MEASUREMENT AND PARTITIONING OF PERSISTENT ORGANIC POLLUTANTS IN THE ENVIRONMENT: APPLICATION OF OCTANOL-AIR PARTITION COEFFICIENTS

by

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A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy
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ABSTRACT

This thesis considers the measurement and partitioning of several classes of persistent organic pollutants (POPs) - namely, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polycyclic aromatic hydrocarbons (PAHs). Octanol-air partition coeffcients (K_{OA}) were measured for 18 PCBs, 24 PCNs, and 4 PAHs over a range of environmentally relevant temperatures. The results show that in all cases the value of K_{OA} varied log-linearly with the inverse absolute temperature and that in general, the enthalpy associated with the transition from octanol to air, ΔH_{OA}, was similar to the enthalpy of vaporization, ΔH_{vap}. Greater partitioning was observed for coplanar and mono-ortho PCBs.

The utility of K_{OA} as a particle-gas partitioning descriptor was tested using results from Chicago air samples. The particle-gas partition coefficient, K_P, was calculated and plotted against K_{OA} and against the subcooled liquid vapor pressure, p^o_L. Log-log plots of K_P versus p^o_L showed enrichment for the coplanar PCBs and PAHs. This enrichment was resolved by K_{OA} for the coplanar PCBs but only partially resolved for the PAHs. A K_{OA}-based absorption model of particle-gas partitioning was compared with the Junge-Pankow adsorption model. The K_{OA} model provided a better fit for PCBs but not PAHs, which were underestimated. An advantage of the K_{OA} model is that it only requires knowledge K_{OA} and the fraction of organic matter on the particle which are both easily measured.

The Chicago field study led to the investigation of a new compound class, PCNs. A method was developed for quantifying PCNs based on the FID response of individual congeners in Halowax 1014, a technical mixture of 2 to 8-Cl congeners. PCNs were quantified in air samples from Chicago and three Arctic locations - a cruise track of the Eastern Arctic Ocean, Alert (Canada), and Dunai Island (Russia). The results show that PCNs contribute significantly to dioxin-type toxicity in air and merit further study.

A review is made of the transport processes, concentrations, and implications of organochlorine contamination of the Canadian Arctic. Speculations are made regarding the relationships of global warming, physical chemistry of the compounds, and future trends of contaminants.

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1. INTRODUCTION

1.1 Background

Persistent organic pollutants (POPs) include a broad range of anthropogenic chemicals with varying structures and properties. Prolonged exposure and uptake to some compounds may result in a variety of negative effects. One common outcome is the impairment of immune system response which makes the affected organism more susceptible to disease. Several classes of POPs are also classified as endocrine disrupters because they are able to mimic or block the action of natural, biological hormones. In humans and other species, this may ultimately affect reproductive system viability and hence species continuity (Patlak, 1996; The Washington Post, 1994).

From a health standpoint, the most important or hazardous POPs are those which are toxic, persistent in the environment, and bioaccumulative. Chemicals which fall into this category include the polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), the organochlorine pesticides (e.g. DDT, toxaphene, hexachlorocyclohexane) and polycyclic aromatic hydrocarbons (PAHs). Many of these compounds are lipophilic or "fat-loving" in nature, and partition strongly into the fat tissues of an organism. Octanol is used as a surrogate for fat and the octanol-water partition coefficient (K_{OW}) is the most commonly used descriptor for assessing the bioaccumulation potential of a compound.

In addition to understanding the biological effects, it is also important to consider a chemical's fate in the environment; where is it released, what physical chemical processes govern its transport, and where in the environment will it accumulate? The answers to questions such as these require the assimilation of a vast spectrum of information and ultimately lead to models of chemical fate. Environmental models require information on the media through which the chemical is being transported (air, aerosols, soil, water and sediment), meteorological conditions (rain rate, wind speed and temperature) and physical chemical data (the "solubility" in air, water, and octanol). With this information, models can be developed for describing inter-media

The transport of chemical through the globe is often compared to chromatography (Risebrough, 1990; Wania and Mackay, 1996) where the air is the mobile phase and terrestrial "lipids" represent the stationary phase. These "lipid" phases include the waxy cuticle on vegetation, the organic matter in soil and the oily film which coats atmospheric particulate matter - these are sinks for lipophilic chemicals. Because octanol is a surrogate for organic or "lipid" phases, the octanol-air partition coefficient (K_{OA}) is recognized as a good descriptor for atmosphere-terrestrial lipid exchange (Paterson et al., 1991; Simonich and Hites, 1995). The temperature dependence of K_{OA} may explain the migration of a chemical from warmer regions where it is released to colder, "polar sinks" where it accumulates.

This thesis will consider the application of K_{OA} to explain some aspects of this transport. Measurements are presented of K_{OA} as a function of temperature for PCBs, PAHs and PCNs (Fig. 1.1, Fig. 1.2, and Table 1) **(papers I & II)**. These results are the first measurements of K_{OA} for these chemicals. The data are then used to test a K_{OA}-based absorption model of particle-gas partitioning against field data from Chicago for these three compound classes **(paper III)**. Accurate models of particle-gas partitioning are essential for describing the long-range transport and particle deposition of semi-volatile chemicals (Bidleman, 1988).

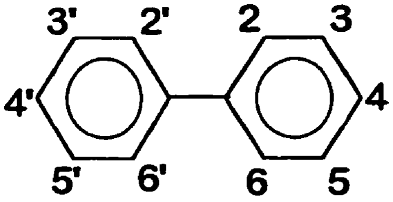
Another aspect of this thesis is the measurement of air concentrations of a new compound class - PCNs **(papers III, IV & V)**. PCNs are "new" in the sense that they have not been routinely monitored in the environment, and measurements of PCN concentrations in air are scarce. Their commercial production began at the beginning of this century when they were primarily used for impregnating wood, paper and textiles but were later replaced by PCBs due to exposure-related health effects (Järnberg, 1997). Despite their toxicity, PCNs continued to be produced to a limited extent and their use is still not prohibited in most countries. It is estimated that the cumulative world production of PCNs is about 750 000 metric tons, approximately 10% of the total PCBs produced (Crookes and Howe, 1993). Because some PCN congeners have dioxin-like toxicity and are detected in biota, PCNs are gaining recognition as a class of chemicals which deserves more scrutiny. A method for quantifying PCNs in air samples was developed and applied to samples collected in Chicago. Air samples were also collected on a cruise track of the Eastern Arctic Ocean **(paper V)** and analyzed for PCNs and coplanar PCBs, the most potent PCBs. These are the first reported air concentrations of PCN and coplanar PCBs in Arctic air. Measurements such as these can be used to investigate the transport of toxic chemicals to polar regions and better assess the toxic load to the Arctic.

The last section **(paper VI)** is a review of the processes and implications associated with POP contamination of the Arctic. Speculations are made regarding future trends, in particular the possible effects of climate change on the global contaminant cycling. Air-surface partition descriptors such as K_{OA} and p^o_L, and their variation with temperature, are highlighted as the most important variables for making these sorts of predictions.

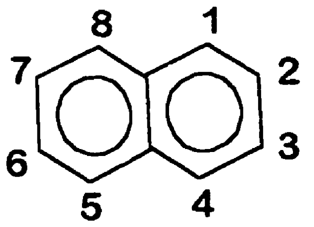
Table 1.1 Properties of selected PCBs, PCNs, and PAHs at 25 °C[a].

compound	Cl position	mol. wt. (g/mol)	T_{melt} (°C)	aqueous sol. (g/m^3)	Log K_{OW}	vap. press. (Pa)	Log K_{OA}[b]
PCBs							
PCB-15	4,4'	223.1	149	0.06	5.3	0.0048	7.66
PCB-77	3,3',4,4'	292	180	0.001	6.5	0.000059	9.71
PCB-171	2,2',3,3',4,4',5	395.3	110	0.002	6.7	0.000027	10.25
PCNs[c]							
PCN-21	1,3,7	231.5	113	0.065	5.35	N.R.	7.92
PCN-52	1,2,3,5,7	300.5	171	N.R.	6.87	N.R.	9.51
PCN-64	1,2,3,4,5,7	335	165	N.R.	7.58	N.R.	10.79
PAHs							
fluorene	$C_{13}H_{10}$	166.2	116	1.90	4.18	0.09	6.79
phenanthrene	$C_{14}H_{10}$	178.2	101	1.10	4.57	0.02	7.57
pyrene	$C_{16}H_{10}$	202.3	156	0.132	5.18	0.0006	8.80
fluoranthene	$C_{16}H_{10}$	202.3	111	0.26	5.22	0.00123	8.88
1-Octanol[d]		130.2	-16.7	390[e]	---	---	---

[a] Mackay et al., 1991, 1992; [b] K_{OA} values from Paper I / II; [c] PCN properties from Crookes and Howe, 1993; [d] Weast, 1980; [e] Arbuckle, 1983 . N.R. = not reported.

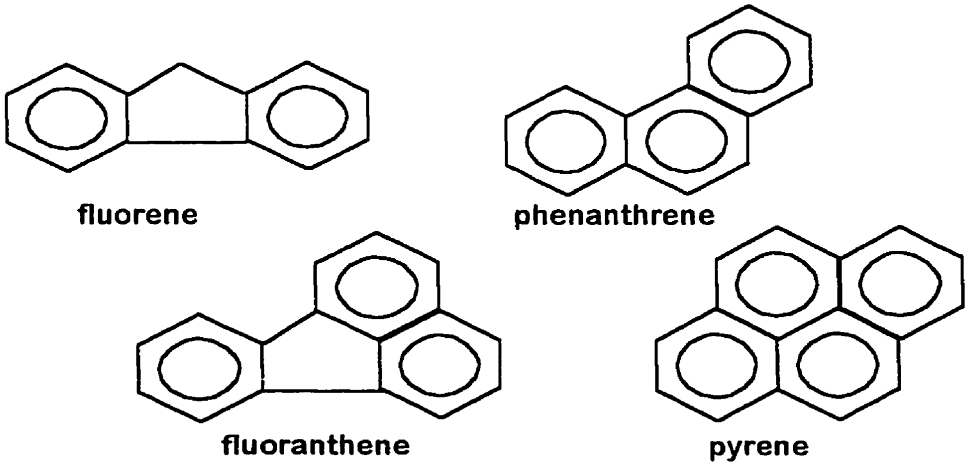


- total global production of PCBs is estimated at 1.5 million tons.
- PCBs are stable molecules and have been mainly used as dielectric fluids.
- although they are no longer commercially produced, they still occur in electrical equipment. Landfills are believed to be the major emission source of PCBs (Harrad et al., 1994).
- the most toxic congeners are the coplanar PCBs, which have no Cl atoms in ortho positions (2,2',6,6') allowing the molecule to achieve a near planar configuration.



- total global production of PCNs is estimated to be approximatley 10% of PCBs. PCNs were produced as technical mixtures which contained varying amounts of chlorine. Kopperscompany in the U.S. which produced Halowaxes, was the largest producer of PCNs. They were produced as Seekay waxes (U.K.) and Nibren waxes (Ger.) (Crookes and Howe, 1993).
- like PCBs, PCNs are chemically and thermally stable and were produced commercially since the early 1900's, before PCBs. Despite their dioxin-like toxicity, PCNs are still not banned.
- PCNs were used for a variety of purposes including dielectric fluids, wire insulators, cutting oils, and as wood preservatives.
-congeners 66 and 67 (1,2,3,4,6,7 and 1,2,3,5,6,7) are believed to be the most toxic and bioaccumulating of the PCNs.

Fig 1.1 Structures and background information for PCBs and PCNs.



- formed as byproducts in combustion processes, PAH are suspected carcinogens and have recently been shown to exhibit estrogenic and /or antiestrogenic activity (Santodonato, 1997).
- mobile combustion sources (cars etc) are believed to be the the major emission source of PAHs in urban areas. Other important sources include residential heating, industrial processes and waste incineration (Wild and Jones, 1995).

Fig. 1.2 Structures and background information for PAHs.

1.2 Overview of Papers

Papers I and II

Harner, T. and Bidleman, T. F. "Measurements of octanol-air partition coefficients for polychlorinated biphenyls". *J. Chem. Eng. Data* **1996**, 41, 895-899.

Harner T. and Bidleman, T. F. "Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs)". *J. Chem. Eng. Data* (accepted).

Temperature dependent values of K_{OA} are presented for three classes semi-volatile compounds - PCBs, PAHs, and PCNs. The apparatus and experimental method for measuring K_{OA} are a modification of the original method developed by this researcher as part of a Master thesis project (Harner and Mackay, 1995). The new system has different configurations for the octanol and the generator column. The adsorbent trap also has a increased dimensions and uses C_8-bonded silica resin as opposed to TENAX GC resin used in the previous design. Instead of thermally desorbing the traps as was done before, the C_8 traps are extracted with solvent. This avoids concerns regarding desorption efficiency and has the advantage that several analyses can be performed on the same sample.

Essentially, K_{OA} is the ratio of the solute concentration in octanol to the concentration in air when the octanol-air system is at equilibrium, i.e. $K_{OA} = C_{octanol}/C_{air}$. It is also possible to calculate K_{OA} as the ratio of the air-water partition coefficient, K_{AW} (K_{AW}=H/RT , where H is the Henry's law constant, R is the ideal gas constant, and T is absolute temperature) and the octanol-water partition coefficient, K_{OW}. A comparison of measured and calculated values shows that there is a tendency for the calculated values to underpredict K_{OA} (Harner and Mackay, 1996 and Paper II). It is therefore desirable to measure K_{OA} directly.

Paper I summarizes K_{OA} measurements for 18 PCB congeners over the temperature range -10 to +30 °C. Regression equations are presented which allow K_{OA} to be estimated for other congeners. In plots of log K_{OA} against log p^o_L (where p^o_L is the subcooled liquid vapor pressure determined by the GC retention method, Falconer and Bidleman, 1994) the mono- and non-ortho chlorinated PCB congeners show greater partitioning than multi-ortho congeners of the same vapor pressure. These results are consistent with field data from Falconer et al. (1995) which showed particle phase enrichments for coplanar PCBs in urban aerosols. This suggests that partitioning onto aerosols may occur via an absorptive mechanism in which chemical is exchanged between air and an organic, octanol-like, film which coats aerosols (Shah et al., 1986; Cotham and Bidleman, 1995) (see paper III).

Similar measurements are reported in Paper II for four PAHs and twenty-four PCNs. The enthalpy of transition from octanol to air, ΔH_O^A for PAHs is calculated from the slope of the log K_{OA} vs 1/T plots. Values are in the same range as those reported for PCBs in Paper I and agree with the temperature coefficient associated with vegetation-atmosphere partitioning (Q_D) for PAHs (Simonich and Hites, 1996).

Paper II highlights the difficulties with using p^o_L as a fitting parameter. The problem lies in the fact that the sub-cooled liquid is a hypothetical state for most semi-volatile compounds which are usually solids at ambient temperatures. Therefore p^o_L cannot be measured directly but must be estimated either from solid phase vapor pressures and entropy of fusion or by the GC retention method (Hinckley et al., 1990). It is no surprise therefore that literature values of p^o_L vary sometimes by more than an order of magnitude.

In light of the difficulties with p^o_L and the fact that atmosphere-lipid partitioning likely occurs via an absorptive rather than an adsorptive mechanism, K_{OA} may be a more suitable descriptor. Paper III tests this hypothesis by applying K_{OA} for describing particle-gas partitioning of semi-volatile compounds.

Paper III

Harner, T. and Bidleman, T. F. "Octanol-air partition coefficient (K_{OA}) for describing particle-gas partitioning of aromatic compounds in urban air". *Environ. Sci. Technol.* (submitted).

This paper reports ambient air concentrations and particle/gas partitioning properties for three classes of compounds PCBs, PAHs, and PCNs in urban air. Samples were collected in Chicago in February 1995 using a high volume train consisting of two glass fibre filters (GFFs) for collecting particles followed by two polyurethane foam plugs (PUFs) to trap gas-phase compounds. A total of 15 - 12h samples were collected with average volumes of approximately 350 m^3. Air concentrations for PCBs and PAHs were consistent with previous studies in Chicago. Results for PCNs are discussed in detail in Paper IV.

The particle/gas partitioning of PCBs, PAHs, and PCNs to aerosols was investigated and modeled according to the adsorption (Junge-Pankow) approach, which utilizes p^o_L as a fitting parameter (Pankow, 1987), and the K_{OA}-based absorption model approach. The results favored the use of the K_{OA} model for PCBs because it was able to resolve differences between the ortho-chlorine classes of PCBs which correlations against p^o_L were not able to explain. Although the Junge-Pankow model provided a better fit for PAHs, neither model was able to explain the particle phase enrichment observed for PAHs. It was hypothesized that combustion aerosols may contain a bound PAH portion which is not free to exchange with ambient air, and that this may account for greater than expected particulate fractions. Alternatively, it may be due to slow re-equilibration of PAH-rich combustion aerosols as they are diluted in ambient air.

In addition to providing a comprehensive and versatile model of particle-gas partitioning, the Chicago field study also led to the investigation of a new compound class. The first ever reported air concentrations of PCN congeners are reported in paper IV.

Paper IV

Harner, T. and Bidleman, T. F. "Polychlorinated naphthalenes in urban air" *Atmos. Environ.* **1997**, 31, 4009-4016.

Because they are thermally and chemically stable, PCNs have historically been used for many of the same purposes as PCBs. They are also released in incinerator emissions (Oehme et al., 1987). More attention has been directed towards this compound class in recent years as a result of studies reporting their dioxin-like toxicity (Hanberg et al., 1990) and their presence in humans (Williams et al., 1993) and biota (Järnberg et al., 1993).

In Paper IV, a method is developed for quantifying PCNs based on Halowax 1014, a technical mixture of 3-Cl to 8-Cl congeners. The flame ionization detection (FID) response is used to assign mass contributions to the components of the technical mixture. A separation scheme utilizing silicic acid columns, and activated carbon columns is used to separate PCNs from other contaminant classes before quantifying them by gas chromatography, negative ion mass spectrometry (GC-NIMS).

The results showed that in Chicago, ΣPCN = 68 pg/m^3 (n=15) which was about five times lower than ΣPCB values. However, despite their lower concentrations PCNs are believed to have similar toxicity contribution as the PCBs. The TCDD (2,3,7,8-tetrachlorodibenzodioxin) toxic equivalent (TEQ) value for one of the PCN congeners (the only reported TEF for PCNs) in Chicago air was on the same order of magnitude as values for the coplanar PCBs, the most potent of the PCBs.

This paper enforces the idea that we should not only focus our attention to the most abundant pollutants but also the most toxicologically active. It is important that more work be carried out with PCNs and coplanar PCBs - more measurements in air and in biota, especially in ecologically sensitive areas such as the Arctic. Concentrations of PCNs and coplanar PCBs in arctic air is the topic of paper V.

