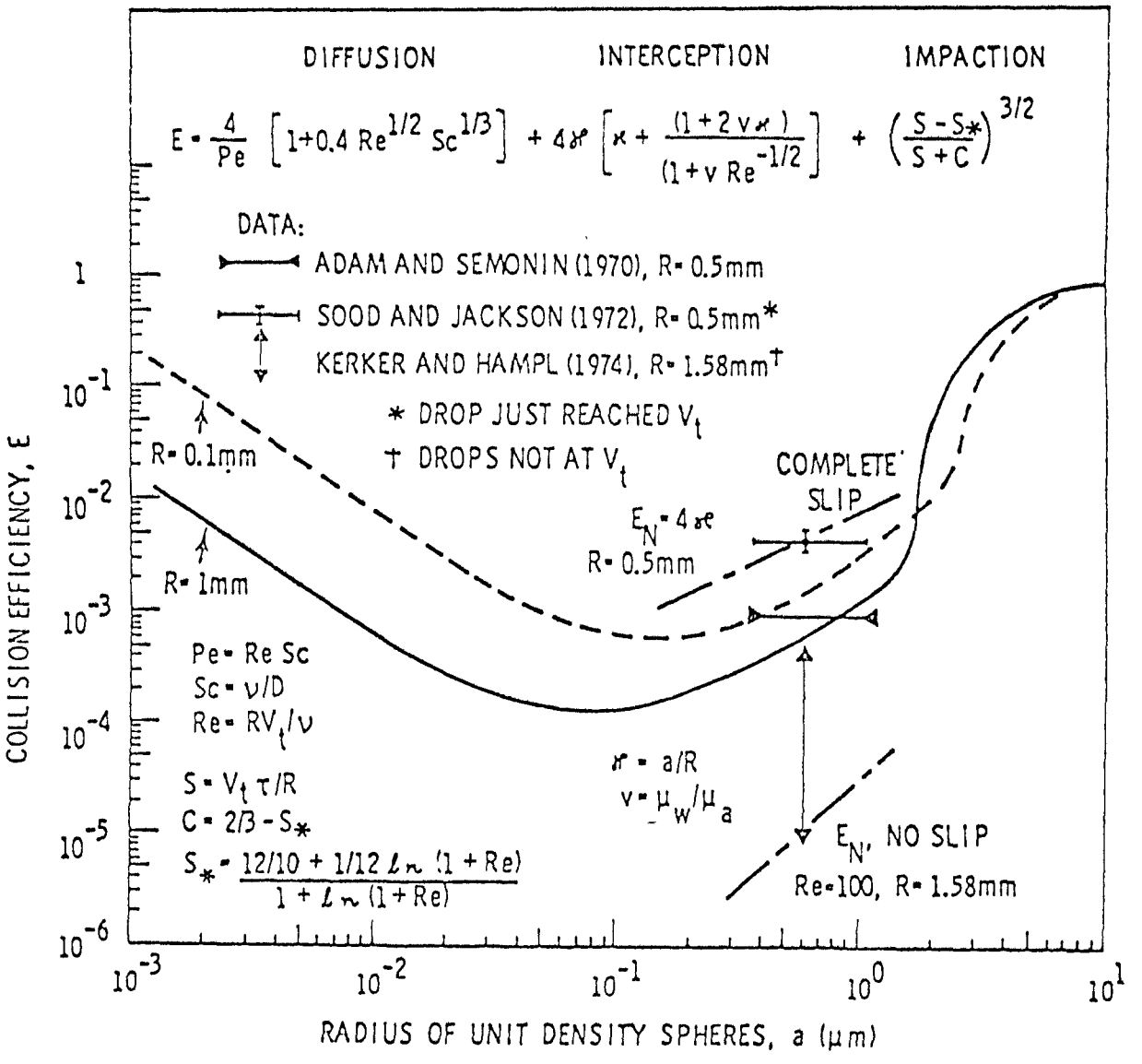


Fig. I-14. Collision efficiency against particle size (49).

Table I-29. Collision efficiencies and washout ratios for different particle sizes

Particle diameter, μm	Collision efficiency,* E_o	Washout ratio, γ
10	5.0×10^{-1}	1.25×10^{6}
2	3.1×10^{-3}	1.75×10^{3}
1	1.2×10^{-3}	3.03×10^{3}
0.2	6.2×10^{-4}	1.55×10^{3}
0.1	9.3×10^{-4}	2.33×10^{3}
0.02	7.9×10^{-3}	1.98×10^{4}
0.01	2.2×10^{-2}	5.5×10^{4}
0.002	2.4×10^{-1}	6.0×10^{5}

*For 0.1 mm drop size.

Table I-30. PCB washout coefficients and particle sizes

Washout coefficient	Particle diameter range, μm
1.45×10^{4}*	0.02 to 0.1
3.84×10^{5}**	0.002 to 0.01
2.08×10^{4}***	0.01 to 0.02
1.31×10^{5}‡	0.002 to 0.01

*Calculated by assumption 1. **Calculated by assumption 2.
***Determined from average washout ratio for two rains and assumption 1.
‡Calculated using assumption 3.

Table I-31. Predicted PCB concentrations in precipitation

Washout coefficients	PCBs in air, ng/m³		PCBs in precipitation, ng/L			
	L. Michigan	L. Superior	L. Michigan		L. Superior	
1.45×10^{4}*	1.0	0.62	15		9	
3.85×10^{5}**	0.13	0.08	50		31	
2.08×10^{4}**	1.0	0.62	21		16	
1.31×10^{5}‡	0.13	0.08	17	) 26‡‡‡	10	) 15‡‡‡
9.86×10^{3}‡	0.87	0.54	9	)	5	)

*,**,***,‡ as for Table I-30. ‡‡Using 20 μg/m³ TSP.
‡‡‡Total PCB in rain, ng/L.

Employing a drop radius of 0.1 mm fit the PCB washout coefficients better than the 1 mm size. The washout coefficients for PCBs and their corresponding particle sizes can be found in summarized form in Table I-30. From the calculated particle sizes it is apparent that PCBs are associated with Aitken particles ($d < 0.2\mu$), which are the smallest of particles present in the atmosphere. Gatz (57) obtained a curve for washout ratios versus mass median diameter of certain particulate associated trace metals. Washout coefficients of the same magnitude as those calculated for PCBs were obtained for particles having mass median diameters $<1\mu$.

To determine how realistic the calculated PCB washout coefficients were, the data for particulate and vapor phase PCBs over Lake Michigan (this study) were used to calculate precipitation concentrations (Table I-31). The generated data would be for rainfalls occurring over the lake which would, under most circumstances, have concentrations less than those found in the Chicago area (104 ng/L). This is to be expected since differences have been observed between air samples taken in urban and remote areas (Section I-3). Murphy and Rzeszutko (2) found a precipitation weighted average rain concentration of 138 ng/L for Beaver Island located in the northernmost part of the lake. The large difference between the calculated and observed values may be the result of contamination of the rain samples by dry fallout.

The available data for concentrations in rain around Lake Superior can also be used to test the calculated washout coefficients. An average concentration for suspended particulates in air for the region is 20 $\mu g/m^3$ (58). The average concentration of PCBs in particulates is 4.0 ppm (this study) which when applied to Lake Superior air, would result in a particulate phase PCB concentration of 0.08 ng/m^3. Assuming 87% of the PCBs are in the vapor phase (this study), the total PCB concentration in air can be calculated as 0.62 ng/m^3. The precipitation data and washout coefficients can be found in Table I-31. Stracha et al. (50) determined an average precipitation concentration of 25 ng/L in areas surrounding Lake Superior. A precipitation concentration of 15 ng/L, predicted by using separate washout coefficients for the particulate and vapor phase, is comparable to the observed value.

Separating the air and rain samples into a particulate and vapor component to calculate washout coefficients, agrees with the precipitation measurements of PCB better than the other calculated coefficients. The washout coefficient calculated under assumption 1 generated precipitation concentrations which were much lower than observed values. This may indicate that airborne PCBs exist partially in the vapor phase. Assumption 2 also generated a washout coefficient which agreed fairly well with the atmospheric data. The basis of the assumption was that a glass fiber filter collects all PCB associated particulates. The assumption may not be as good as the others since the calculated particle sizes are less than those which a glass fiber fiter is known to collect efficiently. The washout coefficient has been found to be a function of the type of rainfall (59). Predicting rain concentrations from washout coefficients obtained during single precipitation events may include larger uncertainties than using annual wet fluxes to predict rain concentrations.

Using vapor and particulate phase washout coefficients of 9.86×10^3 and 1.31×10^5, a Lake Michigan wet flux can be calculated. If it is assumed that the average air concentration of particulate and vapor phase PCBs is 0.13 and 0.87 ng/m^3, respectively (this study), then the wet flux can be calculated as 1101 kg/yr with 369 kg/yr being due to scavenged vapor.

The calculated washout coefficients indicate that PCBs are associated with the smallest particles present in the atmosphere, probably in the range of 0.002 to 0.1μ in diameter. The washout coefficients may also indicate that atmospheric PCB vapor does exist but the extent of the vapor/particulate partitioning cannot be estimated. Until the extent of the partitioning is known, the best method to estimate wet fluxes from air concentrations is to employ particulate and vapor phase washout coefficients. The calculations made in this section were based on data reported in several studies which may produce large errors in the final results; nevertheless, they indicate that more data must be obtained to determine the relationships between vapor and particulate phase PCBs and their capture by precipitation.

Particulate Flux

The following equation can be used to calculate a particulate flux (60):

$$F = V_d \overline{C}_b \qquad \text{Eq. (9)}$$

where

V_d is the deposition velocity
$\overline{C}_b$ is the average concentration of the contaminant in air

Since the deposition velocity depends upon the particle size (61), the size of the particulate associated PCBs must be known. The calculated washout coefficient of 1.31×10^5 corresponds to particle sizes of 0.002 to 0.01μ in diameter. Sehmel and Sutter (61) determined particle deposition rates on a water surface as a function of particle size (Fig. I-15). From the curve it can be seen that particle sizes of 0.01μ in diameter have a deposition velocity of 0.5 cm/sec. Substituting V_d and the average and range of PCB particulate concentrations (0.13, 0.10 to 0.19 ng/m^3) in air over Lake Michigan into Eq. (9), an annual flux to Lake Michigan of 1189 kg/yr was obtained with a range of 915 to 1738 kg/yr. The average is approximately 25% of the wet flux reported by Murphy and Rzeszutko (2).