Paper V

Harner, T., Bidleman, T. F., Halsall, C., Kylin, H. and W. Strachan "Polychlorinated naphthalenes and coplanar PCBs in arctic air" (submitted to ES&T)

For the first time, concentrations of PCNs and coplanar PCBs are reported in arctic air. Samples were collected on a cruise track of the eastern Arctic Ocean and two land-based monitoring stations in Alert (NWT, Canada) and Dunai Island (Russia).

Average concentrations (pg/m^3) of PCNs at the three arctic locations agreed well: 12 pg/m^3 for the eastern arctic ocean (n=13); 6 pg/m^3 for Alert (n=3) and 8 pg/m^3 for Dunai (n=3). Similar congener profiles were observed at the three locations with the 3-Cl homolog contributing between 55-70% of the total PCN mass.

Concentrations of coplanar PCBs (congeners -81, -77, and -126) were more variable at the three locations. Air concentrations (pg/m^3) were on the order of 10-20 for congeners -81 and -126 and on the order of 20-300 for congener -77.

The results showed the dioxin-like toxicity of one of the PCN congeners is on the same order of magnitude as the coplanar PCBs. It is concluded that PCNs are an environmental hazard and there is a definite need to assess the TCDD toxicity for more individual PCN congeners and technical mixtures.

Paper VI

Harner, T. "Organochlorine contamination of the Canadian arctic, and speculation on future trends" *Int. J. Environment and Pollution* **1997**, 8,1/2, 51-73.

This paper reviews the current state of knowledge concerning organochlorine contamination of the Canadian Arctic. The primary pathways by which contaminants migrate to the Arctic (episodic transport and global distillation) are discussed in relation to physical chemical descriptors and the role of temperature.

The sobering message which is presented is that the Arctic ecosystem, now contaminated after decades of careless emissions of POPs, will likely remain contaminated for several more decades despite recent reductions in emissions. The question that now needs to be addressed is, how will the ecosystem be purged of contaminants and on what time scale? The answer has serious implications for the health and welfare of marine mammals and indigenous people who are most affected.

1.3 Conclusion

The octanol-air partition coefficient (K_{OA}) was measured for 18 PCBs, 24 PCNs, and 4 PAHs over environmentally relevant temperatures in the range -10 to +50 °C. The PAH and PCN results are the first reported measurements of K_{OA} for these compound classes. For all measurments, log K_{OA} varied log-linearly with inverse absolute temperature. The enthalpy of octanol-to-air phase transfer, ΔH_{O}^{A}, was in the range 65-90 kJ/mol with larger values for the more chlorinated PCB and PCN congeners. These values were similar to the enthalpy of vaporization (ΔH_{vap}) and the temperature coefficient of vegetation-air partitioning (Q_D) for PAHs.

In log-log plots of K_{OA} against log p^{o}_{L} (subcooled liquid vapour pressure) there was enrichment for the mono- and non-ortho PCBs above multi-ortho PCBs of the same vapor pressure. A similar effect was reported in laboratory experiments of particle-gas partitioning (Falconer et al., 1995) which suggested using K_{OA} as particle-gas partitioning descriptor.

The feasibility of using K_{OA} as a particle/gas partitioning descriptor was tested using field data from Chicago. A comparison was made between two models of particle-gas partitioning - the Junge-Pankow adsorption model and the K_{OA} absorption model. The results indicated that the K_{OA}-based model was a good alternative and perhaps preferred to the adsorption model. It was able to resolve differences between different ortho-classes of PCBs and also explained the partitioning for PCNs. Another advantage of the K_{OA} model is that it only requires knowledge of K_{OA} and the fraction of organic matter on the particle which are both easily measured. Neither model was able to explain the enrichment of PAHs relative to PCBs but it is hypothesized that this may be due to a bound fraction of PAHs which are not exchangeable with the surrounding air.

A method was developed for quantifying PCNs in air samples and was used to determine, for the first time, concentrations of individual PCN congeners in the Chicago samples. Levels of PCNs in Chicago (ΣPCN=68 pg/m^3) were approximately 20% of ΣPCB. The 2,3,7,8-tetrachlorodibenzodioxin toxic equivalent was determined for PCN-66/67 (thought to be the most toxic PCN congener) and was of the same order of magnitude as the coplanar PCBs. PCNs and coplanar PCBs were also quantified in arctic air samples from three locations; a cruise of the eastern arctic ocean, and sampling stations at Alert (Canada) and Dunai Island (Russia). In arctic air, ΣPCN was in the range 5-10 pg/m^3, again about 20% of the reported ΣPCB. The TEQ for PCN-66/67 was found to be similar to the value for PCB-77 and about 1-4% of the value for PCB-126. These results indicate that PCNs are an important compound class which require further study. In particular, more information is needed regarding their toxicity, physical chemical properties, and distribution in the environment.

Lastly, the issue of organochlorine contamination of the Arctic is reviewed. Mechanisms and other factors involved in the transport of contaminants through the globe are discussed and the octanol-air partition coefficient is highlighted as an important descriptor of a chemical's "atmospheric transport potential". Speculations are made regarding the future trends of contaminants and the effect of global warming on the cycling of contaminants.

In closing, environmental chemistry is a relatively new and expanding field of science. In its evolution come new opinions, new concerns, and new questions. Some of these ideas have been manifested in this work and will hopefully lead to an improved understanding of contaminant partitioning and transport in the environment.

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Paper I: Measurements of Octanol-Air Partition Coefficients for Polychlorinated Biphenyls

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Abstract

The octanol-air partition coefficient, K_{OA}, is measured for 15 polychlorinated biphenyls (PCBs) over the temperature range -10 °C to +30 °C using a generator column method. The enthalpy of phase change from octanol to air, $\Delta_O^A H$, is calculated for 18 PCBs and ranges from 66 to 90 kJ/mol. Enthalpy of dissolution of the liquid phase PCB in octanol, $\Delta_{SOL} H$, calculated as $\Delta_{VAP} H - \Delta_O^A H$, has a mean value of 6.6 kJ/mol (n=18) and there is no correlation of $\Delta_{SOL} H$ with homolog group or number of ortho substituted chlorine atoms. Results show that K_{OA} values increase within a homolog group for congeners having fewer ortho chlorine atoms. A $\log_{10}$-$\log_{10}$ correlation of K_{OA} against liquid-phase vapor pressure (p^o_L) shows enhanced partitioning into octanol for mono- and non-ortho congeners. Separate regressions for non/mono-ortho and multi-ortho groups allow K_{OA} to be estimated for other congeners.

Introduction

The octanol-air partition coefficient, K_{OA}, and its temperature dependence is an important descriptor for the partitioning of hydrophobic chemicals between air and environmental lipids (Paterson et al., 1991, Tolls and McLachlan, 1994, Mackay and Wania, 1995, Simonich and Hites, 1995, Finizio et al., 1996). Examples of these compartments include organic carbon in soil, cuticular lipids in vegetation, and oily films on aerosols and other surfaces. Organic contaminants are atmospherically transported to remote, and often pristine, cold climate regions where they accumulate by means of the cold condensation effect (Wania and Mackay, 1993). Significant levels of polychlorinated biphenyls (PCBs), pesticides, and polycyclic aromatic hydrocarbons (PAHs) are found in air, water, snow, and wildlife in the Arctic (Barrie et al., 1992, Muir et al., 1994, Bidleman et al., 1995). The chromatographic migration of these chemicals from source regions to colder climates is greatly influenced by particle/gas partitioning and air/surface exchange. Knowledge of physicochemical factors such as K_{OA} and its temperature dependence can be used to explain the movement of these compounds and identify chemicals which are susceptible to this effect.

It is possible to calculate K_{OA} as the ratio of the octanol-water partition coefficient, K_{OW}, and the dimensionless air-water partition coefficient, $K_{AW} = H/RT$, where H is the Henry's Law constant, T is absolute temperature and R is the ideal gas constant. K_{OA} is calculated as,

$$K_{OA} = K_{OW}\,RT/H \qquad (1)$$

However, K_{OW} represents octanol saturated with water and water saturated with octanol whereas H represents pure water. Arbuckle (1983) estimates that this mutual solubility results in a reduction in the calculated K_{OW} by approximately half a $\log_{10}$ unit for hydrophobic chemicals such as 1,2,3,5-tetrachlorobenzene and pentachlorobenzene. Li and Andren (1994) report a negligible increase in solubility for 4-monochlorobiphenyl (PCB-3), 2,4,6-trichlorobiphenyl (PCB-30) and 2,2',4,4',6,6'-hexachlorobiphenyl (PCB-

155) in a near-saturated solution of octanol in water (0.003125 mol L^{-1}). However, they report experimental difficulties when working with long chain alcohols such as 1-octanol and especially 1-nonanol and 1-decanol due to the formation of microemulsions in water which tend to increase the apparent solubility. Consequently, K_{OA} values which are calculated from K_{OW} measurements are likely to be underestimated with the deviation increasing for chemicals with larger values of K_{OW}. Literature values of K_{OW} and H for individual PCB congeners (Sangster, 1989, Mackay et al., 1991) vary by up to an order of magnitude which further contributes to the error associated with calculating K_{OA}. It is therefore desirable to measure K_{OA} directly for these compounds.

A previous paper by Harner and Mackay (1995) introduced a novel approach for measuring K_{OA} which utilized a generator column. Air was passed through a glass wool column coated with octanol containing 0.5 to 2 g/L of solute (c_O). The vaporized solute was collected on Tenax TA adsorbent traps which were thermally desorbed and analyzed by gas chromatography. The vapor concentration (c_A) was calculated from the amount of chemical desorbed and the total air volume sampled and K_{OA} was calculated as c_O/c_A. Results were presented for six chlorobenzenes, five PCB congeners, and p,p'-DDT over the temperature range -10 °C to +20 °C. Theoretical concepts including mass transfer and equilibrium criteria were discussed. This paper describes a modified and improved method for measuring K_{OA}. Results are presented over the temperature range -10 °C to +30 °C.

Theoretical Background

The octanol-air partition coefficient can be expressed as,

$$K_{OA} = c_O/c_A = s^{o}_{L} / (p^{o}_{L}/RT) \qquad (2)$$

where p^{o}_{L} and s^{o}_{L} are liquid-phase vapor pressure and solubility in octanol. The temperature variation of p^{o}_{L} and s^{o}_{L} are described by the following equations:

$$\mathrm{Log}_{10}\, p^{o}_{L} = -\Delta_{VAP}H / 2.303RT + b_{VAP} \qquad (3)$$

$$\text{Log}_{10}\, s^{o}_{L} = -\Delta_{SOL} H / 2.303RT + b_{SOL} \qquad (4)$$

where the ΔH terms and the b variables are temperature independent. Δ_{VAP} H (J/mol) represents the enthalpy of vaporization and Δ_{SOL} H (J/mol) is the enthalpy of dissolution of the liquid phase compound in octanol. The enthalpy associated with the transition from octanol solution to air is $\Delta_{O}^{A}H$. The temperature dependence of K_{OA} is described by,

$$\text{Log}_{10}\, K_{OA} = \Delta_{O}^{A}H / 2.303RT + b_{OA} \qquad (5)$$

$$\text{Log}_{10}\, K_{OA} = (\Delta_{VAP} H - \Delta_{SOL} H) / 2.303RT - b_{VAP} + b_{SOL} - \log_{10} RT \qquad (6)$$

where $\Delta_{O}^{A} H = \Delta_{VAP} H - \Delta_{SOL} H$ and $b_{OA} = -b_{VAP} + b_{SOL} + \log_{10} RT$. The temperature dependence of K_{OA} is reduced relative to that of p^{o}_{L} because of the enthalpy required for dissolution in octanol, Δ_{SOL} H.

Experimental Section

Chemicals. The chemicals, solvents, and PCB standards used in this work are as follows: 1-octanol (Fisher Chemical). Glass distilled petroleum ether, dichloromethane and isooctane (BDH Inc.) PCB standards and 2,2',5-tribromobiphenyl were purchased from AccuStandard (IUPAC number in parentheses): 3-monochlorobiphenyl (3-monoCBP) (PCB-3), 2,2',4,5'-tetraCBP (PCB-49), 2,2,5,6'-tetraCBP (PCB-53), 2,3',4,4'-tetraCBP (PCB-66), 3,3',4,4'-tetraCBP (PCB-77), 2,2'3,5',6-pentaCBP (PCB-95), 2,2',3,6,6'-pentaCBP (PCB-96), 2,2',4,5,5'-pentaCBP (PCB-101), 2,3,3',4,4'-pentaCBP (PCB-105), 2,3',4,4',5-pentaCBP (PCB-118), 3,3',4,4',5-pentaCBP (PCB-126), 2,2',3,4,4',5'-hexaCBP (PCB-138), 2,2',4,4',5,5'-hexaCBP (PCB-153), 2,2',3,3',4,4',6-heptaCBP (PCB-171), 2,2',3,4,4',5,6-heptaCBP (PCB-180).

Apparatus. The apparatus shown in Figure 1 has several modifications over the original design (Harner and Mackay, 1995). Nitrogen from a compressed cylinder and at a controlled flow rate was sparged through an octanol column approximately 20 cm in height. When performing measurements above room temperature it was necessary to heat the octanol to a temperature T1 which was at least 10 °C greater than the temperature, T2, of the bath. The readout accuracy for the bath was ±0.25 °C. From the octanol saturation stage the air was cooled to the operating temperature, T2, by means of a cooling coil. This ensured the delivery of an octanol-saturated air stream to the generator column. Excess octanol was trapped to prevent any liquid from entering the generator column. The addition of the octanol trap shown in Figure 1 was a technical improvement over the previous "U-tube" design. The octanol-saturated air was passed through the generator column and then through an adsorbent trap which collected the PCBs. An improved design allowed both the generator column and trap to be submerged in the temperature bath to avoid any hot or cold spots which could act as sources or sinks for chemical. Connections were made with vacuum fittings (Swagelok, Weston Valve & Fitting Ltd.) ensuring air and water tight seals.

The generator column consisted of a glass tube 130 mm long x 8 mm i.d. and tapered to 4 mm i.d. at the inlet. Solvent-rinsed glass wool was moderately packed into the column to a length of 90 mm. Increased dimensions of the generator column was another modification which allowed higher flow rates and hence shorter experimental times. However, even at these higher flow rates long sampling times were required to trap a sufficient quantity of gaseous PCB for a single determination. For example, at +30 °C the sampling time for tetrachlorinated and heptachlorinated congeners was approximately 1 and 3 hours respectively but at -10 °C this increased to 48 and 216 hours. A syringe was used to apply the octanol solution evenly onto the surface of the glass wool. This was done by inserting the syringe into the glass wool packing and slowly turning and withdrawing it while delivering 400 μL of solution. Solute concentrations ranged from 0.2 g/L to 0.5 g/L. Traps were 130 mm long x 11 mm i.d. and tapered to 4 mm i.d. at the inlet and packed with 50 mm of C8-bonded silica (Varian Corp.) sandwiched between glass wool plugs.

Experimental flow rates ranged from 70 to 100 mL/min and were measured at the outlet of the system and at ambient pressure. The system itself was under positive pressure caused by resistance to flow through the adsorbent traps. As a result, the true flow through the generator column was less than the flow measured at the outlet. To correct for this effect the system pressure was measured by attaching a pressure gauge (Magnehelic) through a “Tee” connector between the generator column and the adsorbent trap. From this information a pressure correction of approximately 50 cm of water was applied, which decreased the flow rate of each sample by 5%. This translated to higher values for C_A and a negative adjustment of 5% or 0.02 $\log_{10}$ units to all K_{OA} measurements.

Analysis. The C_8 traps were eluted with 5 mL of 30% dichloromethane in petroleum ether. Prior to their next use the traps were washed with 3 mL 2% toluene in dichloromethane and dried using a stream of nitrogen. Sample extracts were blown down under a gentle stream of nitrogen and the solvent was exchanged into 2,2,4-trimethylpentane. Typical final blow-down volumes ranged from 0.2 mL to 1.0 mL, at which point 2,2’,5-tribromobiphenyl was added as an internal standard for volume correction. Recovery tests were performed to correct for blow-down losses. Extraction of the C_8 traps versus thermal desorption was another improvement. It eliminated problems associated with thermal desorption efficiency for heavier compounds from Tenax TA traps and allowed for multiple analyses on trap extracts from an experiment. Samples were analyzed by gas chromatography-electron capture detection (GC-ECD). The GC was equipped with either a 30 m DB-5 or DB-5MS column (J & W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness, operated with hydrogen carrier gas at 50 cm/s. Injections (1 μL) were splitless with the split opened after 0.5 min. The temperature program was 90 °C for 0.5 min., 10 °C/min to 160 °C, 2 °C/min to 250 °C with the detector at 300 °C.

Results and Discussion

Quality Control

Extraction efficiency tests were performed on several traps and showed that essentially all of the chemical was eluted in the first 5 mL of the dichloromethane-petroleum ether solvent mixture with less than 1% carry over to a second 5 mL fraction. The possibility of non-extractable PCBs being retained on the traps was checked by further extraction using dichloromethane alone. Results showed no detectable PCBs in this third fraction thus confirming the adequacy of using 5 mL of the solvent mixture for extraction.

Losses incurred during blow down were quantified by spiking 5 mL of the dichloromethane-petroleum ether solvent mixture with known amounts of PCBs and reducing the volume to 0.2 mL. The percentages lost were reproducible and ranged from 25% for PCB-3 to 10% for PCB-77 and were less than 10 % for the heavier congeners. The analytical results were corrected for these recovery factors. The possibility of PCB vapors breaking through the traps was also of concern especially when air sample volumes exceeded 1000 L. This was investigated by occasionally adding a second trap in series for the higher volume samples. In all cases back-up traps contained less than 1% of the total indicating that a single C_8 trap was sufficient for collecting the gas-phase PCBs.

Equilibration Experiments

Tests were performed to ensure that equilibrium was achieved between air and octanol by comparing the K_{OA} results obtained with two different lengths of generator column. The "standard" column was the 90 mm glass wool bed and was compared to a 10 mm bed. Table 1 shows the results from the 90 mm bed at 70 to 85 mL/min flow and the 10 mm bed at 77 to 240 mL/min flow. The agreement between the 2 sets of measurements indicates that equilibrium is established in these experiments.

A study was also performed to compare K_{OA} measurements for a single-congener octanol solution with those using an octanol solution containing a mixture of congeners. At +20 °C the $\log_{10} K_{OA}$ value for PCB-3 measured individually was 6.95. This agreed well with a value of 7.01 measured for an octanol solution which contained PCB-3 and four tetra-chlorinated congeners.

Results of K_{OA} Measurements

The K_{OA} measurements over the temperature range -10 °C to +30 °C are summarized in Figure 2 and Table 2. K_{OA} increased log-linearly with reciprocal temperature with values increasing by factors of 50 to 300 over the temperature range, clearly illustrating enhanced partitioning to lipid phases at cold temperatures. Equation 7 can be used to calculate K_{OA} at different temperatures using the coefficients in Table 2.

$$\mathrm{Log}_{10} K_{OA} = A + B/T \qquad (7)$$

where $B = \Delta_O^A H / 2.303R$ and $A = b_{OA}$ (equation 5).

The enthalpy of phase change from octanol to air, $\Delta_O^A H$ is calculated from the temperature coefficient as 2.303BR/1000. Values of $\Delta_O^A H$ range from 66 to 93 kJ/mol and average 79 kJ/mol (Table 3). The $\Delta_{VAP} H$ - $\Delta_O^A H$ is the enthalpy of solution in octanol, $\Delta_{SOL} H$, as discussed earlier. Table 3 summarizes $\Delta_{SOL} H$ values for individual congeners. The $\Delta_{VAP} H$ values were estimated from gas chromatographic retention data (Falconer and Bidleman, 1994). Hinckley et al. (1990) compared log vapor pressure - temperature slopes ($\Delta H_{VAP}/2.303R$, equation 3) determined by GC with those measured by other techniques. The average absolute difference was 8.5% for 17 PAHs, PCBs and chlorinated pesticides. The mean value of $\Delta_{SOL} H$ for all PCBs is 6.6 ± 5.9 kJ/mol (n=18). There appears to be no correlation with homolog group or ortho-Cl group (considering PCBs with 4 or more Cl atoms) as shown below.

tetra : $\Delta_{SOL} H = (9.5 \pm 6.0)$ kJ/mol (n=5)

penta : $\Delta_{SOL} H = (4.7 \pm 6.1)$ kJ/mol (n=5)
hexa/hepta : $\Delta_{SOL} H = (7.7 \pm 6.7)$ kJ/mol (n=5)

non/mono-ortho : $\Delta_{SOL} H = (6.9 \pm 7.5)$ kJ/mol (n=6)
multi-ortho : $\Delta_{SOL} H = (7.6 \pm 5.5)$ kJ/mol (n=9)

$\Delta_{SOL} H$ is thus a small term, and $\Delta_O^A H$ is on the average only 7% lower than $\Delta_{VAP} H$.

PCB-3 is the only congener which is common to this work and previous measurements (Harner and Mackay, 1995). Although the temperature slopes differ somewhat a comparison of $\log_{10} K_{OA}$ values at +20 °C shows excellent agreement: 7.01 and 7.01 respectively.

Effect of Ortho-Chlorine Substitution on K_{OA}

It is interesting to compare K_{OA} on the basis of the number of chlorine (Cl) atoms occupying ortho positions. Ortho positions refer to the four sites adjacent to the biphenyl bond having designations 2,2',6,6'. PCBs with no ortho Cl atoms, also known as "coplanar PCBs", are able to obtain a configuration in which both phenyl rings lie approximately in the same plane. The planarity decreases as the ortho Cl atoms are added to the ring. Dihedral angles for different ortho-Cl groups are approximately: non-ortho 40-42°, mon-ortho 57-59°, di-ortho 77-79° and almost 90° for tri- and tetra-ortho congeners (Falconer et al., 1995, Ong and Hites, 1991). Within the same homolog group non- and mono-ortho congeners have lower vapor pressures than congeners with two or more ortho-Cl (Falconer and Bidleman, 1994). We refer to the lowering of vapor pressures as the "primary ortho effect". Because of their lower vapor pressures non- and mono-ortho PCBs sorb to airborne particles to a greater extent (Falconer and Bidleman, 1994).

Table 4 lists K_{OA} values at +20 °C and 0 °C for the tetra and penta homologs and compares them according to number of ortho Cl atoms. K_{OA} values increase by about an order of magnitude from +20 °C to 0 °C. This strong temperature dependence points to a significantly greater retention of PCBs by environmental lipids at cold temperatures. The "primary ortho effect" is also apparent when comparing K_{OA} values for PCBs in the same homolog group. PCBs with fewer ortho chlorines have higher K_{OA} values. For example in the tetra homolog, congener 77 which is non-ortho has a K_{OA} value approximately 40 times greater than congener 53 which is tri-ortho. In the penta homolog, non-ortho congener 126 has a K_{OA} value approximately 70 times higher than for tetra-ortho congener 96.

Subcooled liquid vapor pressure (p^{o}_{L} , Pa) is often used to relate PCB concentrations in air and condensed phases. Figure 3 is a plot of $\log_{10} K_{OA}$ against log p^{o}_{L} at +20°C for congeners containing 2 to 7 Cl atoms. The values of p^{o}_{L} were taken from Falconer and Bidleman (1994). The difference between the non/mono ortho PCBs and the multi-ortho PCBs increases for the higher chlorinated congeners. We refer to this as a "secondary ortho effect" which causes an enhancement of K_{OA} values in addition to the "primary ortho effect" of lower vapor pressure. The secondary effect indicates that non/mono-ortho PCBs have greater K_{OA} values than multi-ortho PCBs of the same vapor pressure. The ratio of these values is defined as the K_{OA} enhancement factor. Studies of particle/gas partitioning also show this secondary ortho effect for non/mono-ortho PCBs (Falconer et al., 1995). The secondary effect on K_{OA} values is substantial for PCBs 77, 126, 105 and 118 which contribute heavily to 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents (TEQ) in biota (Ahlborg et al., 1994). K_{OA} enhancement factors for these congeners range from 2 to 4.

Liquid phase vapor pressures have been reported for 180 PCB congeners (Falconer and Bidleman, 1994). Separate regressions were performed on the non/mono-ortho and multi-ortho groups of congeners containing 2 to 7 Cl atoms which allows K_{OA} at 20 °C to be estimated from p^{o}_{L} for other congeners.

i) non/mono-ortho : $\text{Log}_{10} K_{OA} = (-1.268) \log p^{o}_{L} + 6.135$ $r^2 = 0.995$

ii) multi-ortho: $\text{Log}_{10} K_{OA} = (-1.015) \log p^{o}_{L} + 6.490$ $r^2 = 0.997$

PCB-3, the only monochlorobiphenyl which has a measured K_{OA} value, deviates from both the mono- and multi-ortho regression lines. Foreman and Bidleman (1985) reported abnormal behavior for biphenyl and monochlorobiphenyls compared to the 2 to 7 chlorinated congeners based correlations of p^{o}_{L} against chromatographic retention indices. This discrepancy is consistent with the deviation for PCB-3 in Figure 3.

Conclusions

The mono-ortho and non-ortho PCBs, which are the most toxic, show enhanced partitioning into octanol relative to the multi-ortho congeners. This may explain observations of enhanced partitioning onto aerosols for coplanar PCBs which ultimately facilitates their removal from the atmosphere by wet and dry particle deposition (Falconer et al., 1995). The temperature dependence of K_{OA} may explain the movement of chemicals to colder climates by the cold condensation effect. Until now the "chromatographic" migration of contaminants to cold regions, as they partition between the atmosphere and condensed phases such as soil and vegetation, has been explained using vapor pressure (Wania and Mackay, 1993, Mackay and Wania, 1995). K_{OA} has been proposed as a modelling parameter for air-vegetation exchange (Simonich and Hites, 1995) and the results presented here suggest that K_{OA} is able to resolve different classes of PCBs.

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Table 1. K_{OA} results of equilibration experiments.

congener	90 mm bed[a] mean	90 mm bed[a] Log_{10} mean	n	10 mm bed[b] mean	10 mm bed[b] Log_{10} mean	n
3	$(1.02 \pm 0.05) \times 10^{7}$	7.01	9	$(1.11 \pm 0.25) \times 10^{7}$	7.05	5
53	$(1.74 \pm 0.04) \times 10^{8}$	8.24	9	$(1.80 \pm 0.26) \times 10^{8}$	8.26	5
49	$(3.75 \pm 0.22) \times 10^{8}$	8.57	9	$(4.21 \pm 0.81) \times 10^{8}$	8.62	5
66	$(1.67 \pm 0.23) \times 10^{9}$	9.22	9	$(2.04 \pm 0.38) \times 10^{9}$	9.31	5
77	$(9.16 \pm 1.57) \times 10^{9}$	9.96	5	$(1.30 \pm 0.39) \times 10^{10}$	10.11	5

[a] flow = 70 to 85 mL/min

[b] flow = 77 to 241 mL/min

Table 2. Regression constants for equation 7.

					+20 °C		
Congener	r^2	A	B	Range (°C)	K_{OA} ± S.D.	$\mathrm{Log}_{10}\,K_{OA}$	$\mathrm{Log}_{10}\,p^{o}_{L}$ (Pa)[b]
3	0.9991	-4.82	3470	-10 to +30	$(1.02 \pm 0.05) \times 10^{7}$	7.01	-0.23
3[a]	0.9999	-6.52	3962	-10 to +20	$(1.03 \pm 0.05) \times 10^{7}$	7.01	-0.23
15[a]	0.9999	-5.06	3792	-10 to +20	$(7.54 \pm 0.31) \times 10^{7}$	7.88	-1.37
29[a]	0.9996	-4.77	3792	-10 to +20	$(1.07 \pm 0.37) \times 10^{8}$	8.03	-1.58
49	0.9965	-4.96	3981	-10 to +20	$(3.75 \pm 0.22) \times 10^{8}$	8.57	-2.02
53	0.9974	-5.26	3965	-10 to +20	$(1.74 \pm 0.04) \times 10^{8}$	8.24	-1.79
61[a]	0.9964	-2.89	3464	-10 to +20	$(7.96 \pm 0.72) \times 10^{8}$	8.90	-2.42
66	0.9974	-3.82	3827	-10 to +20	$(1.67 \pm 0.23) \times 10^{9}$	9.22	-2.46
77	0.9997	-3.14	3828	-10 to +20	$(9.16 \pm 1.57) \times 10^{9}$	9.96	-2.92
95	0.9983	-4.30	3904	-10 to +30	$(1.14 \pm 0.09) \times 10^{9}$	9.06	-2.53
96	0.9997	-4.60	3913	-10 to +30	$(5.91 \pm 0.54) \times 10^{8}$	8.77	n.a.
101	0.9923	-3.82	3841	-10 to +30	$(2.06 \pm 0.20) \times 10^{9}$	9.31	-2.73
105	0.9997	-5.68	4678	-10 to +30	$(1.87 \pm 0.13) \times 10^{10}$	10.27	-3.17
118	0.9996	-5.92	4693	-10 to +30	$(1.21 \pm 0.10) \times 10^{10}$	10.08	-3.19
126	0.9992	-5.98	4870	-10 to +30	$(4.08 \pm 0.40) \times 10^{10}$	10.61	-3.60
138	0.9982	-5.57	4584	-10 to +30	$(1.24 \pm 0.21) \times 10^{10}$	10.09	-3.56
153	0.9925	-6.02	4695	-10 to +30	$(1.11 \pm 0.08) \times 10^{10}$	10.04	-3.44
155[a]	0.9944	-2.21	3337	-10 to +20	$(1.44 \pm 0.15) \times 10^{9}$	9.16	-2.66
171	0.9965	-5.71	4757	-10 to +30	$(3.22 \pm 0.23) \times 10^{10}$	10.51	-4.01
180	0.9943	-4.70	4535	-10 to +30	$(5.64 \pm 0.71) \times 10^{10}$	10.75	-4.17

[a] from Harner and Mackay (1995).

[b] from Falconer and Bidleman (1994).

Table 3. Estimation of Δ_{SOL} H from Δ_{VAP} H and Δ_{O}^{A}H.

Congener	Number of Cl atoms	Number of ortho Cl	Δ_{VAP} H [b] kJ/mol	Δ_{O}^{A}H kJ/mol	Δ_{SOL} H kJ/mol
3[a]	1	0	66.79	75.86	-9.08
3	1	0	66.79	66.44	0.35
15[a]	2	0	76.03	72.61	3.43
29[a]	3	1	76.72	72.61	4.12
49	4	2	80.97	76.23	4.75
53	4	3	78.77	75.92	2.85
61[a]	4	1	83.90	66.33	17.6
66	4	1	83.27	73.28	9.99
77	4	0	87.16	73.30	13.86
95	5	3	84.23	74.75	9.48
101	5	2	86.43	73.54	12.9
105	5	1	89.76	89.57	0.19
118	5	1	89.30	89.86	-0.55
126	5	0	94.89	93.25	1.65
155[a]	6	4	82.39	63.89	18.5
153	6	2	91.43	89.90	1.53
138	6	2	91.91	87.77	4.14
171	7	3	95.89	91.08	4.81
180	7	2	96.54	86.83	9.71

[a] from Harner and Mackay (1995).

[b] from Falconer and Bidleman (1994).

Table 4. Increase in K_{OA} for PCBs with fewer ortho chlorines: "primary ortho effect".

Number of ortho Cl atoms	Congener	$Log_{10} K_{OA}$ +20 °C	$Log_{10} K_{OA}$ +0°C
Tetra Homolog			
3	53	8.24	9.28
2	49	8.57	9.64
1	66	9.22	10.21
0	77	9.96	10.88
Penta Homolog			
4	96	8.77	9.72
3	95	9.06	10.02
2	101	9.31	10.31
1	105	10.27	11.43
0	126	10.61	11.81

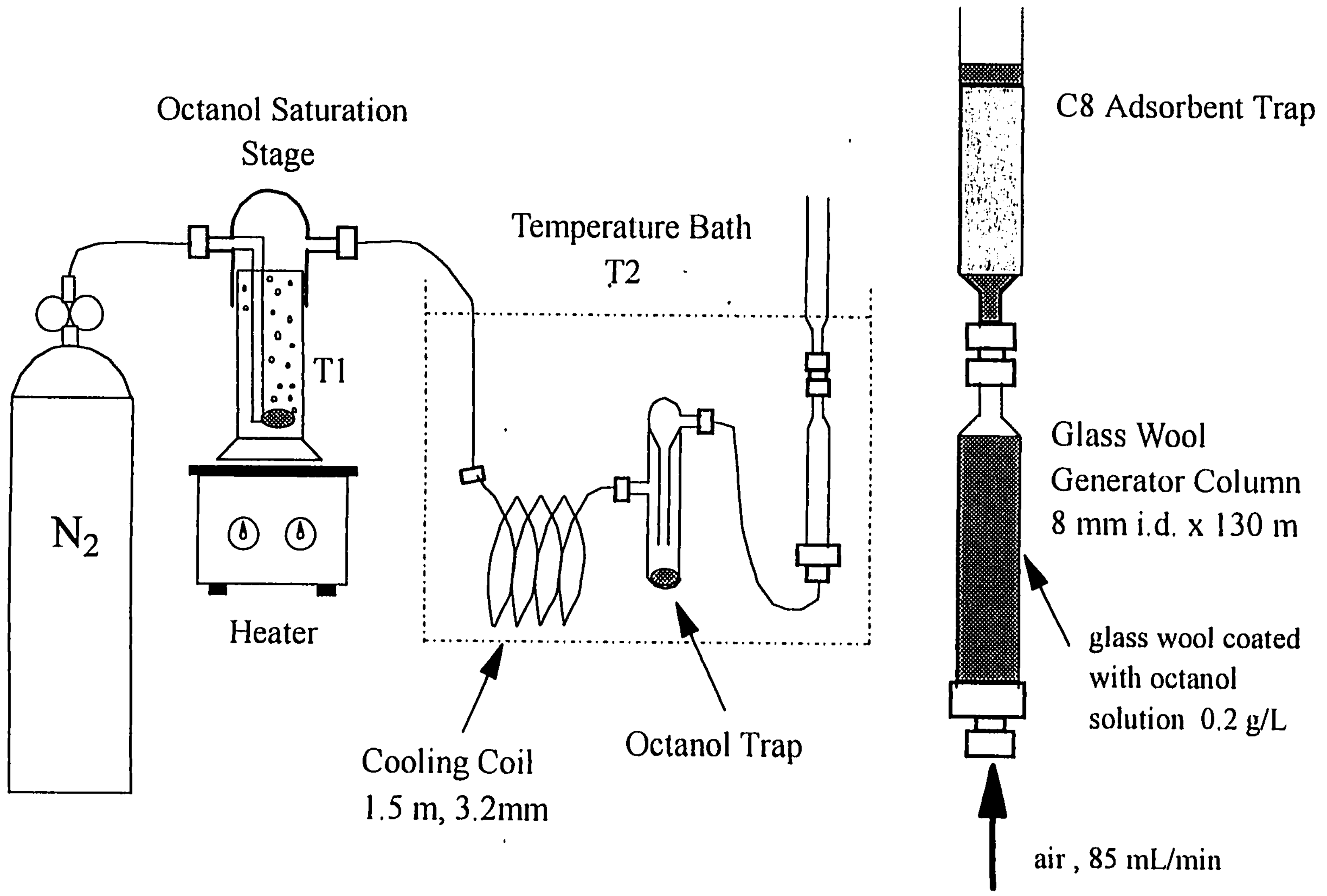

Figure1. Schematic diagram of K_{OA} apparatus, modified from Harner and Mackay (1995).

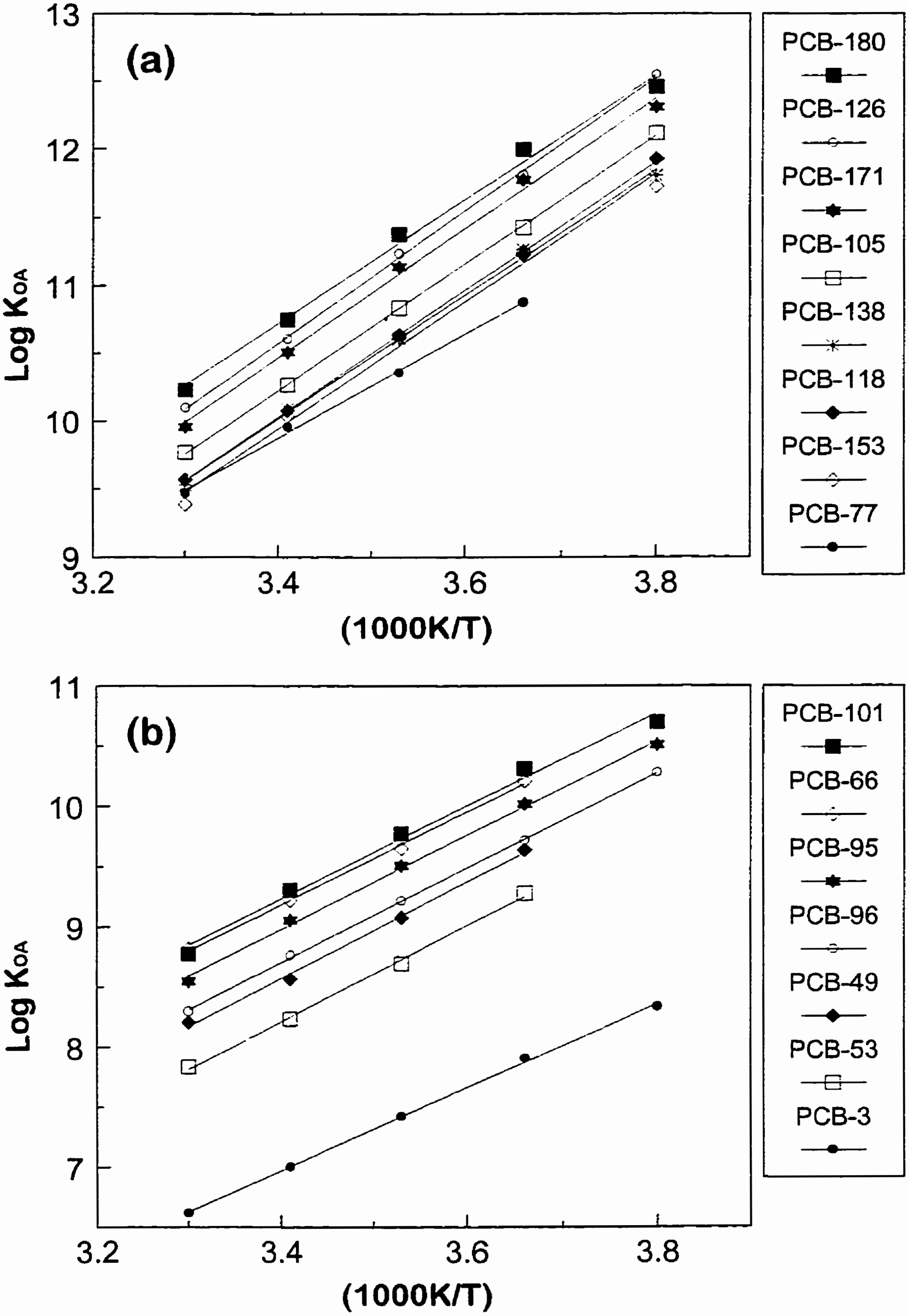

Figure 2. Summary of K_{OA} results over the temperature range -10 °C to +30 °C, plot of equation 7. a) tetra- to heptachlorobiphenyls. b) mono- to pentachlorobiphenyls.