Vapor Flux

PCB vapor deposition on water surfaces has not been investigated. The controlling phase (gas or liquid) of the vapor flux is unknown. Mackay and Leinonen (42) have proposed a model for liquid phase control of low solubility compounds such as PCBs, and estimates of

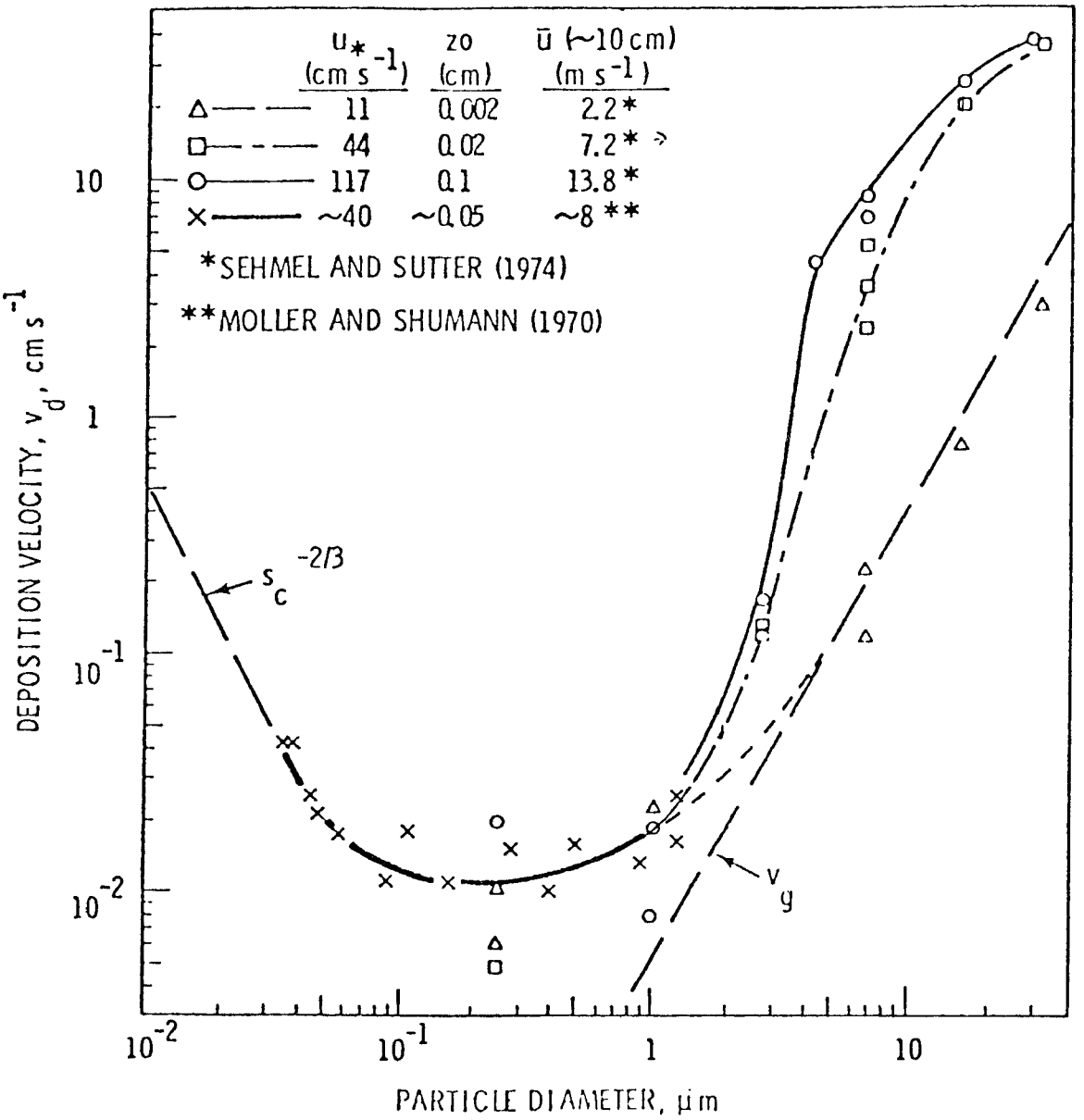


Fig. I-15. Deposition velocity against particle size (61).

PCB evaporation rates from Lake Michigan have been made (5). Due to the scarcity of experimental evidence for liquid or gas phase control of PCBs, the experimental data presented in Part I-6 can be interpreted in two ways. The magnitude of the air/water partition coefficients, which indicated gas phase control, can be used to estimate the flux of PCBs to the lake. Liquid phase control could be assumed and the experimentally determined K_{OL} used to estimate the revolatilization rate of PCBs.

Assuming gas phase control and the microlayer to be a perfect PCB adsorber, Bidelman et al. (21) calculated the vapor flux to the North Atlantic Ocean using the following equation:

$$F = k_G \overline{C}_b \qquad \text{Eq. (10)}$$

where

k_G is the gas phase mass transfer coefficient
$\overline{C}_b$ is the average PCB concentration in air

This relation could be utilized to obtain a maximum value for the influx of vapor phase PCBs to Lake Michigan. Using the values of k_G for Aroclors 1242 and 1254 (Table I-22) and the average vapor concentrations of 0.65 and 0.22 ng/m^3, respectively, the average flux of Aroclor 1242 was found to be 2619 kg/yr while that of Aroclor 1254 was 788 kg/yr (Table I-32). The total PCB vapor flux to the lake, then, is 3407 kg/yr with a range of 1724 to 4347 kg/yr.

A more rigorous approach to calculating the vapor flux to Lake Michigan would be to use the following modified version of the flux equation from Liss and Slater (44):

$$N = K_{OG}(CH-P)/RT \qquad \text{Eq. (11)}$$

where

K_{OG} is the overall gas phase mass transfer coefficient
C is the soluble concentration of PCBs
H is the Henry's Law constant
P is the partial pressure of PCBs
RT is 2.45×10^{-3} atm-m^3/mol at 25°C

K_{OG} was calculated from the following relation (44):

$$1/K_{OG} = 1/k_G + H/k_L \qquad \text{Eq. (12)}$$

where

k_G is the gas phase mass transfer coefficient
k_L is the liquid phase mass transfer coefficient

Maximum and minimum values of K_{OG} and H (Table I-33) determined from the experimental values of K_{OL} (Part I-6) were used to determine the vapor flux (Table I-34). The maximum average value was found to be

Table I-32. Vapor flux to Lake Michigan ($F = K_G C_b$)

Type of value	Aroclor	k_G, m/hr	C_b, ng Aroclor/m^3	F, kg Aroclor/yr	F, kg total PCB/yr
Average	1242	7.93	0.65	2619	3407
	1254	7.05	0.22	788	
Maximum	1242	7.93	0.83	3344	4347
	1254	7.05	0.28	1003	
Range					
Minimum	1242	7.93	0.33	1330	1724
	1254	7.05	0.11	394	

Table I-33. Henry's constants (H) and gas phase mass transfer coefficients (K_{OG}) for Aroclors

Arochlor	H, atm-m^3/mol		K_{OG}, m/hr	
	Maximum	Minimum	Maximum	Minimum
1221	2.59×10^{-6}	2.16×10^{-6}	9.10	9.12
1061	1.02×10^{-5}	2.27×10^{-6}	7.64	8.00
1242	1.08×10^{-6}	1.37×10^{-7}	7.85	7.88
1254	2.94×10^{-7}	6.89×10^{-8}	7.03	7.04

Table I-34. Vapor flux to Lake Michigan [$N = K_{OG}(CH-P)/RT$]

Type of value	Aroclor	K_{OG}, m/hr	H, atm-m^3/mol	C,* mol/m^3	P,** atm	N, kg Aroclor/yr	N, kg total PCB/yr
	1242	7.85	1.08×10^{-6}	7.66×10^{-9}	5.58×10^{-14}	2019	2379***
	1254	7.03	2.94×10^{-7}	2.57×10^{-8}	1.51×10^{-14}	360	2379***
Average	1242	7.88	1.37×10^{-7}			2335	2971‡
	1254	7.04	6.89×10^{-8}			636	2971‡
	1242				6.60×10^{-14}	2457	3208***
	1254				2.33×10^{-14}	751	3208***
Maximum							
	1242					2774	3802‡
	1254					1028	3802‡
Range							
	1242				3.00×10^{-14}	923	857***
	1254				6.17×10^{-15}	66‡‡	857***
Minimum							
	1242					1235	1025+
	1254					210	1025‡

*(Ref. 2).
**This study.
***Calculated using maximum values of Hand K_{OG}.
‡Calculated using minimum values of Hand K_{OG}.
‡‡Flux out of lake.

2335 kg of Aroclor 1242/yr and 636 kg of Aroclor 1254/yr for a total vapor flux of 2971 kg/yr.

Deposition velocities of 0.04 cm/sec for γ-BHC, Dieldrin and p,p'-DDT vapors on turf in wind tunnel experiments have been reported by Atkins and Eggleton (52). While the deposition velocity for a water surface would not be expected to be the same as that for turf, the value could be used to give a lower limit of the vapor flux. Using this deposition velocity and an average vapor phase concentration of 0.87 ng/m^3, an annual flux of 637 kg was obtained.

Another way to interpret the vapor flux would be to assume liquid phase control of PCBs. The liquid phase control model of Mackay and Leinonen (42) can be used to calculate the revolatilization rate of PCBs from Lake Michigan by utilizing the following equation:

$$N = K_{OL}(C-P/H) \qquad \text{Eq. (13)}$$

Using the K_{OL} and H values they theoretically determined and the concentration of PCBs in air and water for Lake Michigan, a revolatilization rate of 3.43×10^5 kg/yr was obtained. The K_{OL} values determined in this study can also be used to calculate a revolatilization rate (Table I-35). Since the K_{OL} values determined in this study are actually a combination revolatilization and desorption rate, the total PCB concentration of PCBs in Lake Michigan were used in the calculation. A maximum flux of 3132 kg/yr was calculated.

Cohen et al. (63) found that the liquid phase mass transfer coefficients of benzene and toluene were a function of the wind and stirring speed in an experimental wind-wave tank. The two relations they obtained were:

$$k_L = 11.4\ Re^{*0.195} - 5.0 \quad 0 \text{ rpm} \qquad \text{Eq. (14)}$$

$$k_L = 11.4\ Re^{*0.195} - 4.1 \quad 540 \text{ rpm} \qquad \text{Eq. (15)}$$

where

Re* is the roughness Reynolds number.

Re* is defined by the following relation:

$$Re^* = z_0 U^* / \nu_a \qquad \text{Eq. (16)}$$

where

z_0 is the effective roughness height
U^* is the friction velocity
ν_a is the kinematic viscosity (1.506×10^{-1} cm^2/sec at 18°C).

Table I-35. Revolatilization rates from Lake Michigan

Aroclor	K_{OL}, m/hr	H, atm-m^3/mol	C,* mol/m^3	P,** atm	N, kg Aroclor/yr	N, kg total PCB/yr
1242		5.73×10^{-4}	7.66×10^{-9}	5.58×10^{-14}	57,200	343,200***
1254		2.76×10^{-3}	2.57×10^{-8}	1.51×10^{-14}	286,000	343,200***
1242	3.47×10^{-4}		4.75×10^{-8}		2,175	3,132‡
1254	8.44×10^{-5}		6.82×10^{-8}		957	3,132‡
1242	4.40×10^{-5}				277	501‡‡
1254	1.98×10^{-5}				224	501‡‡

*(Ref. 2).
**This study.
***(Ref. 42).
‡Calculated using maximum values of K_{OL} in this study.
‡‡Calculated using minimum values of K_{OL} in this study.