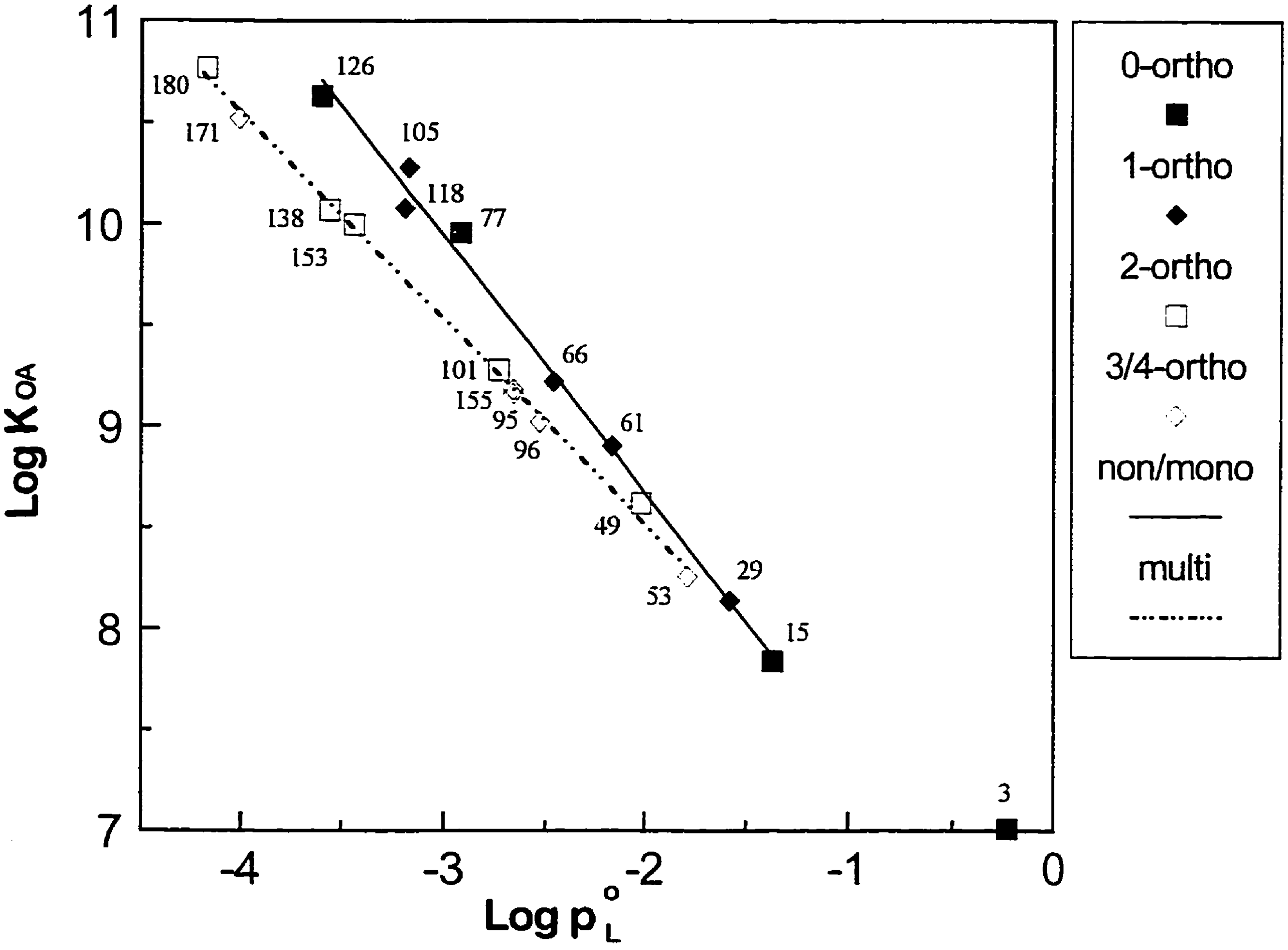

Figure 3. Log_{10}-log_{10} correlation of K_{OA} against p^o_L at +20 °C for non/mono-ortho and multi-ortho congeners for PCBs containing 2 to 7 chlorines, numbered according to congener (Tables 2 and 3).

Paper II: Measurement of Octanol-Air Partition Coefficients for Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Naphthalenes (PCNs)

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ABSTRACT

Measurements of the octanol-air partition coefficient, K_{OA} are reported for four polycyclic aromatic hydrocarbons (PAHs) and 24 polychlorinated naphthalenes (PCNs) as a function of temperature over the range (0 to 50) °C. Results for PAHs are within a factor of 1.5 to 2 of values calculated as the ratio of the octanol-water and air-water partition coefficients. The enthalpies of transfer from octanol to air, $\Delta_O^A H$, for fluorene, phananthrene and pyrene are (82.9, 75.5 and 76.3) kJ/mol respectively. Except for fluorene, these are within the range of reported values of the enthalpy of vaporization, $\Delta_{vap}H$. There is also good agreement between $\Delta_O^A H$ and the temperature coefficient for vegetation-atmosphere partitioning (Q_D). Correlations of $\log_{10} K_{OA}$ against $\log_{10}$ vapor pressure (p°) are compared with previous results for polychlorinated biphenyls (PCBs). Values of log K_{OA} for PCNs show a step-wise change and increase by more than three orders of magnitude from the 2-Cl to 6-Cl homolog groups.

Introduction

Physical chemical properties and their variation with temperature control the cycling and transport of persistent organic pollutants. The octanol-air partition coefficient, K_{OA}, is thought to be the key descriptor of the partitioning of semi-volatile compounds between the atmosphere and terrestrial organic phases (Wania and Mackay, 1996). These include organic carbon in soil, the waxy cuticle and lipid portion of vegetation (Bacci et al., 1990a, 1990b, Paterson et al., 1991, Tolls and McLachlan, 1994, Simonich and Hites, 1995, Kömp et al., 1997), and the organic film which coats atmospheric particulate matter (Finizio et al., 1997).

K_{OA} is the ratio of the solute concentration in octanol, C_O (mass/volume) to the concentration in air C_A (mass/volume), when the octanol-air system is at equilibrium. i.e. $K_{OA} = C_O/C_A$. Hence K_{OA} is dimensionless. It is possible to calculate K_{OA} as the ratio of the octanol-water and air-water partition coefficients i.e. $K_{OA} = K_{OW}/K_{AW}$. K_{AW} is H/RT where H is the Henry's law constant, T is absolute temperature, and R is the ideal gas constant. However, almost no physicochemical data exist for PCNs and the literature values of K_{OW} and H for some PAHs vary by more than an order of magnitude (Mackay et al., 1992, Sangster et al., 1989). These errors will be propagated in the calculation. Another problem is the absence of temperature dependent data for H and K_{OW}. It is therefore desireable to measure K_{OA} directly as a function of temperature.

Previous papers (Harner and Mackay, 1995; Harner and Bidleman, 1996) described a novel method for measuring K_{OA} using a generator column containing glass wool coated with a solution of the chemical in octanol. Values were reported for chlorobenzenes, PCBs, and DDT over the temperature range (-10 to +30) °C. This paper reports K_{OA} values as a function of temperature for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs). PAHs and PCNs are widespread and persistent environmental contaminants. PAHs are combustion products and the 2-4 ring compounds partition between the gas-phase and vegetation according to their vapor pressures or K_{OA} values (Simonich and Hites, 1996, Tremolada et al., 1996). PCNs were introduced in the

1920s as commercial mixtures (e.g. Halowaxes) primarily as dielectric fluids (Crookes and Howe, 1993). PCNs have been reported in incinerator emissions (Oehme et al., 1987), ambient air (Harner and Bidleman, 1997, Dörr et al., 1996) and sediment and biota from the Baltic region (Falandysz et al., 1996a,b, Falandysz and Rappe, 1996, Järnberg et al., 1997). Some congeners have high tetrachlorodibenzodioxin toxic equivalents (TEQs), comparable to those for the coplanar PCBs (Järnberg et al., 1993, Harner and Bidleman 1997).

Theoretical Background

In a previous paper (Harner and Bidleman, 1996) a number of sign errors were made in the equations describing K_{OA} theory. This section is repeated below with proper signs.

The octanol-air partition coefficient can be expressed as,

$$K_{OA} = c_O/c_A = s^{\circ} / \ (p^{\circ}/RT) \qquad (1)$$

where p° and s° are solid-phase vapor pressure and solubility in octanol. The temperature variation of p° and s° are described by the following equations:

$$\mathrm{Log}_{10}\, p^{\circ} = -\Delta_{sub}H \,/\, 2.303RT + b_{sub} \qquad (2)$$

$$\mathrm{Log}_{10}\, s^{\circ} = -\Delta_{sol}H \,/\, 2.303RT + b_{sol} \qquad (3)$$

where the ΔH terms and the b variables are assumed to be temperature independent. $\Delta_{sub}H$ (J/mol) is the enthalpy of sublimation and $\Delta_{sol}H$ (J/mol) is the enthalpy of dissolution in octanol. The enthalpy associated with the transition from octanol solution to air is $\Delta_{O}^{A}H$. The temperature dependence of K_{OA} is described by:

$$\mathrm{Log}_{10}\, K_{OA} = (\Delta_{sub}H - \Delta_{sol}H) \,/\, 2.303RT - b_{sub} + b_{sol} + \log_{10} RT \qquad (4)$$

According to Eq. 4, a plot of log K_{OA} vs 1/T is only approximately linear because the term log RT is a weak function of temperature. Octanol-air partitioning can also be defined by:

$$K'_{OA} = s^{o} / p^{o} = K_{OA}/RT = (\Delta_{sub}H - \Delta_{sol}H)/2.303RT - b_{sub} + b_{sol} \qquad (5)$$

where K'_{OA} has units of concentration/pressure, $\Delta_{O}^{A}H = \Delta_{sub}H - \Delta_{sol}H$, and the intercept ($b_{sub}$-$b_{sol}$) is a constant.

Experimental Section

A description of the apparatus used to measure K_{OA} and an outline of the experimental procedure is presented in an earlier paper (Harner and Bidleman, 1996). Octanol solutions of PAHs were prepared from solids obtained from Accustandard (New Haven, CT). Solutions of PCNs in octanol were prepared by diluting pure Halowax 1014 (United States Environmental Protection Agency, Repository for Pesticides and Industrial Chemicals, Research Triangle Park, NC). Concentrations of individual PAHs ranged from (0.2 to 0.3) g/L. The octanol solution of PCNs contained 3.3 g/L of Halowax 1014. Octanol-saturated nitrogen was passed through a thermostated generator column containing glass wool coated with the octanol solution. Effluent compounds were trapped on C_8-bonded silica (Varian Corp.) which was extracted with 30% dichloromethane in petroleum ether. Flow rates for the PAH and PCN experiments ranged from (70-100) mL/min and measurement temperatures ranged from (0 to 50) °C for PAHs and (10 to 50) °C for PCNs.

PAHs were determined using a Hewlett Packard 5890 Plus GC equipped with a flame ionization detector (FID). Compounds were eluted on a 60 m DB-5 capillary column (J&W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness, operated with hydrogen carrier gas at 50 cm/s. Injections (1 μL) were splitless with the split opened after 0.5 min. The temperature program was 90 °C for 0.5 min., 10 °C/min. to 160 °C, and 2 °C/min. to 250 °C. Injector and detector temperatures were (250 and 300) °C. Peaks were quantified against a mixture of PAH standards (Axact Standards, Commack NY) and PCB-110 (Accustandard, New Haven, CT) was used as internal standard for volume correction.

PCN measurements were performed using an octanol solution of Halowax 1014, a commercial mixture containing mostly 4-7 chlorinated naphthalenes. PCNs in this mixture were quantified by a method which used GC-FID to estimate the mass percent contribution of the individual peaks in the FID chromatogram (Harner and Bidleman, 1997). FID response was assumed to respond to the carbon skeleton of the PCN molecule. Mass percent contributions ($m_i\%$) were assigned using,

$$m_i\,\% = 100(A_i)(M_i)\,/\sum_{i=1}^{n}\,(A_i)(M_i) \qquad (6)$$

where A_i is the area fraction of peak i, M_i is the molecular weight of compound i, and n is the total number of peaks integrated. It was not possible to assign mass percents to all of the congeners since some peaks coeluted on the DB-5 column. A series of n-alkanes was used to calibrate the FID response by normalizing the PCN response to an alkane having similar retention time. Concentrations of the individual PCN congeners in octanol (0.01 to 0.44) g/L were calculated from the Halowax 1014 concentration and the mass percent contributions in Halowax 1014. GC-negative ion mass spectrometry was used to confirm the homolog identity of each peak.

Vaporized PCNs were quantified by GC using electron capture detection (GC-ECD). Halowax 1014 was used as the calibration solution and PCB-103 (Accustandard, New Haven, CT) was used as internal standard for volume correction. Samples were analyzed on the same 60 m DB-5 column that was used for the PAH analysis with the same temperature program and other conditions.

Results and Discussion

Composition of Halowax 1014. Figure 1 is a labelled GC-FID chromatogram showing the 2 to 7 chlorinated PCN congeners. Peaks were labelled according to a new numbering scheme which accounted for peaks not previously identified in the literature. Based on FID response the mass percent contribution of individual congeners in Halowax 1014 was determined. Results are shown in Table 1 in which peaks are also identified by another labelling scheme used by Järnberg et al. (1993). IUPAC congener numbers and structures are also included for peaks which have been identified in the literature (Imagawa et al. 1993, Falandysz et al., 1996a).

Quality Control. The accuracy of the mass percent contribution of individual congeners relied on the accuracy of the GC-FID method for quantifying PCNs in the Halowax 1014 mixture. It was therefore important to validate this method using pure PCN solutions of known concentration. Pure compounds were obtained from the following sources. Congeners 1,2,4,7-TeCN (4b) and 1,2,3,5,7-PeCN (5a) were purchased from Larodan AB (Malmö, Sweden); 1,2,3,4,6,7- / 1,2,3,5,6,7-HxCN (6a), 1,2,4,5,6,8-HxCN (6d) and 1,2,3,4,5,6,7-HeptaCN (7a) were gifts of Åke Bergman and Eva Jakobsson (Department of Environmental Chemistry, Stockholm University, Stockholm, Sweden); 1,2,3,4,5,6,7,8-OctaCN (8) was purchased from Ultra Scientific (Hope, Rhode Island). A solution containing known concentration of these congeners was quantified against the same peaks in Halowax 1014 using the percent composition information from GC-FID analysis. Results showed that the measured values were within ±22% of the true value for 5 out of the 6 congeners (Harner and Bidleman, 1997). The deviation for the sixth peak, CN-52 (1,2,3,5,7-PeCN, may be due to an underlying peak (CN-60) in the Halowax mixture as identified by Imagawa et al. (1993). Overestimation would occur if the response factor for CN-60 were less than for CN-52. However, small errors in estimating the mass percent contribution of individual congeners would not affect the accuracy of K_{OA}, since K_{OA} is a ratio of two concentrations.

In both PCN and PAH determinations of K_{OA}, the C_8 trap extracts were reduced to 0.2 mL by evaporation using a gentle stream of clean nitrogen. To correct for losses due to volatilization of the sample during this "blow-down" procedure a series of spike recovery tests were performed. Recoveries for PCNs (n=3) ranged from 65-85% with good reproducibility (±10%) for individual congeners. PAH recoveries were fluorene 89 ± 2.6%, phenanthrene 93 ± 2.3%, fluoranthene 102 ± 0.6% and pyrene 103 ± 2.3%. Recovery factors for PCNs, fluorene and phenanthrene were applied to trap extract results.

Large air volumes and hence sampling times were required to obtain a quantifiable amount of chemical in the air phase, especially for compounds with large K_{OA} values. In general, the sampling time approximately tripled for every 10 °C decrease in temperature. All experimental determinations of K_{OA} used an octanol solution consisting of several solutes; 2 to 4 compounds in the case of PAHs and approximately 30 components in the Halowax 1014 technical mixture. Earlier work showed no difference in K_{OA} value for a PCB in octanol solution as a single compound or as a component in a mixture (Harner and Bidleman, 1996). This test was repeated with phenanthrene. At 20 °C the K_{OA} value for phenanthrene alone in octanol was 7.78 ± 0.05 (n=6) which was in good agreement with a value of 7.80 from the regression line for phenanthrene measured in the four-component PAH mixture.

Inherent in the measurement of K_{OA} values is the assumption that C_O remains constant. A decrease in C_O is expected due to the depletion of solute as it partitions into the air phase for extended periods of time. However, this change is quantifiable and occurs very slowly. To avoid errors due to a changing C_O, generator columns were replaced when more than 10% of the solute was depleted. This is only necessary for compounds with low K_{OA} values. Another process which can alter C_O (and result in anomalous K_{OA} values) is the accumulation or loss of pure octanol in the generator column. The assumption of a constant C_O was checked by extracting the generator column with a 30% dichloromethane in petroleum ether solvent mixture after several weeks of operation. Analysis of the extract gave values that were (10 to 20)% greater than the original octanol concentrations for a three-component mix of fluorene, pyrene and chrysene. This result validates the assumption that C_O remains relatively constant over the duration of the K_{OA} measurement. However, more significant losses may occur for longer experiments despite pre-saturation of the generator column.

Results of K_{OA} measurements. Values of K_{OA} as a function of temperature are presented in Figure 2 for fluorene, phenanthrene and pyrene over the temperature range (0 to 40) °C and for fluoranthene at (20 , 30 and 40) °C. PCN results are presented over the range (10 to 50) °C. Experimental data (Table 2) demonstrate good reproducibility. Standard deviations were less than 10% for most determinations and never exceeded 50%. The parameters of equation 7, which describes the temperature dependence of K_{OA}, are listed in Table 3 (PAHs) and Table 4 (PCNs).

$$\log_{10} K_{OA} = A + B/T \qquad (7)$$

As explained in the Theoretical Background section, this equation is only approximately linear. Nevertheless, it has been previously used to describe the temperature dependence of K_{OA} (Harner and Bidleman, 1996; Harner and Mackay, 1995; Kömp and McLaughlin, 1997). Alternatively, the octanol-air partitioning data can be treated by plotting log K'_{OA} vs 1/T (eq 5) and then multiplying the fitted K'_{OA} values at each temperature by RT to yield K_{OA}. Values of K_{OA} obtained in this way differed by less than 1% from those calculated from eq. 7, using the parameters A and B in Tables 3 and 4. Enthalpies of transfer from octanol to air, $\Delta_{O}^{A}H = \Delta_{sub}H - \Delta_{sol}H$, were on average only 3% higher when the data were plotted by eq 5. Thus the approximation of linearity in plots of log K_{OA} vs 1/T (eq 7) is satisfactory over the temperature range involved.

Table 3 also compares measured K_{OA} results for PAHs at 25 °C with values calculated using the relation $K_{OA} = K_{OW}RT/H$. Measured results exceeded calculated values by a factor of approximately 1.5 to 2. This is consistent with a previous comparison for PCB data (Harner and Mackay, 1995) and suggests that K_{OA} values calculated using K_{OW} and H systematically underpredict the true value. It is therefore preferable to measure K_{OA} directly.

K_{OA} has a strong temperature dependence with slopes of approximately 4000-4500 for the PAHs and 3248-5040 for the 2-Cl to 6-Cl PCNs. This slope is related to the enthalpy associated with the transfer from octanol to air, $\Delta_O^A H$ (eq 4), which is calculated as 2.303BR, where R is the ideal gas constant. Enthalpies associated with vaporization from the subcooled liquid to air, $\Delta_{vap}H$, have been reported for PAHs (Yamasaki et al., 1984, Hinckley et al., 1990). Values of $\Delta_O^A H$ and $\Delta_{vap}H$ are listed in Table 5. Except for fluorene, the $\Delta_O^A H$ values are within the range of reported $\Delta_{vap}H$ values. For fluorene, $\Delta_O^A H$ exceeds $\Delta_{vap}H$ by (13 to 18) kJ/mol. Harner and Bidleman (1996) found that values of $\Delta_O^A H$ for PCBs were on average about 7% lower than $\Delta_{vap}H$. There is also good agreement between $\Delta_O^A H$ and the temperature coefficient (Q_D) associated with vegetation-atmosphere partitioning of phenanthrene and pyrene, as reported by Simonich and Hites (1994).

In earlier work with PCBs (Harner and Bidleman, 1996), the more nearly planar, mono-ortho and non-ortho PCBs exhibited greater partitioning into octanol compared to the less planar multi-ortho congeners of the same vapor pressure. In Figure 4, PAHs were added to the $\log_{10}$-$\log_{10}$ plot of K_{OA} against p^o_L for PCBs (Harner and Bidleman (1996)). Values of p^o_L were obtained from references 1-3 in Table 5. From the variability in the p^o_L data, it was inconclusive whether PAHs showed any significant "enrichment" in octanol as was previously observed for mono- and non-ortho PCBs containing more than four chlorine atoms. The symbols in Fig. 4 represent p^o_L values from Yamasaki et al. (1984) and result in the regression line: $\log_{10} K_{OA} = -1.040 \log p^o_L + 6.441$ ($r^2=0.992$).

This comparison cannot presently be made for PCNs since unfortunately there are no reported temperature-dependent values of p^o_L. Instead the log K_{OA} values for PCNs were plotted against congener elution order in Figure 5. There is a clear trend of increasing K_{OA} values with PCN homolog, and within a homolog grouping, K_{OA} values increase with congener retention time. The difference between the 2-Cl and the 6-Cl homologs is a factor of more than 1000. Because of their similar shape and size and wide range of partitioning behavior, PCNs are ideal candidates for studies of particle-gas partitioning, long range transport, and global fractionation, and the octanol-air partition coefficient should be a useful descriptor for these processes.

Conclusions

Measurements of K_{OA} as a function of temperature are reported for 24 PCN congeners and 4 PAHs. Measured values for PAHs exceed values calculated using the Henry's law constant (H) and K_{OW} by a factor of approximately 1.5 to 2. Because of the variability in literature values of p°_{L}, it is difficult to conclude whether PAHs show enhanced partitioning into octanol as was previously observed for coplanar PCBs (Harner and Bidleman, 1996).

The enthalpy of transfer from octanol to air, $\Delta_{O}^{A}H$, for PAHs ranges from 75.5 to 82.9 kJ/mol. This agrees well with the temperature coefficient for vegetation-atmosphere partitioning for PAHs, Q_D, and (except for fluorene) with reported values of the enthalpy of vaporization, $\Delta_{vap}H$.

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Table 1: Mass percent contribution assignments for PCNs in Halowax 1014. (GC-FID chromatogram using DB-5 column)

peak		congener	mass contribution (%)	homolog contribution (%)
Dichloronaphthalenes				0.9
2-1		CN-5 (1,4)	0.85	
Trichloronaphthalenes				9.9
3-1	(3a)	CN-19 (1,3,5)	0.58	
3-2	(3b)	CN-24 (1,4,6) CN-14 (1,2,4)	5.87	
3-5			0.36	
3-6			0.16	
3-7			0.30	
3-10		CN-23 (1,4,5)	2.65	
Tetrachloronaphthalenes				14.0
4-1	(4a)	CN-42 (1,3,5,7)	0.31	
4-6	(4b)	CN-33 (1,2,4,6) CN-34 (1,2,4,7) CN-37 (1,2,5,7)	3.32	
4-7	(4c)	CN-47 (1,4,6,7)	1.26	
4-8		CN-36 (1,2,5,6)	0.40	
4-10	(4d)	CN-28 (1,2,3,5) CN-43 (1,3,5,8)	1.27	
4-14	(4f)	CN-32 (1,2,4,5)	0.32	
4-15	(4g)	CN-35 (1,2,4,8)	1.48	
4-16	(4h)	CN-38 (1,2,5,8)	3.78	
4-18	(4I)	CN-46 (1,4,5,8)	1.90	

Table 1. continued

peak (a)	(b)	congener (c)	mass contribution (%)	homolog contribution (%)
Pentachloronaphthalenes				33.9
5-1	(5a)	CN-52 (1,2,3,5,7) CN-60 (1,2,4,6,7)	3.57	
5-2	(5b)	CN-58 (1,2,4,5,7)	0.32	
5-3	(5c)	CN-61 (1,2,4,6,8)	3.78	
5-4	(5d)	CN-50 (1,2,3,4,6)	0.97	
5-8	(5e)	CN-57 (1,2,4,5,6)	5.57	
5-9	(5f)	CN-62 (1,2,4,7,8)	6.46	
5-10	(5g)	CN-53 (1,2,3,5,8)	4.81	
5-11	(5h)	CN-59 (1,2,4,5,8)	8.41	
Hexachloronaphthalenes				32.4
6-1	(6a)	CN-66 (1,2,3,4,6,7) CN-67 (1,2,3,5,6,7)	0.89	
6-2	(6b)	CN-64 (1,2,3,4,5,7) CN-68 (1,2,3,5,6,8)	3.00	
6-3	(6c)	CN-69 (1,2,3,5,7,8)	7.08	
6-4	(6d)	CN-71 (1,2,4,5,6,8) CN-72 (1,2,4,5,7,8)	13.3	
6-5	(6e)	CN-63 (1,2,3,4,5,6)	3.30	
6-6	(6f)	CN-65 (1,2,3,4,5,8)	4.87	
Heptachloronaphthalenes				4.8
7-1	(7a)	CN-73 (1,2,3,4,5,6,7)	0.92	
7-2	(7b)	CN-74 (1,2,3,4,5,6,8)	3.90	
Octachloronaphthalene				0.1
8	(8)	CN-75 (1,2,3,4,5,6,7,8)	0.13	

(a) labelling scheme used in this work. (b) labelling used in Järnberg et al., 1993, 1997. (c) peaks identified by Imagawa et al., 1993 and Falandysz et al., 1996a.

Table 2: Results for PAHs and PCNs (K_{OA} ± S.D.)

PAHs	0 °C, (n=5)	10 °C, (n=9)	20 °C, (n=7)	30 °C, (n=4)	40 °C, (n=3)
fluorene	$(1.36\pm0.27)\times10^{8}$	$(3.17\pm0.60)\times10^{7}$	$(1.35\pm0.48)\times10^{7}$	$(3.28\pm0.77)\times10^{6}$	$(1.24\pm0.09)\times10^{6}$
phenanthrene	$(6.43\pm1.02)\times10^{8}$	$(1.85\pm0.09)\times10^{8}$	$(7.89\pm2.31)\times10^{7}$	$(2.62\pm0.08)\times10^{7}$	$(8.44\pm0.66)\times10^{6}$
pyrene	$(9.24\pm1.89)\times10^{9}$	$(3.37\pm0.29)\times10^{9}$	$(1.43\pm0.53)\times10^{9}$	$(3.52\pm0.78)\times10^{8}$	$(1.32\pm0.05)\times10^{8}$
fluoranthene	n.d.	n.d.	$(1.33\pm0.25)\times10^{9}$	$(4.49\pm1.06)\times10^{8}$	$(1.45\pm0.35)\times10^{8}$

note: for fluoranthene at (20, 30 and 40) °C, n= 5,4 and 2 respectively; n.d.=not determined.

PCNs	10 °C, (n=1)	20 °C, (n=5)	30 °C, (n=2)	40 °C, (n=3)	50 °C, (n=3)
2-1	3.34×10^{7}	$(1.36\pm0.24)\times10^{7}$	5.20×10^{6}	$(2.40\pm0.28)\times10^{6}$	$(1.35\pm0.20)\times10^{6}$
3-1	9.24×10^{7}	$(4.25\pm0.78)\times10^{7}$	1.10×10^{7}	$(4.61\pm0.63)\times10^{6}$	$(2.39\pm0.05)\times10^{6}$
3-2	8.04×10^{7}	$(3.53\pm0.86)\times10^{7}$	1.08×10^{7}	$(4.38\pm0.37)\times10^{6}$	$(2.29\pm0.01)\times10^{6}$
3-10	1.73×10^{8}	$(7.09\pm1.63)\times10^{7}$	1.94×10^{7}	$(7.64\pm0.87)\times10^{6}$	$(3.92\pm0.09)\times10^{6}$
4-6	6.14×10^{8}	$(2.29\pm0.45)\times10^{8}$	6.57×10^{7}	$(2.47\pm0.32)\times10^{6}$	$(1.22\pm0.03)\times10^{7}$
4-7	7.00×10^{8}	$(2.62\pm0.56)\times10^{8}$	7.38×10^{7}	$(2.69\pm0.36)\times10^{6}$	$(1.32\pm0.03)\times10^{7}$
4-14	n.d.	$(7.36\pm1.69)\times10^{8}$	1.97×10^{8}	$(7.60\pm0.70)\times10^{7}$	$(3.31\pm0.09)\times10^{7}$
4-15	1.46×10^{9}	$(4.90\pm1.22)\times10^{8}$	1.38×10^{8}	$(4.88\pm0.62)\times10^{7}$	$(2.32\pm0.04)\times10^{7}$
4-16	1.38×10^{9}	$(5.00\pm1.28)\times10^{8}$	1.39×10^{8}	$(4.84\pm0.59)\times10^{7}$	$(2.30\pm0.05)\times10^{7}$
4-18	1.54×10^{9}	$(5.62\pm1.77)\times10^{8}$	1.55×10^{8}	$(5.30\pm0.55)\times10^{7}$	$(2.49\pm0.05)\times10^{7}$

Table 2 continued

5-1	3.18×10^{9}	$(1.10\pm0.37)\times10^{9}$	2.92×10^{8}	$(9.29\pm1.07)\times10^{7}$	$(4.29\pm0.10)\times10^{7}$
5-2	4.30×10^{9}	$(1.47\pm0.41)\times10^{9}$	3.92×10^{8}	$(1.27\pm0.14)\times10^{8}$	$(5.69\pm0.12)\times10^{7}$
5-3	3.44×10^{9}	$(1.29\pm0.47)\times10^{9}$	3.33×10^{8}	$(1.01\pm0.07)\times10^{8}$	$(4.64+0.05)\times10^{7}$
5-4	5.54×10^{9}	$(1.59\pm0.52)\times10^{9}$	4.22×10^{8}	$(1.31\pm0.17)\times10^{8}$	$(5.67\pm0.09)\times10^{7}$
5-5	1.20×10^{10}	$(3.02\pm0.99)\times10^{9}$	6.37×10^{8}	$(2.00\pm0.43)\times10^{8}$	$(8.13\pm0.31)\times10^{7}$
5-9	6.41×10^{9}	$(2.65\pm1.11)\times10^{9}$	6.77×10^{8}	$(1.88\pm0.07)\times10^{8}$	$(8.59\pm0.13)\times10^{7}$
5-10	9.40×10^{9}	$(2.74\pm1.01)\times10^{9}$	7.20×10^{8}	$(2.18\pm0.33)\times10^{8}$	$(9.06\pm0.05)\times10^{7}$
5-11	n.d.	$(3.11\pm1.35)\times10^{9}$	7.78×10^{8}	$(2.25\pm0.17)\times10^{8}$	$(9.57\pm0.19)\times10^{7}$
6-1	3.77×10^{10}	$(1.03\pm0.27)\times10^{10}$	2.90×10^{9}	$(6.88\pm0.31)\times10^{8}$	$(2.65\pm0.07)\times10^{8}$
6-2	n.d.	$(1.18\pm0.30)\times10^{10}$	3.73×10^{9}	$(8.92\pm0.21)\times10^{8}$	$(3.48\pm0.09)\times10^{8}$
6-3	n.d.	$(1.23\pm0.24)\times10^{10}$	4.13×10^{9}	$(9.73\pm0.22)\times10^{8}$	$(3.71\pm0.10)\times10^{8}$
6-4	n.d.	$(1.38\pm0.48)\times10^{10}$	4.68×10^{9}	$(1.13\pm0.11)\times10^{9}$	$(4.08\pm0.18)\times10^{8}$
6-5	n.d.	$(2.12\pm0.46)\times10^{10}$	8.81×10^{9}	$(2.22\pm0.28)\times10^{9}$	$(7.49\pm0.51)\times10^{8}$
6-6	n.d.	$(4.19\pm1.78)\times10^{10}$	1.61×10^{10}	$(3.62\pm0.77)\times10^{9}$	$(1.08\pm0.08)\times10^{9}$

n.d.= not determined.

Table 3: **Regression parameters for Eq. 7 (PAHs) and measured versus calculated K_{OA} values at 25 °C.**

compound	r^2	A	B	range (°C)	log K_{OW}[a]	H ($Pa.m^3mol^{-1}$)	log K_{OA} (calc.)	log K_{OA} (meas.)	factor difference
PAHs									
fluorene	0.995	-7.74	4332	0 to 40	4.18a	9.75[b]	6.59	6.79	1.58
phenanthrene	0.996	-5.62	3942	0 to 40	4.57a	3.61[b]	7.41	7.57	1.45
pyrene	0.990	-4.56	3985	0 to 40	5.18a	1.21[b]	8.49	8.80	2.04
fluoranthene	0.999	-5.94	4417	20 to 40	5.22a	1.04[c]	8.60	8.88	1.91

[a] Miller et al., 1985; [b] Shiu and Mackay, 1997; [c] Mackay et al., 1992

Table 4: Regression parameters for Eq. 7 (PCNs) and K_{OA} values at 25 °C.

compound	r^2	A	B	range (°C)	log K_{OA}
PCNs					
2-1	0.997	-3.97	3248	10 to 50	6.93
3-1	0.990	-5.39	3786	"	7.32
3-2	0.995	-4.98	3651	"	7.27
3-10	0.994	-5.52	3896	"	7.56
4-6	0.996	-5.34	4000	"	8.08
4-7	0.996	-5.49	4059	"	8.13
4-14	0.991	-5.73	4263	20 to 50	8.58
4-15	0.997	-5.70	4206	"	8.41
4-16	0.997	-5.62	4181	"	8.40
4-18	0.997	-5.66	4206	"	8.45
5-1	0.997	-6.02	4394	"	8.73
5-2	0.997	-5.92	4404	"	8.86
5-3	0.996	-6.05	4417	"	8.78
5-4	0.998	-6.63	4629	"	8.91
5-5	0.996	-7.78	5044	"	9.15
5-9	0.994	-5.88	4452	"	9.06
5-10	0.996	-6.59	4684	"	9.13
5-11	0.995	-6.96	4811	20 to 50	9.18
6-1	0.998	-7.09	5003	"	9.70
6-2	0.996	-6.77	4939	20 to 50	9.80
6-3	0.995	-6.64	4909	20 to 50	9.83
6-4	0.996	-6.63	4923	20 to 50	9.89
6-5	0.990	-5.55	4666	20 to 50	10.11
6-6	0.987	-6.54	5040	20 to 50	10.37

Table 5. Comparison of $\Delta_{vap}H$ and $\Delta_{\sigma}^{A}H$ and Q_D for PAHs.

compound	$\Delta_{\sigma}^{A}H$	$\Delta_{vap}H$	(4)Q_D
	kJ/mol	kJ/mol	kJ/mol
fluorene	82.9	65.3 (1), 69.5 (2)	n.d.
phenanthrene	75.5	72.8 (1), 76.2 (2), 71.1 (3)	81.8
pyrene	76.3	72.0 (1), 86.7 (2), 78.6 (3)	79.4

1. heat of sublimation for the solid, converted to heat of vaporization for the liquid using the experimentally determined heat of fusion. Literature values from articles cited in Bidleman, Anal. Chem. 56:2490-2496 (1984) and Hinckley et al., J. Chem. Eng. Data 35:232-237 (1990).

2. enthalpy of vaporization determined by GC. Yamasaki et al. (1984).

3. enthalpy of vaporization determined by GC. Hinckley et al. (1990).