Values of z_0 and U* were obtained from a graph presented in their study and used along with ν_a to calculate k_L for different wind speeds. It was then assumed that the profile of the wind speed versus PCB mass transfer coefficient curve would be the same as that of the benzene and toluene curves. Using this assumption and the K_{OL} values obtained in this study, PCB liquid phase mass transfer coefficients were calculated for different wind speeds (Table I-36). Since the stirring speed in the experiment presented in this study (Part I-6) was unknown, 540 rpm was assumed. The exact dependence of stirring speed on k_L has not been determined (63). Revolatilization rates as a function of wind speed were calculated using Eq. (13) (Table I-37). Wind speed data taken periodically over 3 summers on Lake Michigan showed an average of 4.7 m/sec (35). Under these wind speed conditions the PCB revolatilization rate for Lake Michigan would be 1.72×10^5 to 1.13×10^6 kg/yr.

The validity of the revolatilization rates can be checked by determining if they can account for the enrichment observed in the microlayer. Elzerman (64) reported microlayer concentrations on Lake Michigan of 78 to 1090 ng/L with concentrations in the bulk water being 5 to 64 ng/L. The screen technique he employed to collect the microlayer is thought to sample the top 300μ of the water surface. Knowing this fact, the amount of PCB in 1 m^2 of surface area can be calculated. The wet flux (4800 kg/yr) and particulate flux (1189 kg/yr) were combined to give the downward flux of PCBs. The revolatilization rates under quiescent conditions were used as the upward flux. The residence time of the microlayer was calculated by subtracting the time involved in depositing an amount of PCB equal to that in the microlayer from the time involved in stripping that amount (Table I-38). It is apparent that the microlayer would not exist under the conditions of the K_{OL} calculated by Mackay and Leinonen (42). The evaporation rate estimated by Versar (5) and the maximum and minimum K_{OL} values determined in this study are more realistic in that they give residence times >1 hr.

Two interpretations have been given to elucidate the direction and magnitude of the PCB vapor flux. Gas phase control of PCBs is a new interpretation. Besides the experiment performed in this study and that of Hetling et al. (22), experimental evidence is lacking. Further experimentation must involve the determination of accurate Henry's Law constants for PCBs. Liquid phase control of PCBs has been hypothesized (42). The K_{OL} values determined in this study show that adsorption of PCBs to particulate matter slows the rate of revolatilization. Extrapolating the K_{OL} values to Lake Michigan may involve certain errors. The desorption rate of the particulate matter used in this study may not be the same as that of Lake Michigan particulates. Also, all the PCBs in Lake Michigan water may be adsorbed to particulate matter and unless desorption kinetics are rapid and the revolatilization rate is faster than the sedimentation rate, revolatilization may not occur. Another uncertainty is the effect of the microlayer on revolatilization rates. Factors which may affect the revolatilization rate must be further explored.

Table I-36. K_{OL} against wind speed

Wind speed cm/sec	K_L,* cm/hr	K_{OL}(1242), cm/hr		K_{OL}(1254), cm/hr	
		Maximum	Minimum	Maximum	Minimum
0	2.00	3.47×10^{-2}	4.40×10^{-3}	8.44×10^{-3}	1.98×10^{-3}
300	2.97	1.00	9.88×10^{-1}	9.78×10^{-1}	9.72×10^{-1}
600	8.38	6.41	6.38	6.39	6.38
1150	30.50	28.50	28.50	28.50	28.50

*(Ref. 63).

Table I-38. Microlayer residence times against revolatization rates

Revolatilization rate, kg/yr	Deposition rate, kg/yr	PCB in microlayer,* g/m^2	Residence time, hr
343,000**	5,989	2.34×10^{-8}	0
1,160***			8
3,132‡			2
501‡‡			22

*Calculated using minimum observed concentration (78 ng/L) (64).
**Estimate based on data in (Ref. 42).
***(Ref. 5).
‡Calculated from maximum K_{OL} in this study.
‡‡Calculated from minimum K_{OL} in this study.

Table I-37. Revolatilization rates from Lake Michigan against wind speed

Aroclor	Wind speed, cm/sec	K_{OL}, m/hr	H,* atm-m^3/mol	C,** mol/m^3	P,*** atm	N, kg Aroclor/yr	N kg total PCB/yr
1242		0.0099	5.73×10^{-4}	4.75×10^{-8}	5.58×10^{-14}	6.22×10^{4}	
	300						1.72×10^{5}
1254		0.0097	2.76×10^{-3}	6.82×10^{-8}	1.31×10^{-14}	1.10×10^{5}	
1242		0.064				4.02×10^{5}	
	600						1.13×10^{6}
1254		0.064				7.24×10^{5}	
1242		0.285				1.79×10^{6}	
	1150						2.11×10^{6}
1254		0.285				3.22×10^{5}	

*(Ref. 42).
**(Ref. 2).
***This study.

Bubble Ejection

Bubble ejection of particulate matter must be considered as a potentially important water to air transport process. The ocean is a major natural source of atmospheric particulate matter (47,48). The process which produces the particulates is bubbles breaking at the air/water interface (65). These bubbles strip off a layer of 0.025 to 0.75 μm of the air/water interface. The composition of the scavenged material depends upon the composition of both the surface microlayer and the bubble skin. It has been estimated that the ocean produces 10^{15} to 10^{16} g/yr of atmospheric sea salt particles (47,48). Estimates of this kind have not been performed for freshwater lakes.

To estimate the amount of PCBs injected into the atmosphere from Lake Michigan, the composition and enrichment of the microlayer must be known. Andren et al. (66) perpared a review paper dealing with some of the physical and chemical aspects of surface microlayers in freshwater lakes. Elzerman (64) performed a study on surface organic microlayers in Lake Michigan. He determined the enrichment of PCBs in the microlayer in several locations finding an average microlayer concentration of 245 ng of Aroclor 1254/L while that of the bulk water was 22 ng of 1254/L. The maximum enrichment observed was under conditions where the microlayer and bulk water concentrations were 664 ng/L and 5.2 ng/L, respectively. The actual depth sampled by the screen technique is thought to be about 300μ (64). Most freshwater surface microlayers are 10 to 30 nm thick (67). Knowing the concentration in the bulkwater, the concentration in the microlayer and the actual depth sampled, a simple calculation can be performed to obtain the concentration in the actual surface microlayer. The average concentration in a 30 nm thick microlayer was calculated to be 2.2 ppm while that of the maximum enrichment case was 6.7 ppm.

To estimate the flux of particulate PCBs from Lake Michigan to the atmosphere, the particulate flux for the ocean must be recalculated to compensate for the differences in area of the two environments. Due to the salinity differences of the two bodies of water, a salt correction must also be applied since the composition of the ejected material over the ocean would be expected to be more enriched in salt than the material ejected from Lake Michigan. The average total dissolved solids concentration of Lake Michigan is 157 mg/L (68) while the average salinity of the ocean is 35 g/L, the salt correction factor is then 0.157/35. The estimated amount of particulate matter ejected from Lake Michigan was calculated to be 7×10^8 to 7×10^9 g/yr.

An assumption must then be made that the PCB concentration of the microlayer is similar to that of the material ejected. This is logical since a jet droplet carries away part of the microlayer (65), although other factors may dilute or enhance the concentration. The composition of the bubble skin also contributes to the amount of material ejected. Wallace and Duce (69) have shown that bubbles may also adsorb materials in the water column before they reach the surface. Employing a concentration of PCBs in the microlayer of 2.2 ppm, a range of the annual flux of PCBs of 2 to 16 kg was obtained. If the maximum microlayer enrichment values are used, a flux of 5 to 46 kg/yr is calculated. If the microlayer depth is 10 nm the fluxes would be three times as great as the ones calculated.

These calculations would seem to indicate that the ejection of PCBs into the atmosphere from Lake Michigan is not as important a process as it could be in the ocean. The numbers obtained should be considered a rough estimate since the significance of bubbles bursting in freshwater lakes has not been investigated.

Photolysis

Photolysis must be considered as a degradative pathway which may alter the amount of PCB deposition. Photolysis of PCBs in water as well as in a number of solvents has been reported (36,37,38,70). The significance of PCB photolysis in the atmosphere has not been investigated. The main reaction of photolysis of PCBs is stepwise dechlorination. If extrapolation from a solvent media to the atmosphere could be made, this would mean photolysis of airborne PCBs would change the composition of an air sample with the extent of the process depending upon the residence time in air.

Bunce et al. (70) performed some calculations to estimate the impact of PCB photolysis in Lake Erie. The quantum yield of PCBs must be known in order to adapt their model to calculate the impact of photolysis in the atmosphere. The quantum yields they reported were determined in solvents such as acetonitrile-water and isooctane. Information is not available for the determination of quantum yields in the atmosphere. Solvents can influence the rate of photolysis. Ruzo et al. (38) found different rates of tetrachlorobiphenyl photolysis in different solvents. They also found that the presence of O_2 decreased the photolysis rate, sometimes by a factor of four. Herring et al. (36) found that Aroclor 1254 degraded most rapidly in hexane, then water, and slowest in benzene. Since the solvent plays an important role in the rate of photolysis, it is extremely difficult to extrapolate rates, taken in any other media except air, to the atmospheric environment. Studies on the photolysis of PCBs under simulated atmospheric conditions must be performed before a reasonable estimate of its importance can be made.

The fluxes both to and from Lake Michigan have been estimated in the preceding discussion. Models for both the liquid and gas phase control of PCBs have been discussed. Table I-39 contains net atmospheric input estimates to Lake Michigan based upon the two models. The Lake Michigan estimates show that vapor deposition or revolatilization, depending upon which model is the correct one, are the most important fluxes.

Combining the data obtained in this study with the input data reported by Murphy and Rzeszutko (Table I-1), it is apparent that the atmosphere is now the major source of PCBs to Lake Michigan (Table I-40). as also concluded by Murphy and Reszutko (2). The known industrial discharges prior to 1975 are an order of magnitude greater than the annual atmospheric input. Further experimentation must be performed to determine which phase controls the vapor flux of PCBs so more accurate estimates can be made.

Table I-39. Estimated net atmsopheric inputs to Lake Michigan based on gas and liquid phase control model

Flux	Gas phase control, kg PCB/yr		Liquid phase control kg PCB/yr	
Particulate	1189		1189	
Vapor	2675		0	
Wet	4800**	1101***	4800**	1101***
Bubble ejection	9		9	
Revolatilization	0		3132+	
Net atmospheric input	8655		2848	

*Average using maximum and minimum values of H found in this study.
**Data taken from (2).
***Estimate based on air concentrations found in this study.
+Based on K_{OL} values determined in this study under quiescent conditions.