4. temperature coefficient of PAH-vegetation binding. Simonich and Hites (1994), n.d.= not determined.

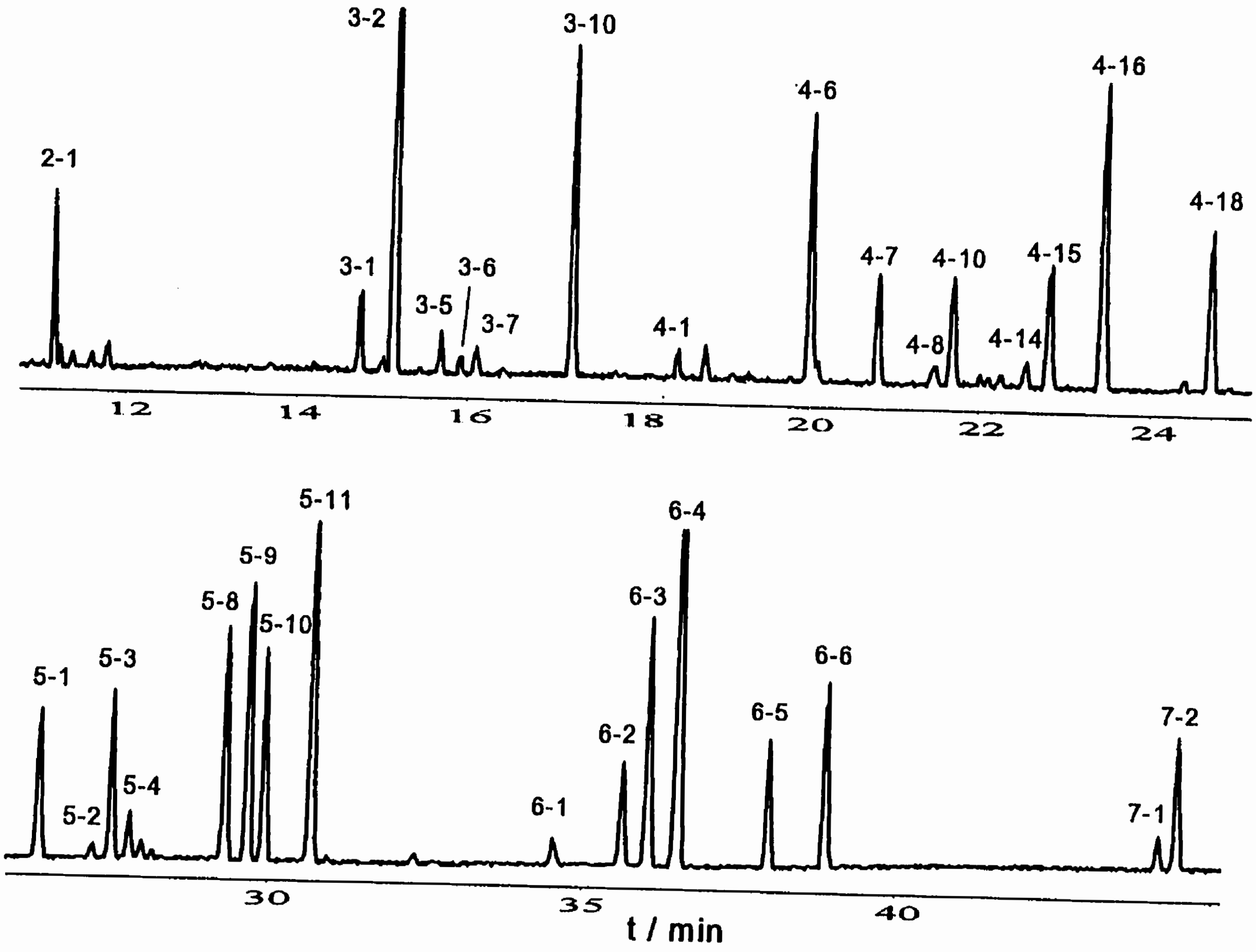

Figure 1. GC-FID chromatogram of Halowax 1014 with major PCN peaks identified (see Table 1), 60 m, DB5-MS column.

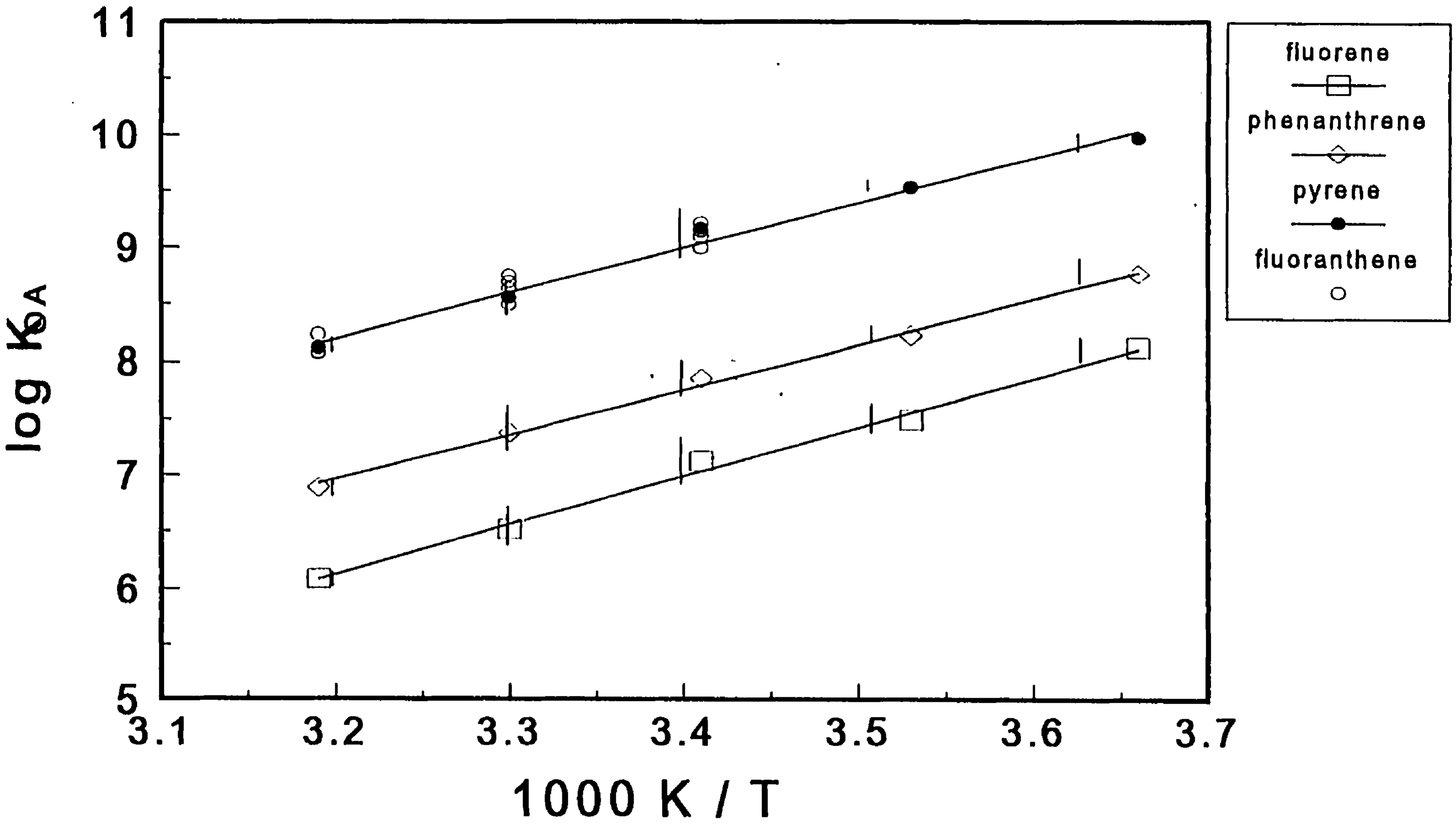

Figure 2. Summary of K_{OA} results for PAHs over the temperature range (0 to 40) °C, plot of eq 7. Symbols and bars represent mean and range of values for fluorene, phenanthrene and pyrene; single data points are plotted for fluoranthene at (20, 30 and 40) °C.

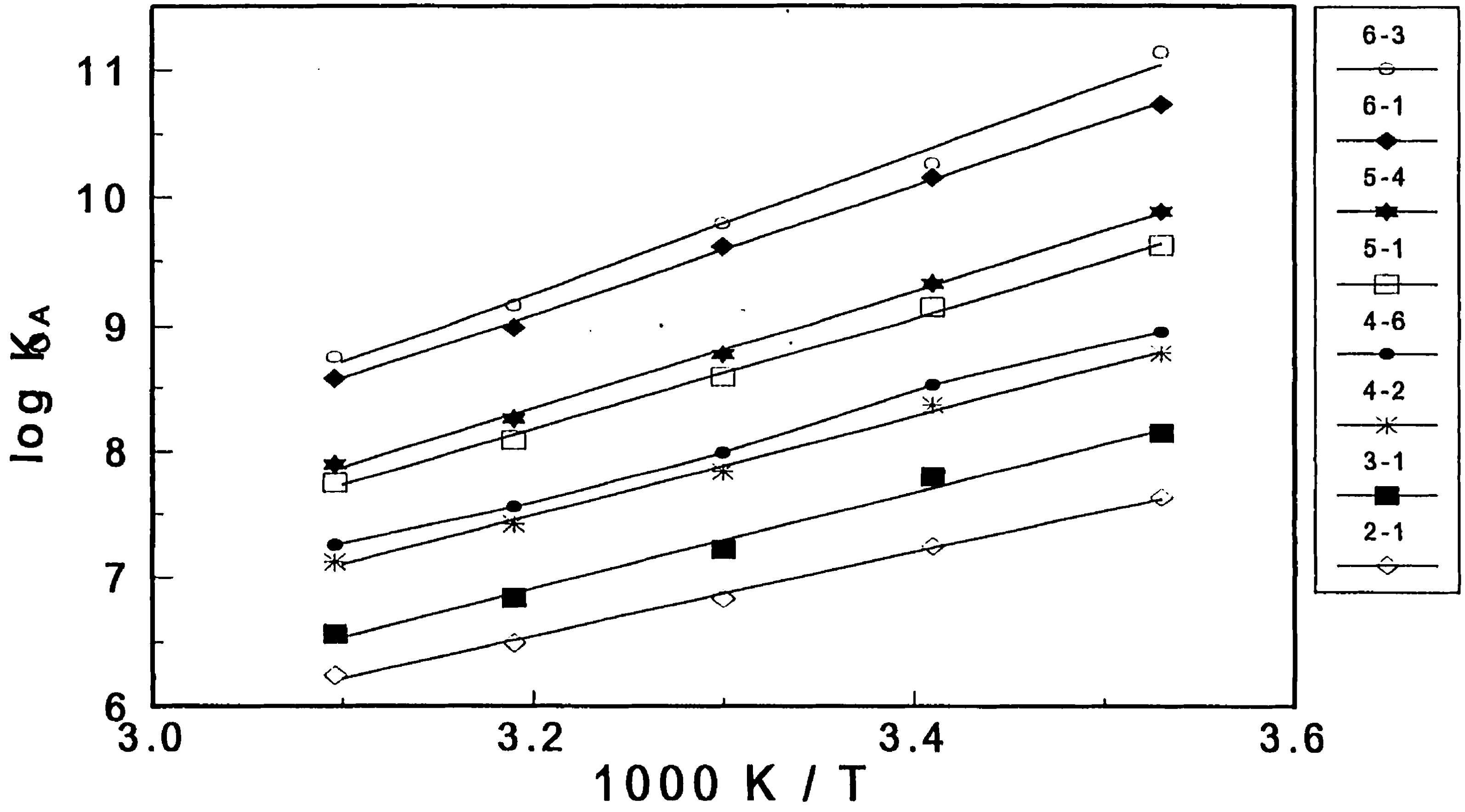

Figure 3. Selected K_{OA} results for PCNs over the temperature range (10 to 50) °C, plot of eq 2.

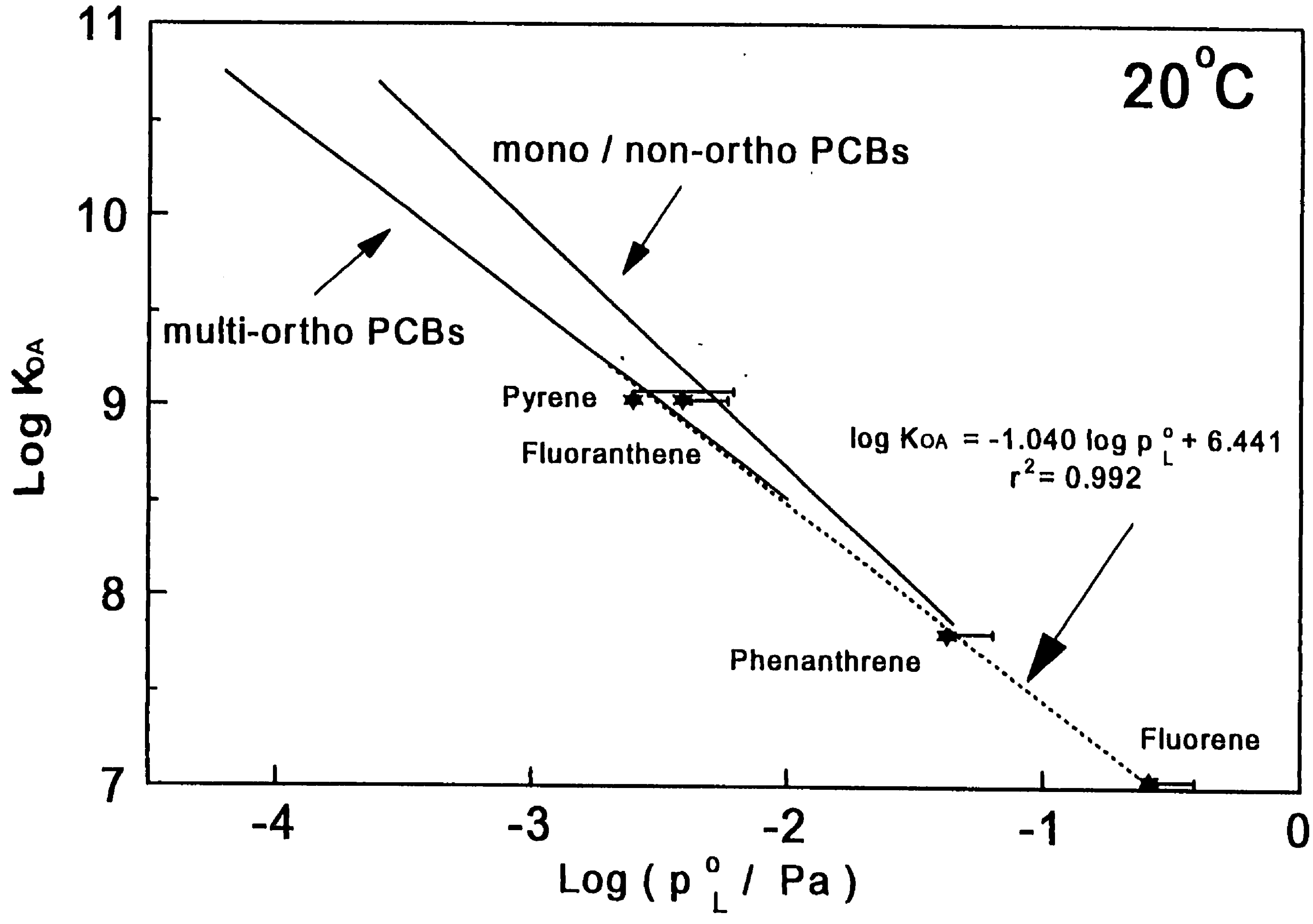

Figure 4. $\log_{10}$-$\log_{10}$ correlation of K_{OA} against p^0_L at 20 °C for mono/non-ortho PCBs, multi-ortho PCBs, and PAHs. Range bars represent variability in literature values of p^0_L. Symbols and regression line are for data from Yamasaki et al. (1984).

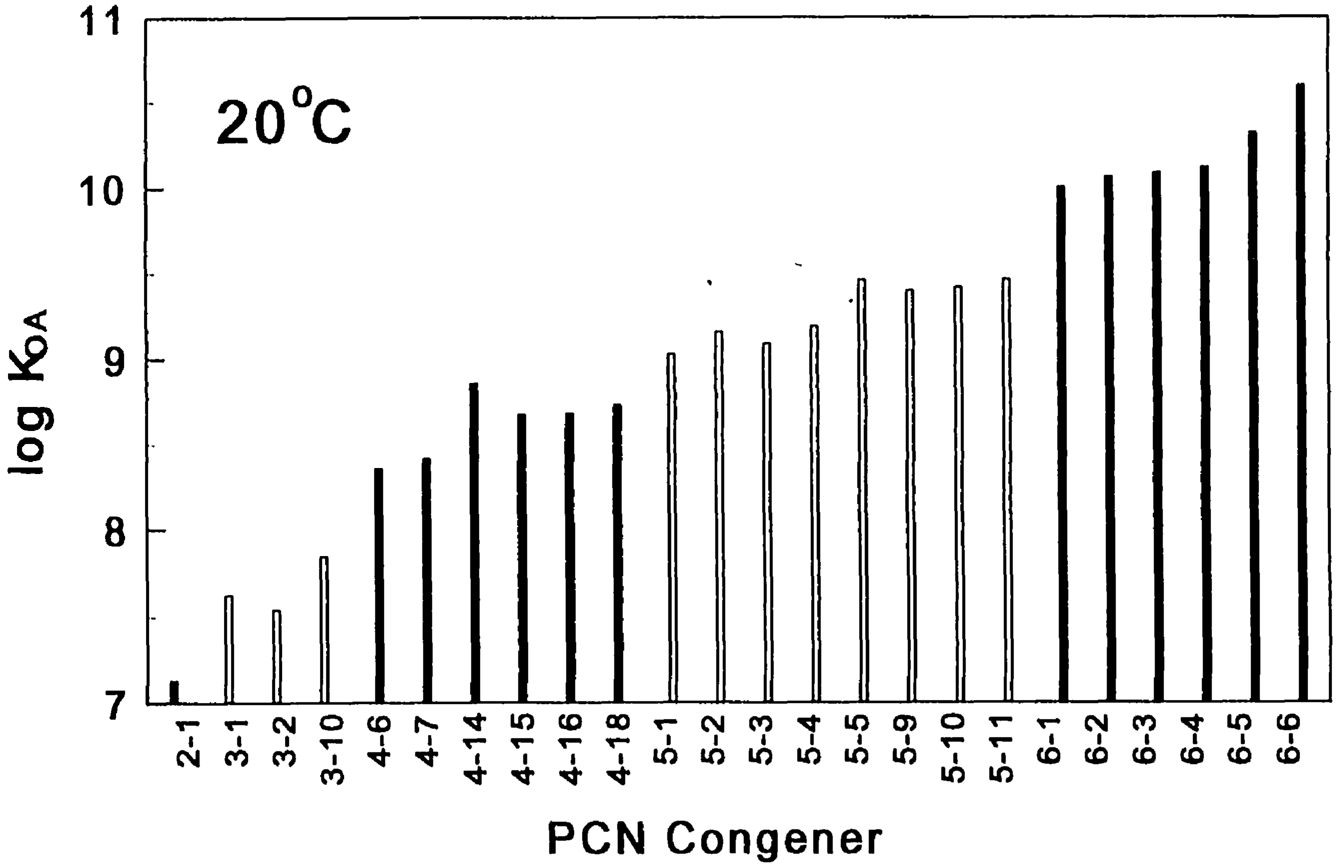

Figure 5. Plot of $\log_{10}$ K_{OA} values for PCN congeners at 20 °C.

<u>Paper III:</u> Octanol-Air Partition Coefficient (K_{OA}) for Describing Particle-Gas Partitioning of Aromatic Compounds in Urban Air

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Abstract

Atmospheric concentrations and particle/gas partition coefficients were measured for PAHs, PCBs and PCNs in urban Chicago in Feb./Mar. 1995. Average (n=15) concentrations (pg m^{-3}) were: ΣPAH=58 000, ΣPCB=350 and ΣPCN=89. The partitioning of these compounds between the particle phase and the gas phase was investigated and modeled according to the adsorption (Junge-Pankow) approach, which utilizes the sub-cooled liquid vapor pressure (p^o_L) as a fitting parameter, and the K_{OA} absorption model approach. The K_{OA} model was able to resolve differences between ortho-chlorine PCB substitutions which correlations against p^o_L were not able to explain. Partitioning of PCNs was also well described by the K_{OA} model. Sorption of PAHs to particles agreed with both models when the wind was predominantly from the S-W sector. For samples containing mostly N-E sector air, PAHs showed particle phase enrichments relative to the chlorinated aromatics in log-log plots of the particle/gas partition coefficient, K_P versus p^o_L. Enrichment factors calculated as $K_{P\,(PAH)}$ / $K_{P\,(multi\text{-}ortho\ PCB)}$ were 27-100 from the N-E sector compared to 2-4 for the S-W sector. This suggests source region effects on K_P for PAHs. It is hypothesized that the enrichment may be due to non-exchangeable PAHs trapped inside combustion aerosols or a result of a slow re-equilibration of these aerosols as they are diluted in ambient air.

Introduction

Atmospheric transport and particle deposition is an important pathway for the movement of contaminants from urban and industrial centers to nearby lakes *(1-4)* and far away regions such as the Arctic *(5,6)*. Semivolatile compounds of concern include PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), and PCNs (polychlorinated naphthalenes) which partition appreciably onto atmospheric particulate matter.

Conventional models of particle/gas partitioning assume that chemical adsorbs to active sites on the surface of the particle. The particle/gas partition coefficient (K_P) is usually plotted on a log-log scale versus the subcooled liquid vapor pressure (p^o_L) of the compound *(7-9,4,5)* and the resulting correlations are often quite good. A disadvantage however, is that different correlations are found among compound classes and even within a compound class different trends are sometimes observed. For instance, Falconer et al. *(10)* showed enhanced partitioning (K_P values) for non-ortho (coplanar) PCBs relative to multi-ortho PCBs having the same p^o_L value.

An alternate absorption model *(11,12)* considers that atmospheric aerosols are coated with a lipid-like organic film. Hence, it is likely that an important aspect of particle/gas partitioning is absorption of chemical into this organic phase. Liang and Pankow *(13)* found that partitioning of semivolatile compounds to environmental tobacco smoke (almost entirely organic carbon) and urban air particulate matter (~10-20% organic carbon) was nearly the same when normalized to the organic carbon content of the aerosol. Odum et al. *(14)* modeled the mass transfer of semivolatile organics in and out of combustion aerosols which they described as a solid core coated with a viscous, organic layer.

For several years, K_{OA} has been used to describe plant/air partitioning *(15-17)* but only recently has it been demonstrated to be a useful descriptor of particle/gas partitioning *(18)*. This paper compares the Junge-Pankow adsorption model with the K_{OA}-based absorption model for describing the particle/gas partitioning of PCBs, PCNs, and PAHs in air samples collected in urban Chicago (February-March, 1995).

Experimental

Collection of Air Samples

Air samples (n=15) were collected in Chicago approximately 2 km inland from the shore of Lake Michigan on the roof of Farr Hall, Illinois Institute of Technology (IIT), in February/March 1995. A high volume sampling train consisting of double glass fiber filters (20 × 25 cm, Gelman A/E) followed by two polyurethane foam (PUF) plugs was used. All PUF plugs were pre-cleaned by soxhlet extraction with acetone (24 h) followed by a second extraction with petroleum ether (24 h) and dried in a vacuum desiccator at ~40 °C *(19)*. Filters were baked at 400 °C for 12 h and then wrapped in aluminum foil and sealed in air-tight plastic bags prior to sample collection. PUFs were stored in glass jars with teflon lined lids before and after sample collection.. Used PUF plugs and glass fiber filters were stored at -10 °C until they were ready to be analyzed.

Chicago samples were taken over 12 h day or night periods to avoid diurnal temperature variations and thereby minimize filtration artifacts. Meteorological data were provided by the Illinois State Water Survey monitoring stations at Farr Hall and Indiana Dunes National Lakeshore near the southern tip of Lake Michigan. Collection information is summarized in Table 1.

A separate sampling train consisting of a single glass fiber filter and two PUF plugs was used for total suspended particle determinations (TSP, μg particles m^{-3} air). The filters were preweighed after equilibration in a constant humidity chamber for 48 h at 20 °C over a saturated sodium chloride solution. The same procedure was used after sampling to ensure that any changes in filter mass were only attributed to particulate matter and not to differences in water content.

Analytical Methods

Air samples were analyzed for PCBs, PCNs, and PAHs. Concentrations of PCNs in air are reported in a previous paper *(20)*. Polyurethane foam plugs were spiked with a solution containing a mixture of $^{13}C_{12}$-labelled mono- and non-ortho PCBs - 77, 81, 105, 114, 126, 156 and 169 - and then soxhlet extracted overnight with petroleum ether (PE) or hexane. Filters were also spiked and extracted for the same time period using dichloromethane (DCM). After volume reduction to 2 mL and transfer to isooctane the samples were fractionated on a column containing 3 g silicic acid (3% added water) topped with 2 g neutral alumina. The column was prewashed with 25 mL DCM followed by 25 mL PE. The sample was applied, PCNs/PCBs were eluted in the first fraction (F1) with 20 mL PE and the PAHs were eluted in the second fraction (F2) with 20 mL DCM. Both fractions were reduced by blowing down with a stream of nitrogen.

After an additional cleanup by shaking with 18M sulfuric acid, F1 was reduced to 1 mL and further fractionated on a mini-column containing AX-21 activated carbon mixed 1:20 with silicic acid (SA) prepared as described by Falconer et al. *(10)*. The carbon-SA mix (100 mg) was sandwiched between 50-mg layers of SA in a disposable pasteur pipet containing a small plug of glass wool at the lower end. The column was prewashed with 5 mL toluene followed by 5 mL 30% DCM in cyclohexane. The first fraction (F1-1) was eluted with 5 mL 30% DCM in cyclohexane and contained the multi- and mono-ortho PCBs. The second fraction (F1-2) was eluted with 5 mL toluene and contained mono-ortho PCBs (mono-ortho PCBs were split between F1-1 and F1-2), PCNs and non-ortho (coplanar) PCBs. Both fractions were reduced to 0.2-0.4 mL and F1-1 was transferred to isooctane.

Analysis

<u>PCNs</u>

PCNs in fraction F1-2 were quantified by GC-negative ion mass spectrometry (GC-NIMS) in selected ion mode (SIM) using NIMS response factors derived from the weight percentages of the individual congeners or congener groups in Halowax 1014, a commercial mixture of PCNs (Reference standard, EPA-Research Triangle Park, NC). A more detailed account of the quantification procedure is found elsewhere (Harner and Bidleman, 1997a). Ions monitored in SIM mode were (target, qualifier) 3-Cl: 232, 230; 4-Cl: 266, 264; 5-Cl: 300, 298; 6-Cl: 334, 332; 7-Cl: 368, 366; 8-Cl: 404, 402. The criterion for acceptance was a target/qualifier ion ratio within ±20% of the standard. Capillary gas chromatography (GC) was carried out with Hewlett-Packard 5890 instruments equipped with either a 30 m DB-5 or DB-5MS column (J&W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness, operated with hydrogen carrier gas at 50 cm s^{-1}. Injections (1 μL) were splitless with split opened after 0.5 minutes and the injector at 250 °C. The temperature program was 90 °C for 0.5 min., 10 °C min^{-1} to 160 °C, 2 °C min^{-1} to 250 °C. Other operating conditions were: transfer line 250 °C, ion source 150 °C, quadrupole 100 °C, and methane reagent gas at ~1.0 Torr.

PCBs

PCBs were analyzed in two steps. First, total PCB concentrations were determined from fraction F1 of the silicic acid column. PCB congeners were quantified against a PCB mixture which was prepared from solutions of 56 individual congeners (Accustandard, New Haven, CT 06511). Tribromobiphenyl (Accustandard) was used as the internal standard for volume correction. Quantification was carried out using a Hewlett Packard gas chromatograph (5890) equipped with an electron capture detector. Peaks were separated on a 60 m DB-5 column (J&W Scientific, 0.25 mm i.d., 0.25 μm film thickness) operated with hydrogen carrier gas at 50 cm s^{-1}. Sample injections (1 μL) were splitless with split opened after 0.5 minutes and the injector at 250 °C. The temperature program was 90 °C for 0.5 min, 10 °C min^{-1} to 160 °C, 2°C min^{-1} to 250 °C with the electron capture detector at 300 °C.

Analysis of the mono- and non-ortho PCBs in carbon column fractions F1-1 and F1-2 was performed by GC-NIMS in SIM mode. Ions monitored were (target, qualifier): PCBs-81 77 (292, 290); PCBs-118, 114, 105, 126 (326,324); PCBs-156, 169 (360,358); $^{13}C_{12}$-PCBs- 81, 77 (304, 302); $^{13}C_{12}$-PCB-126 (338, 336); $^{13}C_{12}$-PCB-105 (340, 338); $^{13}C_{12}$-

PCB-169 (372,370). Ions 289 and 291 were monitored for PCB-103 which was used as the internal standard for volume correction. GC and MS conditions and temperature program were the same as used for the analysis of PCNs.

PAHs

Samples (n=15) were analyzed by GC/MS using electron impact (GC-EIMS) with the source at 200 °C and quadrupole at 100 °C. GC conditions were the same as reported for PCNs. Quantification was performed using a calibration solution of 16 PAH compounds (EPA method 610/8310, AXACT, Commack, NY 11725). Deuterated chrysene (Cambridge Isotope Laboratories, Andover, Massachusetts 01810-5413) was added as internal standard for volume correction. Ions monitored were (target, qualifier): fluorene (166, 165), phenanthrene, anthracene (178, 176), fluoranthene, pyrene (202, 200), chrysene-d_{12} (240, 241), benz(a)anthracene, chrysene (228, 226), benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene (252, 250), indeno(1,2,3-cd)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene (276, 138).

Results and Discussion

Quality Control

At the sampling site, several PUF plugs and filters were spiked with PCNs (Halowax 1014) and a standard solution of 56 PCB congeners. All samples, including spikes, were fortified prior to extraction with a surrogate standard solution containing several mono-ortho and non-ortho $^{13}C_{12}$-labelled PCBs. The surrogate was applied to PUFs which were contained in the soxhlet apparatus just prior to extraction. In the case of the filters the surrogate was applied in small drops to the surface of the filter which was then cut into 1cm wide strips and placed in the flask of the soxhlet apparatus. PUF recoveries for PCBs and PCNs were 80-120% and 50-80% respectively. Filter recoveries were of similar magnitude for the higher molecular weight congeners but substantially lower for the lower molecular weight PCBs (2-Cl and 3-Cl) and PCNs (3-Cl and 4-Cl). Subsequent laboratory tests attributed these low recoveries to evaporative losses when the surrogate was applied to the surface of the filter. Hence, PUF surrogate recoveries were used for both PUF and filter samples.

F1 from the silicic acid column was reduced to 1 mL and analyzed by GC-ECD for all PCBs. Spike recoveries for this fraction ranged from 80-120%. Carbon column fractions F1-1 and F1-2 were reduced to approximately 0.2 mL to increase the detectability. Evaporative losses for the mono- and non-ortho PCBs were accounted for by the recovery factors for $^{13}C_{12}$-labelled PCB-81, 77, 126 and 169 and PCB-105, which were specific to each sample. Recoveries of these ranged from 50-85%. Recoveries for PCNs ranged from 50 % for the 3-Cl congeners to 80% for the heavier congeners. Method recoveries for PAHs were determined by spiking clean PUF plugs with the PAH standard solution and then treating the PUF as a sample. PAHs were contained in fraction F2 of the silicic acid separation and mean (n=3) recoveries were: fluorene 72 ± 11%, phenanthrene 93 ± 8%, anthracene 93 ± 6%, fluoranthene 100 ± 8%, pyrene 95 ± 7%, benz(a)anthracene 87 ± 6%, chrysene 99 ± 8%, benzo(b)fluoranthene 75 ± 7%, benzo(k)fluoranthene 83 ± 9%, benzo(a)pyrene 72 ± 5%, indeno(1,2,3-cd)pyrene 73 ± 5%, dibenz(ah)anthracene 67 ± 7% and benzo(ghi)perylene 82 ± 8%.

Quantities of semi-volatile compounds on back PUF plugs were used to correct the samples for blanks. These were expressed as concentrations by dividing by the sample air volume. Field blanks were also collected at the sample location by periodically placing a clean PUF plug in the sample train and then restoring it to the glass sample jar. The larger of these two blank values was used for sample correction. Limit of detection values (L.O.D.= blank + 3 s.d.) for the different compound classes were: PAHs 0.01-0.1 ng m^{-3}, PCBs 0.03-3 pg m^{-3}, and PCNs approximately 0.025 pg m^{-3}. Since PCNs were virtually non-detectable in the blanks, L.O.D. values were calculated based on the area of the smallest peak that could be integrated. Samples exceeding L.O.D. values were corrected for average blanks and method recovery factors.

Average (n=6) recoveries of 10 PCBs and 11 PAHs from NIST urban dust standard reference material 1649 (National Institute of Standards and Technology, Gaithersburg, Maryland 20899) were 84-125% for PCBs (using NIST values from Shantz et al. *(21)*) and 42-127% for PAHs (using NIST values from Wise et al. *(22)*). Individual recoveries are listed: PCB-28 84 ± 18% ; PCB-31 114 ± 20%; PCB-52 86 ± 8%; PCB-101 125 ± 8%; PCB-105 126 ± 11%; PCB-118 86 ± 7%, (GC-MS, 110 ± 9%); PCB-138/137 84 ± 4%; PCB-153 98 ± 5%; PCB-156 91 ± 11%; PCB-180 99 ± 2%; phenanthrene 49 ± 3%; anthracene 64 ± 17%; fluoranthene 42 ± 3%; pyrene 47 ± 3%; benz(a)anthracene 57 ± 3%; chrysene 58 ± 5%; benzo(b)fluoranthene 122 ± 13%; benzo(k)fluoranthene 128 ± 21%; benzo(a)pyrene 97 ± 18%; indeno(1,2,3,cd)pyrene 101 ± 22%; benzo(ghi)perylene 85 ± 14%.

Ambient Air Concentrations - PAHs, PCBs,and PCNs

Atmospheric concentrations of PAHs, PCBs and PCNs in Chicago are listed in Table 1, with corresponding average mass percent distributions summarized in Figure 1.

Levels of PAHs were the highest of the three compound classes, with mean ΣPAH = 57.9 ng m^{-3}. The mass distribution was dominated by fluorene, phenanthrene, fluoranthene and pyrene while other PAHs individually accounted for less than 2% of the total (Fig. 1). These data are approximately a factor of three lower than measurements taken in a heavily industrialized region of Chicago in February, 1988 *(9)* and are in the same range as reported by Simcik et al. *(23)* (i.e. ΣPAH = 51-162 ng m^{-3}) for air samples collected at the IIT site three weeks prior to this study.

The average value for ΣPCB in Chicago was 350 pg m^{-3}. Again, PCB levels were about five times lower than previous measurements taken near a more heavily industrialized region in Chicago *(9)* and within the same range (i.e. 270-910 pg m^{-3}) as values reported by Simcik et al. *(23)*. The mass profile of PCBs in Chicago was typical of urban air and was dominated by the tri- and tetra-chlorinated biphenyls.

Results for PCNs represent the first reported air concentrations for this class of compounds near the Great Lakes *(20)*. The average value for ΣPCN was 89 pg m^{-3}. The air profile was dominated by the 3-, 4- and 5-chlorinated (Cl) congeners as shown in Fig. 1, where the first number represents the homolog group (3-Cl, 4-Cl, etc) and the second is its elution order within that group on a DB-5 column. Identities of individual congeners are given by Harner and Bidleman *(20,24)*. One of the 3-Cl congeners (2,4,6-trichloronaphthalene) accounted for more than 40% of the total mass. This may reflect the large market share (65%) of the technical mixtures Halowax 1001 and 1099 which consist of 80% 3- and 4-Cl congeners.

Several PCNs exhibit dioxin-like toxicity. These include PCN-42 (4-1), PCN-52+60 (5-1) and PCN-66+67 (6-1). Mean values for these congeners in Chicago air (pg m^{-3}) were (4-1) 1.06 ± 0.69, (5-1) 1.44 ± 0.73, and (6-1) 0.32 ± 0.36. These levels are about an order of magnitude greater than mean concentrations of coplanar PCBs; PCB-77=0.43, PCB-126=0.061, and PCB-169 <0.030 pg/m^3 . Hanberg et al. *(25)* reports TCDD toxic equivalence factors for PCNs and coplanar PCBs {i.e. 0.0005 (PCB-77), 0.1 (PCB-126), 0.005 (PCB-169) and 0.002 (6-1, i.e. PCN-66+67)}. Based on these values and the respective concentrations of these compounds in Chicago air, it is estimated that the TCDD toxicity of PCN-66+67 is 2-5 times greater than the values for PCB-77 and PCB-169 and represents approximately 8% of the toxicity attributable to PCB-126 *(20)*. The contribution of the bioaccumulating PCNs may be higher if PCN-42, PCN-52 and other PCNs were included but TCDD toxic equivalence factors have not been assigned for these compounds.