Table I-40. Inputs of PCBs (kg/yr) to Lake Michigan*

Sources	Prior to 1975		1977	
	LPC	GPC	LPC	GPC
Industrial discharges	25,000	25,000		
Atmospheric	2,848	8,655	2,848	8,655
Streams and wastewater	750	750	750	750
Total	28,598	34,405	3,598	9,405

*Data in Table I-1 incorporated into estimates. LPC and GPC are liquid and gas phase control, respectively.

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APPENDIX I-A

XAD-2 CLEANUP PROCEDURE

1. Dry XAD-2 for 24 hr at 60°C.
2. Clean XAD-2 by soxhlet extraction using petroleum ether for 72 hr, changing the solvent every 24 hr.
3. Dry XAD-2 overnight at 60°C.
4. Weigh out 70 g quantities of clean resin and store in glass jars with foil lined caps.

SAMPLE CLEANUP PROCEDURE

1. Soxhlet extract XAD-2 for 24 hr with 500 ml of petroleum ether.
2. Concentrate XAD-2 extract to 10 ml using a Kuderna-Danish concentrator.
3. Dry extract through disposable pipette containing sodium sulfate.
4. Concentrate to 2 ml using a slow stream of purified nitrogen.
5. Transfer to 4 g alumina (6% w:w H_2O) column (1 cm ID) topped with a small amount of sodium sulfate.
6. Drain column to top of sodium sulfate level collecting the eluate in an appropriate receiving vessel.
7. Add more petroleum ether to collect PCB fraction.
8. Total volume collected should be 13 ml.
9. Concentrate to a suitable volume with a slow stream of purified nitrogen.
10. To soxhlet extract filter, cut into strips small enough to fit in the thimble of a 250 ml soxhlet extractor.
11. Soxhlet extract with petroleum ether for 24 hr.
12. Treat filter extract in the same manner as XAD-2 extract.

PART II

PAHs IN AIR OVER LAKE MICHIGAN

by

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ABSTRACT

Aerosol sampling was conducted over Lake Michigan for a 3-yr period to develop and adapt methods of analysis for measuring low concentrations of polycyclic aromatic hydrocarbons (PAHs) and to determine the qualitative nature and possible cycling of these compounds over the lake's surface. Twelve PAHs were identified in the air over Lake Michigan. Their wet and dry fluxes were approximately 10^5 kg/yr and relatively high levels were found for two potent carcinogens--benz(a)anthracene and benz(a)pyrene. Neither bubble ejection nor volatilization proved to be significant as pathways for PAH return to the atmosphere. The atmosphere is postulated to act as a source and the sediment as an eventual sink for these compounds.

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II-1. INTRODUCTION

The increased use of fossil fuels as a source of energy has resulted in an increase of organic combustion by-products in the air. In heavily populated areas the concentration of these compounds can reach undesirable levels (1). Although this pollution has been recognized, little information exists on the composition and fate of the organic fraction of aerosols. Once organic aerosols are formed those physical, chemical and meteorological factors that can influence their deposition from air to water, as well as other pathways, have not been documented adequately and real values to work with are meager or nonexistent. The total composition of organic matter in aerosol particles has never been fully investigated and no information, to date, exists on the organic fraction of aerosols directly over Lake Michigan or the size fractionation of polyaromatic hydrocarbons over Lake Michigan. This becomes important in view of work done on aerosol trace element input and the small drainage basin to surface area ratio of the lake.

The principal objective was to systematically develop and adapt methods of sampling and analysis to measure low (ng/m^3) concentrations of 16 selected PAHs in aerosols directly over Lake Michigan.

II-2. CONCLUSIONS

Twelve polycyclic aromatic hydrocarbons were identified in aerosols sampled directly over Lake Michigan. This constituted the first measurements of this kind on a large inland lake. Concentrations ranged from 0.1 to 4.2 ng/m^3 which were found on single filters exposed for <24 hr. These values correlated well with those from shoreline data in the literature and added to the meager qualitative and quantitative data obtained to date on PAHs in this unique environment. The highest concentrations of these compounds were found for the smallest PAH ring sizes, and may be an unexplained lake effect on organic aerosols and vapor.

Concentrations of PAHs in the Lake Michigan microlayer ranged from 0.15 to 0.45 μg/liter, representing on a relative scale, 10^6 times the concentration in air. This suggests that aerosols are a source of these compounds and that the microlayer serves as a repository until the PAHs are removed.

The wet and dry fluxes of individual polycyclic aromatics were virtually the same and approximately an order of magnitude lower than the total organic carbon flux to the lake. High levels of two important aromatics, benz[a]anthracene and benz[a]pyrene, emphasize the need for data on the atmospheric input of water pollutants such as these known carcinogenic agents.

Neither bubble ejection nor volatilization of polycyclic aromatics proved to be significant routes for the return of PAHs to the atmosphere from the lake, compared to the inputs of wet and dry deposition.

It appears that PAHs in aerosols originate from man-made combustion processes. It is hypothesized that the controlling mechanism is a gas-to-particle formation associated with particles from 0.001 μm (molecular) to 1 μm (submicron). This conversion for PAHs is made rapidly at ambient temperatures and pressures. By the nature of the particle sizes PAHs are formed on, their residence times are long and removal from air is principally by impaction. Thus, the flux from air to water is slow but significant. The atmosphere acts as a large source and the lake as a sink, with little or no return. Once the PAHs reach the lake their build up in the microlayer seems evident, until adsorption and sedimentation to the lake bottom remove them from further cycling.

II-3. BACKGROUND

Gas Chromatography of PAHs in Aerosols

Gas chromatography (GC) for the determination of PAHs in air was used by Liberti et al. (2). The GC analysis of PAHs in other matrices was reported previously. Extraction of urban aerosols was achieved by dividing into cyclohexane, methanol-water and nitromethane fractions. This procedure allowed quantitative recovery of PAHs in the nitromethane fraction and complete separation of aliphatic and aromatic fractions. Subsequent separation of the aromatic fraction was performed using a 35 m capillary column coated with SE-30. Good separation of 19 PAHs was achieved. However, isomer resolution was not completed. Analysis was carried out with flame ionization detectors using 1,3,5 triphenylbenzene as an internal standard.

Cantuti et al. (3) evaluated SE-30, SE-52 and XE-60 liquid phases, temperature programming and the electron capture detector for improved PAH analysis. The SE-52 and XE-60 columns provided mixture separation of the difficult pairs benz[a]- and benz[e]pyrene, chrysene and benz[a]anthracene. It was found that retention indices for programmed runs were in agreement with isothermal values, indicating programming could be used with reliability.

Other researchers have utilized the resolution of GC to analyze PAHs in atmospheric samples (4,5).

Extensive evaluation of GC liquid phases was conducted with PAH separation in mind. Apiezon L, silicon oil and polystyrene were examined by Abraham and Marks (6) and JXR, OV-1, DC-200 and Dexsil 300 were compared by Birchfield et al. (7). Of these phases, Dexsil 300--a borane-silicone copolymer--showed best thermal stability, but was incapable of resolving certain refractory pairs such as benz[a]- from benz[e]pyrene. Others have found Dexsil 300 to be a superior liquid phase. For example, Natusch (8) used 1.5% Dexsil 300 on 40/60 mesh Chromosorb W coupled with temperature programming and flame ionization, which yielded a clean separation of 20 to 30 PAHs. Kubota et al. (9) used a 4.6 m x 3.2 mm glass column of 3% Dexsil 300 on 80/100 mesh Chromosorb W(HP), with programming from 110 to 320°C, to elute 2 through 7 ring systems.

Because of the interest in PAHs as carcinogens, there has been a proliferation of publications on their occurrence, distribution and methodology.

The chemical characteristics of the organic matter found in air which is extracted by benzene in a soxhlet procedure have been examined by infrared spectra, empirical formula, functional groups and particle sizes (10,11). Variation of organic chemical content with size was shown to occur. This finding is important because it delineates the kinds of substances which will enter the human lung.

Grimmer and Bohnke (12) used capillary column gas chromatography to provide high resolution of over 100 PAHs in airborne dust collected at Bochum and Marz, Federal Republic of Germany. The acetone extract was partitioned successively between cyclohexane, dimethylformamide and cyclohexane again, to give an enriched aromatic fraction. Clean up of the complex mixture was facilitated with silica and Sephadex LH-20 column chromatography prior to GC.

Analysis of fourteen PAHs in a large area of Los Angeles County showed a correlation with inversion height (13). The higher the median inversion height the lower the concentration of benz[a]pyrene, or the larger the volume of air a pollutant has to disperse in, the greater its dilution. The major source of benz[a]pyrene was traffic with an average emission value of 0.43 ng/m^3 (14,15).

Until recently, the lack of an effective separation scheme was the most serious hindrance to the understanding of airborne PAHs. Schemes typically entailed liquid-liquid extraction, column-, thin layer- (TLC) or paper-chromatography (PC) followed by luminescence or absorption spectroscopy. These techniques met with varying degrees of success due to serious limitations, including loss of sample, tailing and loss of reproducibility.

It has been recognized that small differences in the structure of PAHs cause great differences in their tumorgenicity. To remedy this problem emphasis has been focused on high resolution columns.

Zoccolillo (16) developed a high efficiency packed column of 1% SE-52 on 60/80 mesh Chromasorb G that was comparable to a 35 m capillary column with respect to resolution and time of analysis. This was accomplished by selecting a solid support of low surface area and minimizing the liquid phase coating. The column was applied successfully to routine analysis of PAHs in airborne particulates in Rome, Italy.

Doran and McTaggart (17) utilized glass capillary columns for the routine analysis of benz[a]pyrene and benz[a]anthracene. High temperature stationary phases such as the OV-series and the Dexsil series were used to allow temperature programming with minimum bleed.

While suspected previously, the complexity of airborne PAHs has been made more clear with the use of high resolution capillary columns. Lao et al. (18) and Lee et al. (19) reported >100 PAHs in extracted airborne matter using capillary columns. A systematic extraction scheme for airborne PAHs was described by Novotny

et al. (20) involving several partitioning steps, lipophilic gel fractionation, high resolution liquid chromatography (LC) on chemically-bonded stationary phases, followed by capillary column GC.

Using the sensitive flame ionization detector (FID) and high resolution capillary columns, unique profiles of polyaromatic compounds were obtained (21). This technique was used to screen sources of atmospheric pollution.

Lao et al. (18) was the first to evaluate the potential of combined GC-mass spectrometry (MS) for PAH analysis in airborne pollutants. Mass spectra of more than 70 major PAHs in air were obtained and compared to reference standards. It was found that MS could be used as a sensitive detector for GC (22,23,24).

Lao et al. (25) extended their GC-MS work to a quadrupole system for qualitative analysis and micro-processor controlled GC-FID for quantitative analysis of PAHs. Comparisons of Dexsil 300, 400 and 410 packed columns showed small differences in retention times or response factors.

Fourier transform nuclear magnetic resonance spectroscopy (NMR), GC and MS were used to characterize PAHs and alkylated PAHs in air pollution particulate matter over Gary, Indiana (19). Emphasis was placed on hitherto unresolved toxicologically important isomers by using glass capillary columns and NMR to locate positional isomers. It was found that Gary gave a distinct "finger print" of PAHs and concentrations that could be used as a tracer.

Recent publications on high pressure liquid chromatography indicate separations of airborne PAHs comparable to GC (26,27).

It has been demonstrated that gas-liquid chromatography (28) gave baseline separations of isomeric 3 to 5 ring PAHs using a nematic liquid crystal *N*, *N*'-bis (*p*-methoxybenzylidene)α, α'-bi-*p*-toluidene (BMBT). This liquid phase also yielded unique resolution of steroid epimers (29), polychlorinated biphenyls (30) and methoxybenzanthracene isomers (31). Separations were superior to any published to date on packed or capillary columns, however, BMBT showed bleed at elevated temperatures and prolonged operation. To remedy this, a new liquid crystal *N*, *N*'-bis (*p*-butoxybenzylidene)α, α'-bi-*p*-toluidene (BBBT) was synthesized and shown to have diminished bleed with the same separation (32). It was found, however, that analysis of high molecular weight PAHs (22 to 24 carbon atoms) on BMBT or BBBT resulted in prolonged retention times and peak broadening. A new high temperature liquid crystal *N*, *N*'-bis (*p*-phenylbenzylidene)α, α'-bi-*p*-toluidene (BPhBT), compatible with GC-MS and extending the analysis of PAHs to 5 to 7 ring systems was synthesized (33). With BBBT and BPhBT, PAHs from 2 to 7 rings can be separated and analyzed by packed column chromatography. Baseline separations of 22 to 24 carbon PAHs were performed in <10 min with small injection volumes.

Airborne particulate matter from an urban area was fractionated and analyzed on a 5 m, 4% Dexsil 300 column and Finnigan 3100 mass spectrometer. Interpretation and comparison with standards led to identification of more than 100 compounds (34).

Recent determinations of PAHs in the environment were achieved with glass capillary GC on a 20 m column of SE-52 (35). The method was applied to samples of recent lake and river sediments, river particulates, street dust and airborne particles.

A unique separation of airborne PAHs was achieved using a 2 hr Soxhlet extraction. The extract was concentrated without separation and analyzed by GC using a high performance ultra-thin, thermally treated Carbowax 20M column (36). In the past, use of composite extracts from as many as 300 high volume filters was reported. However, for the first time they were capable of analyzing a single 24 hr filter (36). A rapid procedure for the analysis of nearly 100 organic compounds was developed, allowing a series of 50 comparative survey analyses from a single site in <8 hr/sample.

For quantitative GC analysis of PAHs, pentatricontane (C_{35}) has been used as an internal standard (37).

Pierce and Katz (38) examined the size dependence of PAHs in air. Using Anderson cascade impactors, eight PAHs and two oxygenated arenes were separated by TLC and analyzed by absorption and fluorescence spectrophotometry. The size distribution of PAHs followed a log normal relationship, with the majority of PAHs associated with particles <3 μm diameter. Little other information on particle or mass distribution of PAHs in air is known. DeMaio and Corn (39) showed that >75% of the weight of selected PAHs was associated with particles <2.5 μm in diameter. Kertesz-Saringer et al. (40) reported that from 70 to 90% of the total benz[a]pyrene was associated with aerosols with a radius of <1 μm. Thomas (41), however, showed that the amount of benz[a]pyrene per unit weight of soot obtained from the combustion of various fuels was constant for all particle size fractions. Other studies (38) showed that photo-oxidation by-products of PAHs also are size dependent.

Only one paper has been published on PAHs in airborne matter over a large body of water (42). Eighteen different PAHs with from 2 to 6 ring structures, were collected over the North Atlantic Ocean. The ether soluble fraction of these aerosols was separted according to a scheme yielding organic acids, phenols, organic bases, aliphatics, aromatics and neutral polar compounds (43).

Work on the total organic carbon content of aerosols over a large (marine) body of water showed a decrease in the amount of organic matter with increasing salt content (44,45).

II-4. EXPERIMENTAL METHODS

Glass Fiber Filter Treatment

Glass fiber filters have a basic pH when untreated. This poses a problem when used in weight measurements. Gases, such as sulfur dioxide, can be adsorbed on the surface of the glass fiber and, at a basic pH be oxidized to sulfate (46). To avoid this weight anomoly, the glass filters were soaked in 6N H_2SO_4 prepared from XAD-2-extracted water. To lower their organic blank, all glass filters were then extracted with ether and combusted for 3 hr at 450°C (43,47).

Glass fiber filters are hygroscopic to a certain extent although less than other filter media. In order to minimize weight changes with fluctuations in relative humidity (RH) or temperature the filters were weighed before and after collection at constant temperature and relative humidity (48).

Glass fiber filters were placed in the chamber, equilibrated for 1 hr, and their mass determined by weighing on either an analytical balance (±0.0001 g) or an electromagnetic ultramicrobalance (±0.0001 mg). The difference before and after collection yielded particle mass.

Ship Aerosol Sampling

Sampling was conducted aboard several ships during a 3-yr period and once from land on the shoreline of Lake Michigan. The ships utilized were the University of Michigan's R/V Laurentian, the University of Wisconsin Systems the Neeskay and the R/V Roger R. Simons of the Environmental Protection Agency. Sampling was conducted during the spring, summer and fall, although not at all these times each year. Transects for the cruises were both north and south of Milwaukee and stationary samplings in connection with cruises under the direction of Dr. Herman Sievering of Governors State College were also carried out.

Equipment including high volume aerosol samplers, high volume cascade impactors and Delron cascade impactors were run in duplicate and located on the bow of each ship ahead of smoke stacks, ventilation systems and from 2 to 7.6 m above the water line. These samplers were positioned such that they were as far apart as possible. Precautions were taken to secure all samplers with rope, tape and foul weather proofing which was water proof polyethylene bags.

It was found that inorganic contamination of filters was possible from air recirculated by the pump. The source of this inorganic copper in filters is wear on the armature of the pump (49). A study of the production of carbon aerosol by high volume samplers from abrasive wear of motor brushes yielded average concentrations of 150 ± 10 $\mu g/m^3$ (50). This is an appreciable value compared to the range of 1.7 to 19.8 $\mu g/m^3$ found over Lake Michigan (this work). Recirculation was found to be very low, i.e., <0.1%, and could be ignored in monitoring environmental samples. Caution should be exercised in operating two or more samplers in that they should have ample spacing or exhaust tubes to preclude interference.

In a recent report (51) volatile polychlorinated naphthalenes (PCNs) were found in the plastic parts of motor assemblies of certain high volume samplers and contaminated the filters for subsequent analysis. To avoid recirculation of PCNs, a collapsible exhaust duct 3 m in length was connected to the housing of each high volume sampler. This allowed the exhaust to be channeled away from the intake (52). An evaluation of plastic components in our samplers has shown no PCNs to be present. However, exhaust tubing was mounted as a precaution.

To avoid contamination of the filters from the smokestack of the ship while sampling, the high volume samplers and Delron samplers were turned off whenever the wind came within their arc. While underway there was little problem with smokestack contamination. However, when on station, samplers were often turned off.

Flows for the Delron cascade impactors were corrected by calibration in the laboratory against a mercury manometer. Flow rates for the high volume samplers and high volume cascade samplers were calibrated in the laboratory before each cruise with a top loading orifice and water manometer.

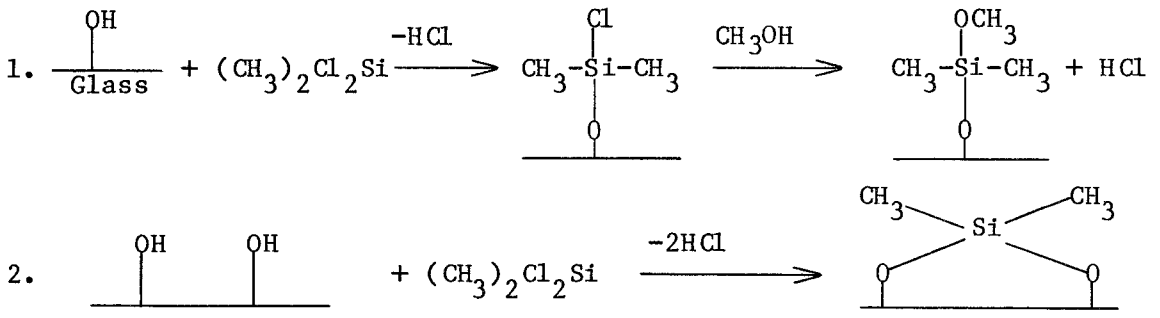
It has been shown that some PAHs are sufficiently volatile to evaporate during collection if prolonged sampling procedures and slow flow rates are used. This is especially true for the lower-molecular-weight hydrocarbons, that is, it is not possible to collect anthrancene, phenanthrene, pyrene or fluoranthene efficiently. It is evident that accuracy requires collecting samples at high flow rates during short periods (about 24 to 48 hr) and analyzing them in the laboratory as soon as possible. Samples were stored in clean aluminum pouches, in the dark at 4°C. The organic fraction of samples remains stable for up to 5 yr if treated in this way (53). In a study on the stability of PAHs collected on glass fiber filters, no tetracyclic and larger PAHs were lost with a 2-hr collection at a flow rate of 1.2 m^3/min followed by 2-hr of filtered air at 1.2 m^3/min (54). The same study showed some tetracyclic PAH loss with 24 hr filtration.

Gas Chromatographic Analysis

A Hewlett-Packard 5730-A gas chromatograph equipped with a dual flame ionization detector and a linear temperature programmer was used. Chromatograms were generated on a 1 mv full scale, 1 cm/min chart speed linear electronic strip chart recorder fitted with an electronic integrator. Nitrogen carrier gas flow was regulated by calibrated Brooks mass flow controllers. Air flow rate was maintained at 240 ml/min and hydrogen at 39 ml/min to optimize FID response (55). In-line screens and molecular sieve traps were placed on all gas lines. The carrier gas line also was fitted with an Oxisorb cartridge (Altech Association). Hydrogen and nitrogen were of >99.99% purity. High temperature, low bleed HT-10 septa (Applied Science) were used with on-column injection. Sample volumes ranging from 1 to 3 μL were introduced using a Hamilton 701-N syringe.

GC Column Silanization and Operation

Before packing a gas chromatographic column, a water aspirator was attached to one end by means of a disposable pipette and tubing. Spectrograde chloroform and acetone (300 ml) were drawn through the columns to remove oil and grease. A 10% solution of dimethyldichlorosilane (DMCS, Supelco) in glass distilled toluene was added and allowed to stand for 10 min. The DMCS was removed, the column rinsed with toluene, filled with methanol and allowed to stand for 10 min. The methanol was removed by suction and the column rinsed with fresh methanol followed by acetone. The reactions for deactivating (silanizing) the surface sites on glass are:



Graphitized ferrules were used on the inlet and outlet ends of each column. Temperatures reported were those on instrument dials. Baseline drift and column bleed were minimized by using a differential electrometer. The packing (3% Dexsil 300 on 60/80 mesh Chromosorb 750, Analabs Inc.) was placed in a stainless steel drying tube, pressurized with 40 psi N_2 and blown into 4.6 m columns. Air in the columns was flushed out for 30 min with N_2 (60 psi maximum flow), followed by conditioning from 70 to 320°C at 4°C/min overnight under N_2 flow. The packing 2.5% BBBT on 100/120 mesh Chromosorb W-HP was prepared from a chloroform solvent slurry and packed in 1.3 m columns. The

columns were conditioned from 190 to 270°C at 1°C/min overnight under maximum N_2 flow. The packing 2.5% BPhBT on 100/120 mesh Chromosorb W-HP was prepared in a boiling dimethyl formamide (DMF) solvent slurry and packed in 1.85 m columns. The columns were conditioned from 160 to 270°C at 1°C/min overnight under maximum N_2 flow. A 1 cm plug of Chromosorb W coated with 4% SE-30 was packed on the column inlet side to retard deterioration. The packing--Ultra-Bond Carbowax-20 M on 100/120 mesh Chromosorb W (RFR Corporation)--was packed into a 1.85 m column. The column was conditioned under maximum N_2 flow, at 200°C overnight and then 240°C for 2 hr.

Several problems occurred in the packing and operation of the Dexsil 300 columns. Extensive bleed and packing separation occurred due to bad batches of the liquid phase supplied by Analabs. New packing was ordered. A large pressure drop was found across the 4.6 m 80/100 mesh columns. During temperature programming, the flow rate dropped to 10 ml/min, causing extensive baseline drift. A change from 80/100 mesh to 60/80 mesh solved this problem. Although the solid support caused no contamination, the highest purity support--Chromosorb 750--was used for the larger mesh size. As a result, 3% Dexsil 300 on 60/80 mesh Chromosorb 750 provided no bleed and no flow decrease during temperature programming.

The stringent requirements of resolution, stationary phase thermal stability and detector sensitivity demanded by the presence of trace levels of closely related, nonvolatile PAHs over Lake Michigan challenge the analytical capabilities of GC. Only the most sensitive GC detector was used, the flame ionization detector (FID). The advantage of the Hewlett-Packard FID was its wide dynamic range (10^7) and sensitivity (5×10^{-12} amps full scale). The FID signal was proportional to the number of carbon atoms in similar oxidation states, providing a quantitatively comparable detector response for most PAHs.

The "solvent flush" injection technique was used to insure that all analytes entered the column. The method involves drawing a plug of solvent into the syringe then the analytical solution. The solvent behind the solution washes the barrel clean, sweeping all material onto the GC column.

Linear PAHs are more readily oxidized than non-linear (angular) PAHs. Therefore, PAHs such as tetracene usually are not found in the atmosphere, although angular compounds such as benz[a]anthracene and chrysene are. The stability of PAHs suspended in the atmosphere depends on molecular structure, the amount of available light and the presence of oxidizing pollutants. For example, half-lives of <1 day to several days have been given for benz[a]pyrene on soot in the presence of sunlight (1). A PAH within the soot probably has a much longer half-life. Smaller PAHs would disappear in sunlight more rapidly than larger ones and summer temperatures would accelerate this loss. The PAHs absorb light between 350 and 450 nm and photooxidize at these wavelengths (1). In order to minimize sample or standard losses, yellow fluorescent lights were installed in the laboratory.

In analyzing PAHs, factors affecting the reproducibility of analysis are: the solvent, adsorbent, laboratory environment and quality of reference compounds. Errors related to these factors cannot be overcome with internal standards and can be avoided only by purifying solvents and working in a clean, ventilated laboratory.

Sixteen PAHs were chosen as standards based on those PAHs most prevalently found in aerosols and known to be carcinogenic.

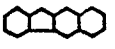
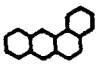
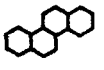
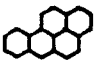
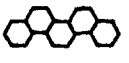
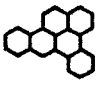
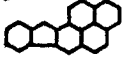
Two solvents--cyclohexane and glass distilled methylene chloride--were used for disolution of PAH standards. It was found that the PAHs were more soluble in methylene chloride than in cyclohexane at the high concentrations (100 ppm) utilized. The high dielectric constant of methylene chloride (8.93) allowed immediate solvation of PAHs whereas several hours at room temperature were required for PAH solution in cyclohexane with a dielectric constant of 2.22.

The PAHs used for qualitative and quantitative analysis were fluorene, anthracene, phenanthrane, fluoranthene, pyrene, 2,3-benzofluorene, triphenylene, benz[a]anthracene, chrysene, benz[a]pyrene, perylene, picene, 1,2,4,5-dibenzpyrene, *o*-phenylene pyrene, benzo[ghi]perylene and coronene. Each compound was weighed (2.5 mg) and dissolved in 25 ml of solvent. Standards of 10 and 1 ppm were made by diluting 1 ml of 100 ppm stock solution to a 10 ml volume and 1 ml of 10 ppm standard to a 10 ml volume. The chemical, physical and biological properties of the PAH standards are listed in Table II-1.

During analysis, organic solvents are evaporated to concentrate the PAHs. The loss of PAHs during this procedure was reduced or avoided by working at pressures above 12 mm Hg and at a water bath temperature <45°C. Contamination and systematic errors were recognized and corrected by including blanks with standards and samples (56).

No universally acceptable quantitative values are available for the precision and accuracy of measurement techniques for PAHs. Accuracy data reported in the literature usually are based on the recovery of added material or the recovery of an added radioactive standard bound in the ambient atmospheric matrix, exactly as the compound of interest, still remains unanswered. The accuracy of PAH analysis depends on collection techniques as well as on analytical methodology. To date no standard reference materials are available for trace level PAHs in natural matrices, thus precluding absolute PAH analysis. It is more meaningful to talk about relative precision and sensitivity. For PAH analysis a sensitivity of $\pm$ 0.1 ng/m^3 and a relative precision of $\pm$ 25% are considered reasonable (54).

Table II-1. Chemical and physical properties and carcinogenicity* of PAHs (1,57,58)

Compound, formula	Structure	Molecular weight	Melting point, °C	Boiling point, °C
Fluorene $C_{13}H_{10}$		166.23	116-117	293-295
Anthracene $C_{14}H_{10}$		178.24	216.2-216.4	340
Phenanthrene $C_{4}H_{10}$		178.24	101	340
Fluoranthene $C_{16}H_{10}$		202.26	110	393
Pyrene $C_{16}H_{10}$		202.26	156	393
2,3-Benzo-fluorene $C_{17}H_{12}$		216.29	?	?
Triphenylene $C_{18}H_{12}$		228.30	199	425
Benz[a]anthracene $C_{18}H_{12}$		228.30	159-161	435
Chrysene $C_{18}H_{12}$		228.30	255-256	448
Benz[a]pyrene $C_{20}H_{12}$		252.32	176.5-179.3	475
Perylene $C_{20}H_{12}$		252.32	273-274	500
Picene $C_{22}H_{14}$		278.36	367-369	518-520
1,2,4,5-Dibenzpyrene $C_{24}H_{14}$		302.38	233-234	?
o-phenylene-pyrene $C_{22}H_{12}$		276.34	162.5-164	?
Benzo(ghi)perylene $C_{22}H_{12}$		276.34	?	?
Coronene $C_{24}H_{12}$		300.36	438-440	525

*Benz[a]pyrene is strongly carcinogenic; benz[a]anthracene and o-phenylene-pyrene are weak carcinogens; chrysene, triphenylene, picene and 1,2,4,5-dibenzpyrene have uncertain or unknown carcinogenicity; the remainder are not carcinogenic.

II-5. RESULTS AND DISCUSSION

PAH Concentrations and Fluxes to Lake Michigan

The environmental role of PAHs in air is of particular concern because they pose a potential health hazard to man. Although this work does not address itself directly to the health aspects of PAHs, it does so indirectly by focusing on sources and types of PAHs emitted, physical and chemical characteristics in the atmosphere, and methods of collection, separation, detection, and quantitation. PAHs are found in small detectable amounts in air, water, and soil. PAH solubility determines the specific aquatic interactions; biodegradation controls the soil interactions; and association with particulate matter dictates the prevailing interaction in air. Many--but not all--PAHs can be attributed to man's activities. However, those that are formed by man originate exclusively from combustion processes. Emitted vapor cools and condenses on particles already prsent or forms small particles of pure condensate. The physical properties that influence PAHs include particle size, surface area, shape and density for which little information exists. The PAHs are subject to the same processes as airborne particles. They are dispersed by turbulence, transported by wind, and removed from the atmosphere by sedimentation, impaction, washout and rainout.

Most previous PAH measurements are for benz[a]pyrene alone. For this reason a broad range of three to seven ring PAHs was examined.

PAHs are either cycled through or stored in the environment. Pathways of cylcing were explored to determine if the lake acts as a sink for aerosol depsotion and where their concentrations are highest.

Table II-2 lists abbreviations for the PAHs found in aerosols over Lake Michigan and the PAHs found in microlayer water. These PAHs were chosen because of their broad range of ring sizes, sources, synergism and biological activity.

Measured values for single filters ranged from 0.1 ng/m^3 for several compounds to 4.2 ng/m^3 for pyrene sampled in late October, 1975 (Table II-3). Average annual airborne BaP concentrations from 1966 to 1970 in urban areas of the United States National Air Sampling Network ranged from a low of 0.2 ng/m^3 over Hawaii to a high of 29.5 ng/m^3 at Altoona, Pennsylvania (54). The same 5 yr study also produced nonurban annual average concentrations of BaP which were generally an order of magnitude less than those for the urban concentrations, i.e., 0.1 to 2.1 ng/m^3 (59). These ranges fit well with overall individual PAH compounds and the values found for BaP over Lake Michigan, 0.3 to 1.8 ng/m^3. It is reasonable to believe that southern Lake Michigan might lie somewhere between an urban and nonurban range, with urban generated aerosols being transported, diluted and deposited to the lake. The BaP values for cities located on Lake Michigan are listed for comparative purposes (Table II-4). If the urban-industrial area on the western shore of

Table II-2. Abbreviations for polycyclic aromatic hydrocarbons

Abbreviation	Chemical name
Fl	Fluorene
Ph	Phenanthrene
An	Anthracene
Flu	Fluoranthene
Blf	2,3 Benzofluorene
Py	Pyrene
BaA	Benz[a]anthracene
Per	Perylene
Tri	Triphenylene
BaP	Benz[a]pyrene
O-Pp	*O*-phenylenepyrene
B[ghi]P	Benz[ghi]perylene

Table II-4. Annual average ambient concentrations (ng/m^3) of BaP

Station	1966	1967	1968	1969	1970
Chicago	3.3	3.0	3.1	3.9	2.0
East Chicago	6.8	5.7	1.9	6.8	5.3
Hammond	3.9	2.5	2.1	3.3	1.7
Grand Rapids	ND	ND	1.4	1.6	0.8

ND is not determined.

Table II-3. PAH concentrations (ng/m^3) for Lake Michigan cruises

Compound	Cruise number											
	II	III	III	IV	V	V	VI	VIII	VIII	XI	XI	XII
Fl	0.51	0.4	0.2	1.2	--	--	2.2	0.6	1.1	2.2	--	1.3
Ph	--	0.2	0.1	0.8	--	0.8	--	0.8	0.4	1.0	--	0.5
An	--	0.1	0.1	0.8	--	0.8	--	0.8	0.4	1.0	--	0.5
Flu	1.7	--	0.2	0.8	1.3	1.2	--	1.3	0.9	1.2	0.8	0.9
Blf	4.1	0.2	0.1	--	2.5	1.5	--	1.3	--	1.1	--	0.9
Py	4.2	0.1	0.1	3.4	--	1.8	0.2	0.4	0.2	0.5	--	0.4
BaA	0.8	0.2	--	0.9	--	--	2.5	0.3	0.2	--	2.2	0.4
Per	--	0.1	0.1	1.7	--	--	--	--	--	--	--	--
Tri	--	0.1	0.1	0.5	--	--	--	0.4	0.2	0.3	--	--
BaP	--	--	--	--	1.8	--	--	--	--	--	--	0.3
O-Pp	--	--	--	--	--	0.9	--	--	--	--	--	--
B[ghi]P	2.0	--	--	1.5	--	--	--	--	--	--	--	--

*Relative precision ± 25% ranging from 1.05 to 0.03 ng/m^3.

the lake was the principal BaP source, the levels shown in Table II-4 could produce those levels found over the lake. No PAH values were found in the literature for on-lake sampling, and no other PAH values besides BaP were found for shoreline comparison.

From samples collected on cruise number III which was conducted in the northern part of the lake, it appears that definite lower concentrations of PAHs exist compared to the southern portion of the lake. This fact correlates well with total suspended particulate matter (TSP) and total organic carbon (TOC) values which showed similar north to south gradients. Concentrations of individual PAHs, collected consecutively, showed similar values. The sources, meteorology and precision of sampling apparently were stable in order to provide this data. A similar trend was seen for samples run simultaneously on cruise number VIII.

Three to six-membered ring systems were detected over Lake Michigan with the bulk of those being contained in 2 to 4-membered ring. It is not clear whether this reflects a natural environmental portioning over the lake or an analytical bias. Small rings elute from a GC column first, yielding sharper peaks. Since the flame ionization detector responds to mass flow rate (dm/dt), the narrower the band the greater the sensitivity, favoring the detection of these low molecular weight compounds.

The major mode of PAH removal from the atmosphere is through chemical reactions (59). These include photooxidation, and reaction with oxidants, nitrogen oxides and sulfur oxides. Reactions of the large PAH ring systems adsorbed on the surface of soot are rapid and sensitive to electrophilic substitution and oxidation (1). Evidence exists that destruction of aromatics on soot is accelerated by photochemical smog (53) and that SO_2, SO_3 and H_2SO_4 react rapidly with PAHs on aerosols (1). Ozone is also known to react with PAHs by oxidation of a double bond, the nuclear ring, or side chains (60). All of these compounds are polar, thus water-soluble, and would not be found in an aromatic enriched fraction. If the larger PAHs are selectively oxidized and removed as polar organics in an analytical workup scheme, this might explain the higher concentrations of the smaller rings found over Lake Michigan. Chemical half-lives may be only hours or days under intense sunlight, whereas in dry unpolluted atmospheric conditions, residence times of particles <5 μm in diameter may exceed 100 hr (61).

These arguments are contrary to what would be expected for collection of PAHs on filters, in that smaller rings are more volatile and the collection process less efficient. Pupp et al. (62) reported losses of volatile PAHs from filters for high equilibrium vapor concentrations and sublimation. If the collection methods do not recover all ambient PAHs, then the atmospheric concentrations would be lower than the true value. It is interesting to note that one of the most volatile PCBs--Aroclor 1242--was found to associate in highest concentration with particulate matter over Lake Michigan versus the vapor phases (63). This fact and the higher levels of small ringed PAHs may be an unexpected--and as yet unexplained--lake effect on organic aerosols and vapor.

Size fractionated PAH sample values are presented in Table II-5. For the May and June cruises similar compounds and similar concentrations were observed on the same stage. No trend was seen for increasing concentrations of PAHs on small-sized particles. However, the limited number of samples

Table II-5. PAH concentrations (ng/m^3) for hi-volume size fractionated samples

	Roger Simons May 17, 1977	Roger Simons June 11, 1977	Roger Simons Aug. 14, 1977*
Stage 1	Fl 2.4 Blf 0.7 Py 3.0 BaA 0.3	Fl 0.5 Flu 0.1	
Stage 2	An 0.5 Ph 0.5 BaA 0.2	Fl 0.5 An 0.3 Ph 0.3 Flu 0.1 Blf 0.2	Fl 0.04 Tri 0.02
Stage 3	Fl 2.0 An 0.3 Ph 0.3	Fl 1.2	
Stage 4	An 0.8 Ph 0.8 Flu 0.9 Blf 0.5 Py 0.3 BaA 0.4	Fl 0.2 An 0.15 Ph 0.15 Flu 0.9 BaA 0.2	
Stage 5	An 0.5 Ph 0.5 Flu 0.4 BaA 0.2	Fl 1.3 Py 0.1	Blf 0.3
Backup stage	Fl 1.1 An 0.4 Ph 0.4 Flu 0.2 BaA 1.2	Fl 1.4 An 0.3 Ph 0.3 Flu 0.3	

*Combination of nine filters.

obtained precludes any conclusions on size fractionation. Approximately 85 to 90% of the PAH content of sized aerosols collected in Toronto were associated with particles <5 μm in diameter for the same size during the summer period (38). It was evident that the dependency of PAH content on size varied significantly with sampling locations, seasons and emission sources. Particles having a diameter <5 μm in the respirable range are most likely to be deposited in the pulmonary region of the respiratory tract. These values agree with those of De Maio and Corn (39) who found particles <5 μm contained more than 75% of the weight of selected PAHs. More recently, Kertes-Saringer (40) reported that from 70 to 90% of the total BaP was associated with aerosols of <1 μm in Bucharest, Hungary.

The concentrations of PAHs in Lake Michigan microlayer water are given in Table II-6. Values range from 0.15 to 0.45 μg/L which are similar to the range (0.05 to 3 μg/L) found for surface waters (64). Fewer PAHs were detected in the microlayer compared to the atmospheric samples, and no PAHs were seen in a 5 L bulk water sample with a 2 ng absolute limit of detection. These concentrations represent--on a relative scale--values 10^6 times greater than the concentrations of PAHs found in air. This might suggest an atmospheric route such as deposition to the lake surface as a source of high PAH levels. Garrett (65) observed organic microlayers are contained in a surface monomolecular slick which was roughly 2×10^{-3} μm thick. In a calculation of the number of monolayers that the mid-lake total organic matter of 4.3 $\mu g/m^3$ would yield, Andren et al. (66) determined that nearly 1000 layers would occur for this value. It was further stated that this calculation suggests the importance of atmospheric deposition. However, the proteinaceous nature of the microlayer also suggests that the lake itself is a source of TOM. From the scanning electron microscope results, it is evident that anthropogenic aerosol input occurs to Lake Michigan. Glassy sphericals found in the air were similar to those found in Lake Michigan microlayer samples (67). The similarity of these particles indicates that they are formed from similar processes such as coal combustion. Annual consumption of coal around southern Lake Michigan is approximately 21×10^6 Tonnes (68), thus fly ash is probably an important source of particles in the microlayer.

Table II-6. PAH concentrations (μg/L) for the Lake Michigan microlayer samples*

Cruise	Roger Simons June 8, 1977	Roger Simons June 19, 1977
Sample 1	Fl 0.35	An 0.45 Ph 0.45
Sample 2	An 0.15 Ph 0.15 Flu 0.35	Flu 0.3

*A bulk water sample of 5 L collected on August 3, 1976 showed no PAHs. Relative precision of ± 25%.

The presence of PAHs in the microlayer cannot be attributed solely to atmospheric input. Certain bacteria and plants produce PAHs as biological bi-products in their normal development (59), e.g., the alga *Chlorella vulgaris* is known to synthesize several PAHs (69). The presence of these tiny plants and animals that live in the microlayer (neuston) could be the main source of high PAH concentrations. Strains of *Chlorella* have been bred that are 80% oil by weight (70). Once the PAHs have been synthesized, *in situ*, they are likely to remain in the microlayer. The proteinaceous wet surfactants in the microlayer which are known to be glycoproteins and proteoglycons (70), effectively trap organic molecules and, due to their hydrophobic nature, might retain PAHs at the air-water interface. Another mechanism for the microlayer enrichment of PAHs might be rising bubbles which are capable of transporting a substantial portion of particulate matter to the surface (71). As wind-induced bubbles move toward the surface, adsorptive scavenging occurs on surface-active particulate organic carbon. Transport rates for particulate organic carbon in the open ocean have proved to be rapid, with the bulk of the collection occurring in the first minute (71). Bubble flotation as a mechanism for PAH concentration in the microlayer may not be a valid argument. Samples were collected under stable atmospheric and lake conditions, minimizing bubble formation.

The appearance of the low molecular weight PAHs may be a reflection of solubility and extraction efficiency. Acheson et al. (72) investigated factors affecting the extraction and analysis of PAHs in water. These included the initial concentration of the PAHs, the presence of suspended solids and prolonged storage of the sample prior to analysis. In general extraction efficiency of pyrene (a lower molecular weight PAH) and benzo[ghi]perylene (a higher molecular weight PAH) were diminished if initial concentrations were low, suspended solids high, and storage prolonged. Suspended solids, however, had a greater effect on benzo[ghi]perylene than on pyrene. This may be due to the higher solubility of small ring systems such as pyrene in water and their more efficient recovery from water by an XAD-2 column. No quantitative information was given on the relative degree of ring system adsorption on the glass wall of the collection flask or chemical or biological degradation. However, it was recommended that extraction should be carried out as soon as possible after sample collection. Because the solubilities of most PAHs in water are extremely low, PAHs often have been assumed to exist entirely on particles. Studies on the partitioning of ^{14}C-anthracene between dissolved and particulate phases in natural waters showed that a significant fraction--35 to 85%--is in solution (73). The fractionation also was found to be highly dependent on yeast cell concentration (used as a model for suspended organic matter) and suspended organic solids encountered in natural waters but not as dependent on adsorption to mineral surfaces. This soluble fraction of the low molecular weight anthracene may explain the frequency of detection of this compound (Table II-3).

The inconclusive results of size-fractionated PAHs for this work led to the choice of a particle size of 1 μm as the most representative value. This was done on the basis of Kertesz-Saringer's (40) investigation of the total BaP concentration and the aerosol size it was associated with. This value is probably a liberal estimate since BaP was correlated to particles <1 μm. Deposition velocities (74) are almost the same for particles between 0.1 and 1 μm, thus PAH deposition should not be unduly distorted by small particles.

For this particle diameter and a mean wind velocity for the Lake Michigan cruises of 4.7 m/sec, the deposition velocity is 2×10^{-2} cm/sec. The V_d for field measurements (75) of 1 μm diameter particles and a wind speed of 4.7 m/sec was determined to be 32×10^{-2} cm/sec. The two values were used as a range to bracket those depositions which might be seen for environmental PAH aerosols. For dry deposition, the mean concentrations of individual compounds for all cruises was selected. The dry flux of individual PAH compounds is listed in Table II-7. The flux to the northern sector of Lake Michigan is less than the flux to the southern sector for all compounds and generally the range of concentrations was an order of magnitude lower than dry TOC flux to the respective parts of Lake Michigan. The highest flux occurred for fluorene in the northern part of the lake and the highest fluxes were seen for benzo[ghi]perylene, perylene, 2,3-benzofluorene and fluorene in the southern part of the lake. High levels of benz[a]anthracene were seen for northern and southern parts of the lake and the potent carcinogen benz[a]pyrene also was found at relatively high levels in the southern third of Lake Michigan.

Wet PAH deposition was calculated for a particle of mass median diameter of 1.0 μm. The scavenging ratio for this size is 160 (76) and rainfall to the lake was taken as 75.2 cm/yr (77).

The wet flux of individual PAH compounds to the southern and northern parts of Lake Michigan is given in Table II-8. The values are virtually the same for the upper range of dry deposition and are similar to the trend seen for total suspended paticulate matter.

Bubble Ejection of PAHs from Lake Michigan Microlayer Water

In an attempt to understand the importance of the return of PAHs to the atmosphere, bubble ejection was explored as a possible source for atmospheric PAHs. The surface area of the ocean was taken as 3.61×10^{14} m^2 (78), the surface area of Lake Michigan as 5.8×10^{10} m^2 (79) and a range for the bubble ejected organic carbon transported from the ocean to the atmosphere from 5×10^{13} g/yr to 5×10^{14} g/yr (80). Scaling these values for the amount of organic matter (1.5 x organic carbon) (81), and knowing the surface area of Lake Michigan, a range from 1.2×10^{10} g/yr to 1.2×10^{11} g/yr of bubble ejected organic matter released from the microlayer can be calculated. This assumes that the number of bubbles formed in the open ocean is the same as the number of bubbles produced per unit area of Lake Michigan, and that the organic carbon and the PAH concentrations in the microlayer are the same as those ejected into the air. As the bubble bursts, it peals off the microlayer (70). A microlayer thickness of 300 μm was assumed, and the calculated organic matter in the microlayer was determined to be from 0.69 to 6.9 g/L. Using the organic matter concentrations, the ejected organic matter in air and the mean concentrations of PAHs in the microlayer (Table II-6), the bubble ejected flux from water to air for selected PAHs is: fluorene--6.1 kg/yr; anthracene--5.2 kg/yr; phenanthrene--5.2 kg/yr; and fluoranthene--5.7 kg/yr. This hardly would be significant compared to the 10^3 kg/yr flux of wet and dry PAH deposition from air to water. However, the organic matter flux from water to air calculated to be from 1.2×10^7 kg/yr to 1.2×10^8 kg/yr more than exceeds that of the organic matter dry flux from the air to the water at

Table II-7. Dry flux of polycyclic aromatic hydrocarbons to Lake Michigan

Compound	Northern 2/3 of Lake, kg/yr x 10^2	Southern 1/3 of Lake, kg/yr x 10^2
Fl	0.72 - 11.5	1.6 - 25
Ph	0.36 - 5.8	0.9 - 14
An	0.24 - 3.8	0.9 - 14
Flu	0.48 - 7.7	1.4 - 22
Blf	0.36 - 5.8	2.3 - 36
Py	0.24 - 3.8	1.7 - 28
BaA	0.48 - 7.7	1.3 - 20
Per	0.24 - 3.8	2.1 - 33
Tri	0.24 - 3.8	0.43 - 6.8
BaP	---	1.2 - 19
O-Pp	---	1.1 - 17
B[ghi]P	---	2.8 - 44

Table II-8. Wet flux of polycyclic aromatic hydrocarbons to Lake Michigan

Compound	Northern 2/3 of Lake, kg/yr x 10^2	Southern 1/3 of Lake, kg/yr x 10^2
Fl	1.1	2.4
Ph	0.57	1.3
An	0.37	1.3
Flu	0.73	2.0
Blf	0.57	3.5
Py	0.37	2.6
BaA	0.73	1.8
Per	0.37	3.1
Tri	0.37	0.65
BaP	--	1.8
O-Pp	--	1.7
B[ghi]P	--	3.3

13.3×10^6 kg/yr and would become important during high wind conditions when numerous bubbles are formed.

Volatilization of PAHs from Lake Michigan

The approximate rates of evaporation of low water soluble PAHs were examined as a route for entrance back to the atmosphere and to compare this with the deposition flux from air to water. It has been shown that PAHs have high activity coefficients in water resulting in a high evaporation rate (82).

The theoretical basis for mass transfer across the air-water interface is:

$$K_L = \frac{Hk_g k_\ell}{Hk_g + k_\ell} \qquad (1)$$

where

K_L is overall mass transfer coefficient

H is Henry's Law constant, a distribution coefficient (mole/L_{air}: mole/L_{water})

k_g is gas phase mass transfer, the rate transport away from the air interface (m/hr)

K_ℓ is liquid phase mass transfer, the rate of transport to the water interface (m/hr)

The gas phase and liquid phase mass transfer are affected by mixing and temperature. Wind influences kg, water turbulence k_ℓ and temperature influences H most significantly, although each environmental property affects the other parameter properties to some degree.

In order to take the action of wind and water velocities into account, the equations of Southworth (83) were utilized:

$$k_g = 1137.5\ (V_{wind} + V_{current})\left(\frac{18}{\text{mol. wt. PAH}}\right)^{1/2} \qquad (2)$$

$$k_\ell = 23.51\frac{V_{current}^{0.969}}{R^{0.673}}\left(\frac{32}{\text{mol. wt. PAH}}\right)^{1/2} \qquad (3)$$

for

$V_{wind} \leq 1.9$ m/sec

and

$$k_\ell = 23.51 \frac{V_{current}^{0.969}}{R^{0.673}} \left(\frac{32}{\text{mol. wt. PAH}}\right)^{1/2} \left(e^{0.526(V_{wind}-1)}\right) \qquad (4)$$

where

V_{wind} is wind velocity (m/sec)

$V_{current}$ is current velocity (m/sec)

R is mixing depth (m)

The laboratory estimates of Henry's Law coefficient and estimates based on the ratio of equilibrium vapor pressure to aqueous solubility were chosen for anthracene (2.66) and benz[a]pyrene (2.1×10^{-5}) (83). These PAHs were selected to cover a wide molecular weight range with available coefficients. The mean wind speed of 4.7 m/sec for Lake Michigan was used and a current velocity at 2% of this wind speed or 0.094 m/sec was selected on the basis of the Hutchinson (84) discussion of wind generated currents. A mixing depth of 1 m was assumed as the depth at which instantaneous mixing equilibria were obtained.

On the basis of the above values, equations and assumptions, coefficients were calculated for anthracene and benz[a]pyrene. For anthracene, the mass transfer results were: kg = 1732 cm/hr; k_ℓ = 1.04 cm/hr; and K_L = 1.04 cm/hr; and for benz[a]pyrene k_g = 1456 cm/hr; k_ℓ = 0.87 cm/hr; and K_L = 2.95×10^{-2} cm/hr. The mass transfer rates for the two compounds are liquid phase controlled, thus factors directly affecting k_ℓ, such as current velocity dramatically affect volatilization. Overall mass transfer follows the expected trend, with the highest rate for low molecular weight anthracene and the lowest rate for higher molecular weight (five aromatic rings) benz[a]pyrene.

The mass flux, N_i, of PAHs across a phase boundary necessary to predict a steady state exchange rate of these compounds between the atmosphere and the water body can be written in terms of the bulk liquid concentration and the partial pressure in the atmosphere:

$$N_i = K_{iL}(C_i - P_i/H_i) \qquad (5)$$

where

N_i is mass flux (mol/m^2-hr)

K_{iL} is overall liquid transfer coefficient (m/hr)

C_i is bulk liquid concentration (mol/m^3)

H_i is Henry's Law coefficient (atm m^3/mol)

P_i is $C_i P_{is}/C_{is}$

P_{is} is vapor pressure (atm)

C_{is} is solubility in water (mol/m^3)

Substituting the calculated K_L, the Henry's Law coefficient and 0.3 μg/L or 1.68×10^{-6} mole/m^3 (Table II-6) as an estimate of bulk liquid concentration for anthracene, the flux from Lake Michigan to the atmosphere was determined. The conversion from Southworth's (83) Henry's Law constants was made by making a density correction and multiplying by RT for the correct units:

$$833 \cdot H \cdot RT \qquad (6)$$

where

T is absolute temperature (298°K)

R is gas constant (8.2×10^{-5} atm m^3/mol °K)

The Henry's Law constant was 54.1 atm m^3/mole for anthracene and the equilibrium partial pressure for anthracene, assuming a vapor pressure of 1 mm or 1.3×10^{-13} atm at 25°C and a solubility of 4.1×10^{-4}/mole m^3 (85), was 5.3×10^{-6} atm. The calculated flux of anthracene was -1.3×10^{-4} mole/m^2-hr, indicating that no anthracene is leaving the lake by volatilization, although the flux is in the opposite direction from atmospheric vapor to the lake. No calculation of flux was made for benz[a]pyrene due to the lack of solubility and vapor pressure data, however, it is unlikely that this higher molecular weight compound would volatilize to a greater extent than anthracene. It appears from these approximations that volatilization is not a significant flux and that wet and dry deposition dominate input with little return to the atmosphere from the lake.

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16. ABSTRACT

The air over Lake Michigan was sampled during 1977 to develop a collection method for PCBs and obtain data about their atmospheric transport and dry deposition onto the lake. A resin, XAD-2, was the most efficient collection medium for PCB vapor and was incorporated into standard high volume air samples for the collection of particulate and vapor phase PCBs. PCB concentrations in air samples taken over Lake Michigan were lower than those taken from urban areas; i.e., Milwaukee. Aroclors 1242 and 1254 were the main components of vapor phase PCBs while in some instances the particulate phase PCBs contained Aroclor 1260. The particulate phase PCBs over Lake Michigan contained a larger percentage of the more volatile mixtures than those reported in urban areas such as Chicago and Milwaukee. PCBs tend to associate with particulates 0.002 to 0.1 um in diameter. The amount and organic carbon content of the particulate phase appear to control vaporization and revolatilization of PCBs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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