Particle-Gas Partitioning of PAHs, PCBs and PCNs in Chicago Air

Semivolatile aromatics such as PAHs, PCBs and PCNs are present in the gas phase and attached to particles. It is a common practice to describe the phase distribution using the particle-gas partition coefficient, $K_P = C_p / C_g$ *(4,26,27,9)* The fraction (ϕ) of compound in the particle phase is:

$$\phi = C_p(TSP) / [C_g+C_p(TSP)] = K_P\,(TSP) / [1 + K_P\,(TSP)] \qquad (2)$$

where C_p is the concentration on particles (ng/μg particles), C_g is the gas phase concentration (ng/m^3 air), and TSP is the total suspended particle concentration (μg/m^3). To partially correct for adsorption of gaseous compound to the filter, C_p and C_g were calculated from:

$$C_p = (FF\text{-}BF) / \mu g \text{ particles} \qquad (3)$$

$$C_g = (PUF + 2BF) / m^3 \text{ air} \qquad (4)$$

where FF and BF are the quantities of chemical on the front and back glass fibre filters and PUF is the quantity found on the polyurethane foam plug *(28,27,9)*.

The particle-gas partition coefficient is often correlated with the subcooled liquid vapor pressure ($p^o{}_L$) using eq. 5.

$$\log K_P = m \log p^o{}_L + b \qquad (5)$$

Under equilibrium conditions and for compounds of the same class, the expected slope (m) of eq. 5 is -1. Interpretation of the intercept term (b) depends on the assumed mechanism of particle-gas interaction. If compounds are adsorbed to active sites on the particle surface, b is related to the specific surface area of the particle and the excess heat of desorption from the particle surface *(7,26)*. If the mechanism is absorption into a liquid-like film on the aerosol, b depends on the fraction of organic matter in the particle that is involved in the partitioning process and the activity coefficient of the compound in the organic film *(11)*. Sampling artifacts and/or non-equilibrium conditions may lead to values of $m \neq 1$ *(8,9)*.

Figure 2 (A series) shows log-log plots of K_P versus p°_L for PAHs (FE, PH, FLA, PY) and PCBs in Chicago air. PCNs are not included since no congener-specific vapor pressure data are available. The plots show enhanced sorption to the particle phase for PAHs and non-ortho (coplanar) PCBs relative to the multi-ortho PCBs. The correlations are made using liquid-phase vapor pressures from Falconer et al. *(20)* for PCBs and Yamasaki et al. *(30)* for PAHs. Both sets of vapor pressures are based on GC retention data. The enhancement of PAHs over PCBs is greater if the PAH vapor pressures of Hinckley et al. *(31)* are used. The latter are based on GC-retention data or conversion of solid- to liquid-phase vapor pressures, and are ~2-3 times higher than Yamasaki's values.

The reason for this enhancement is not clear. A possibility for PAHs is that during their formation in combustion some PAHs become bound within the particle and are non-exchangeable with the atmosphere. Some of this PAH pool may be extracted during analysis, however. The "non-exchangeable" effect usually causes curvature in plots of eq. 5 *(28,32)* although the number of PAH points in Figure 2A is insufficient to see this effect if it were present. PCBs, on the other hand, are likely to partition onto particles already present in air and may more easily approach a true equilibrium. In other words, the discrepancy between PAHs and PCBs may be explained by their being bound in different ways or even to different types of particles, with the PAHs skewed toward particles originating from combustion sources. The heat of desorption from the particle surface may also be greater for PAHs than PCBs *(7)*.

Figure 3a shows that the largest K_P enrichment factors (EFs) for PAHs (i.e. EF = $K_{P\,(PAH)}$ / $K_{P\,(\text{multi-ortho PCB})}$) were found for samples which contained more than 50% contribution of air from the N-E sector (315° - 135°) (n=9). This sector represents downtown Chicago. Geometric mean K_P EF values for air containing greater than 50% N-E sector air were: fluorene (60), phenanthrene (30.2), fluoranthene (18.1) and pyrene (16.5). For 100% N-E sector air (n=4) the K_P EF values were: fluorene (100), phenanthrene (47.4), fluoranthene (27.8) and pyrene (27.1).

In contrast, much smaller particle phase enrichments were observed for PAHs in air originating from the S-W sector (135° - 315°). This sector represents a mix of residential and heavily industrial regions. Geometric mean K_P EF values for samples containing >50% S-W sector air (n=6) were: fluorene (2.4), phenanthrene (2.2), fluoranthene (3.8) and pyrene (3.0). For 100% S-W sector air (n=3), the K_P EF values were: fluorene (2.1), phenanthrene (2.5), fluoranthene (4.0) and pyrene (3.4). Cotham and Bidleman *(9)* found that PAHs were sorbed to a greater extent than PCBs in the south Chicago industrial section. From their log-log correlations of average K_P vs p^{o}_{L}, the EF for PAHs is 2.6-3.5, similar to what is observed in this study during transport from the S-W sector.

These results suggest that the K_P values for PAHs are dependent on source region and hence aerosol type. Inspection of data from of a study by Holsen et al. *(33)* at the same sampling location revealed a connection between aerosol type and wind direction. They found that when the air came from the S-W sector 15% of the time, coarse particles (2.5-10 μm) contributed 40% of the total particle mass. This increased to 57% when the air arrived from the S-W 30% of the time. The samples with greater contributions of S-W sector air also had higher levels of calcium which is indicative of crustal origin. Hence, at this sampling location, the S-W sector appeared to contribute more larger particles which were primarily a result of mechanical abrasion and erosion. Conversely, samples for which the contribution of N-E sector air was greater had higher proportions of fine particles (<2.5 μm) due to combustion (<0.1 μm) and accumulation mode (0.1-2.5 μm) aerosols *(33)*.

In summary, higher K_P values for PAHs (relative to PCBs) were found for Chicago aerosols. The K_P EFs were on the order of 2-4 for S-W and significantly higher (27-100) for air arriving from the N-E sector. We speculate that aerosol size distribution may be related to these differences but no conclusions can be drawn without information on the particle size distributions of PAHs and PCBs. Other complicating factors may be the presence of some non-exchangeable PAHs in the particles *(32)* and slow re-equilibration of combustion aerosols as they are diluted in ambient air. Kamens et al *(34)* showed that under cool, outdoor conditions (-1 to -4 °C), tens of hours were required for compounds like phenanthrene and pyrene to re-establish 90% of equilibrium once they had departed from equilibrium in the particle phase.

Alternatively, it may be a physical characteristic of PAHs and non-ortho PCBs which gives them a "partitioning advantage" compared to other PCBs. As seen in Figure 2, vapor pressure is not able to explain this effect. Rather than adsorbing to active sites on the particle surface, it is possible that the chemical is actually absorbing or dissolving into an organic layer on the particle *(11)*. Aerosols contain about 10% organic carbon and greater amounts of organic matter. The organic matter on aerosols is a mixture of non-polar compounds and polar material that is formed by oxidation and gas-to-particle conversion, i.e. "secondary organic aerosol" *(12,34,35)*. If absorption is the dominant process, a more appropriate descriptor may be the octanol-air partition coefficient, K_{OA}.

The relationship of K_P to K_{OA} is *(36)*:

$$K_P = 10^{-9} K_{OA} f_{om} (\gamma_{oct} / \gamma_{om}) (M_{oct} / M_{om}) / \rho_{oct} \qquad (6)$$

where f_{om} is the fraction of organic matter in the aerosol involved in partitioning, γ_{oct} and γ_{om} are the activity coefficients of the absorbing compound in octanol and aerosol organic matter, M_{oct} and M_{om} are the molecular weights of octanol (130 g mol^{-1}) and the organic matter, and ρ_{oct} is the density of octanol (820 kg m^{-3}). With the assumptions that γ_{oct}/γ_{om} and $M_{oct}/M_{om} = 1$:

$$\log K_P = \log K_{OA} + \log f_{om} - 11.91 \qquad (7)$$

Figure 2 (B series) shows log-log plots of K_P versus K_{OA}. In these plots the non-ortho PCBs which fell above the multi-ortho line in the p^o_L correlation (A-series) now fall in line with the rest of the PCBs. The ability of K_{OA} to resolve the difference in the PCB types is also illustrated in Figure 3b which shows enrichment factors ($EF = K_{P\,(non\text{-}ortho)} / K_{P\,(multi\text{-}ortho)}$)

for the non-ortho PCBs (congeners 77 and 126) in the fifteen Chicago air samples. $K_{P\ (multi\text{-}ortho)}$ values were taken from regression lines of individual sample events, e.g. in Fig. 2A plots. Several (although not all) of the samples show enrichment of the coplanar PCBs. The average EFs for PCB-77 and -126 are approximately 3.5 and 4 and indicate that these congeners are partitioning onto particles 3.5 to 4 times more strongly than a multi-ortho PCB having the same vapor pressure. Figure 3b also shows that K_{OA} values for PCB-77 and -126 show similar enrichment (i.e. $K_{OA\ non\text{-}ortho}$ / $K_{OA\ multi\text{-}ortho}$) compared to multi-ortho PCBs of the same vapor pressure *(37)*. Consequently, log-log plots of K_P versus K_{OA} resolve the differences between non-ortho and multi-ortho PCBs. Partitioning onto particles for another class of chlorinated aromatics - PCNs - was also well described by K_{OA} (Fig. 2 B-Series). These results encourage the use of K_{OA} as a particle/gas partitioning descriptor and support the hypothesis that the mechanism of particle/gas partitioning is absorption into an organic film which coats atmospheric particulate matter.

Preferential sorption of coplanar PCBs was also found in a previous study of aerosols from southeast Chicago *(10)*. In this case, the authors were able to account for the enrichment by the more nearly planar configuration of the non-ortho and mono-ortho PCBs.

PAHs, which have planar structures, also have higher K_P values than non-planar PCBs of the same vapor pressure (Fig. 2 A-Series). This enrichment cannot be resolved by K_{OA} (Fig 2. B-Series) since preferential absorption into octanol (i.e. $K_{OA\ (PAH)}$ / $K_{OA\ (multi\text{-}ortho\ PCB)}$) is not larger for PAHs *(24)*. This suggests that some other mechanism is involved, as discussed earlier.

The regression equations for log-log correlations of average K_P (n=15) against K_{OA} and p^o_L are as follows:

(all PCBs): $\log K_P = 0.654 \log K_{OA} - 9.183$; $r^2=0.876$; n=33

(PCNs): $\log K_P = 0.735 \log K_{OA} - 9.947$; $r^2=0.918$; n=22

(PAHs): $\log K_P = 0.829 \log K_{OA} - 10.263$; $r^2=0.999$; n=4 and

(all PCBs): $\log K_P = -0.715 \log p^\circ_L - 5.141$; $r^2=0.886$; $n=33$

(PAHs): $\log K_P = -0.745 \log p^\circ_L - 4.666$; $r^2=0.999$; $n=4$

Models of particle-gas partitioning - adsorption versus absorption

Junge-Pankow Adsorption Model

First proposed by Junge *(38)* and later critically reviewed by Pankow *(7)*, the Junge-Pankow model (eq. 8) is the most common method for estimating adsorption of semivolatile organic compounds to aerosols.

$$\phi = c\theta / (p^\circ_L + c\theta) \qquad (8)$$

This model relates the fraction of chemical adsorbed to particles (ϕ) to the subcooled liquid vapor pressure of the pure compound (p°_L, Pa) and the particle surface area per unit volume of air (θ, cm^2 aerosol cm^{-3} air). The parameter c (Pa cm) is based on the heat of desorption from the particle surface (Q_d, J mol^{-1}), the heat of vaporization of the compound (Q_v, J mol^{-1}), and the moles of adsorption sites on the aerosol (N_s, mol cm^{-2}).

$$c = 10^6 RTN_s \exp[(Q_d - Q_v)/RT] \qquad (9)$$

where T is temperature (K), R=8.314 Pa m^3 mol^{-1} K^{-1} = J mol^{-1} K^{-1} and the factor 10^6 converts m^3 to cm^3. A value of c=17.2 Pa cm is typically used although Pankow *(7)* suggests that this may vary with the class of compound. Values for the surface area parameter, θ, are often assumed to be 1.1×10^{-5} for urban air and 4.2×10^{-7} to 35×10^{-7} for rural air *(39)*.

Absorption Model

It has been recently proposed by Pankow *(11,12)* that absorption of gas-phase compounds into an organic film coating the particle makes an important contribution to the overall particle-gas partitioning process. Gas absorption can be expressed as,

$$p_L = \gamma_{om} X p^{o}_L \qquad (10)$$

where p_L is partial pressure in equilibrium with a compound having mole fraction X and activity coefficient γ_{om} in the organic film ($\gamma_{om} \rightarrow 1$ as $X \rightarrow 1$, Raoult's Law). Pankow's expression for K_P based on absorption is:

$$K_P = 10^{-6} RT f_{om} / M_{om} \gamma_{om} p^{o}_L \qquad (11)$$

where f_{om} is the fraction of the particle mass that consists of absorbing organic matter having molecular weight M_{om} (g mol^{-1}). A substantial portion of this organic matter may be "secondary organic aerosol", which is formed by oxidation of hydrocarbons and is therefore polar *(12)*. The combined relationship for both adsorption and absorption is:

$$K_P = (1/p^{o}_L)\ \{RTN_s A_{tsp} \exp[(Q_d - Q_v)/RT] + 10^{-6} RT f_{om} / M_{om} \gamma_{om}\} \qquad (12)$$

where A_{tsp} is the aerosol specific surface area ($A_{tsp} = 10^{6}\,\theta$ / TSP). The above expressions (eq 9-12) have been modified from those originally presented. In previous papers R does not appear in the pre-exponential term because it was incorporated into other constants. Also here we use consistent units of R (Pa m^3 mol^{-1} K^{-1} = J mol^{-1} K^{-1}) and vapor pressure (Pa) whereas some earlier papers used Torr for vapor pressure and varying units of R. The utility of eq. 12 is questionable however. Will an aerosol which is covered with an organic film have any active sites available for adsorption to occur ?

Two logarithmic forms of equation 11 are:

$$\log K_P = \log 10^{-6} RT f_{om} / M_{om} \gamma_{om} - \log p^{o}_L \qquad (13)$$

$$\log K_P = \log f_{om} + \log 10^{-6}\ RT / M_{om} \gamma_{om} p^{o}_L \qquad (14)$$

Both the adsorption (eq. 8) and absorption (eq. 13) models predicts the same functional dependence of K_P on p^o_L. Absorption may also be viewed according to eq. 14 where the term $10^{-6}RT/M_{om}\gamma_{om}p^o_L$ is related to the partition coefficient of the compound between the organic matter and air. This suggests using the octanol-air partition coefficient (K_{OA}) as an alternative to vapor pressure for describing absorption to aerosols *(18,40,37)*.

$$K_{OA} = C_{oct}/C_{air} = 10^3\rho_{oct}\,RT\,/\,M_{oct}\gamma_{oct}p^o_L \qquad (15)$$

where C_{oct} and C_{air} are the moles of compound per m^3 of octanol or air. Other terms were defined in the presentation of eq 6, which results from combining eq 14 and 15.

Values of K_{OA} have been reported as a function of temperature for several PCB congeners, chlorobenzenes, PAHs and polychlorinated naphthalenes (PCNs) *(40,37,41,24)*.

The K_{OA} absorption model (eq 7) can be used to predict values of K_P from knowledge of only K_{OA} and the organic fraction of the aerosol, f_{om}, if it is assumed that all of the aerosol organic matter is available to absorb gaseous compounds. The fraction on particles (ϕ) is then calculated from K_P and TSP by eq 2.

Comparison of Adsorption and K_{OA} Absorption Models

Figure 4 compares the percent ($\phi \times 100$) fraction on particles as predicted by the Junge-Pankow adsorption model (using c=17.2 Pa cm and $\theta = 1.1 \times 10^{-5}$) with the average experimental values for PCBs and PAHs (n=15). PCNs are not included due the lack of p^o_L values. The Junge-Pankow model gives particulate percentages which are in good agreement with sampling data for PAHs, but overpredicts sorption of PCBs. The same trend was found in an earlier study in south Chicago *(9)*. Comparisons of several data sets from urban and rural locations also shows that sorption of PAHs in urban air is well represented by the Junge-Pankow approach *(36,42,43)*.

Agreement between the model and sampling results is no guarantee that either gives the correct result. Filtration air samplers are subject to "blow off" artifacts which result in loss of semivolatile compounds from filtered particles. Parallel experiments with denuders yield higher particulate fractions for PAHs *(44,45)*. In the J-P model, θ can be expected to vary with aerosol size distribution *(46)* and Q_d may vary for different compounds *(7,47)*.

The K_{OA} absorption model can be applied in the same manner using eq 2 and knowledge of the organic matter content of the aerosols. Shah et al. *(48)* reported an average organic carbon content of airborne particles in U.S. cities of 8.4%. Cotham and Bidleman *(9)* reported total carbon (organic + elemental) levels of 23% in Chicago urban aerosol. This corresponds to 15% organic carbon if an organic/elemental ratio of 1.8 is assumed (Shah et al., 1986). Conversion from organic carbon to organic matter is possible if we assume that organic compounds present on urban aerosols have, on average, the molecular formula of octanol (74% carbon). Hence, 15% organic carbon corresponds to approximately 20% organic matter.

Figure 5 shows the particulate fractions predicted by the absorption model assuming organic matter fractions of 10% and 20% which is in the range expected for urban aerosols. The K_{OA} model fits the PCB data better than the Junge-Pankow model, resolves differences between multi-ortho and non-ortho PCBs, and also explains the partitioning data for PCNs. The particle/gas distribution of PAH is underpredicted (see also Fig 2 B-series and 3b). As hypothesized earlier, this may be related to the presence of "non-exchangeable" PAHs or due to the long times required for aerosol-air re-equilibration.

It is increasingly accepted that partitioning of semivolatile organics to environmental lipids (soil, vegetation, aerosols) is controlled by an absorptive rather than, or in addition to, an adsorptive mechanism. The octanol-air partition coefficient is a good descriptor for the partitioning of PCBs and PCNs between the air and atmospheric particulate matter. Correlations of K_P against K_{OA} are able to resolve differences between the ortho-chlorine substitution classes of PCBs which correlations against p^{o}_{L} are not able to explain, and partitioning of PCNs to Chicago aerosols is also accounted for by K_{OA}.

The K_{OA} absorption model described here requires knowledge of only K_{OA} and the organic matter fraction of the aerosol which are both more easily measurable than the parameters of the Junge-Pankow model. Thus, there is an incentive to utilize the absorption model for chlorinated aromatics and to measure K_{OA} as a function of temperature for other compounds of interest or concern.

Sorption of PAHs was not well represented by either model, especially for air arriving from the N-E sector. It may be that particle/gas distribution of PAHs is more complex and involves both adsorption and absorption as well as being influenced by non-exchangeable PAHs.

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Table 1. Collection data and concentrations of semi-volatile compounds in Chicago.

sample	date 1995	day (D) or night (N)	m^3 air	mean temp (°C)	TSP ($\mu g\ m^{-3}$)	ΣPAH ($pg\ m^{-3}$)	ΣPCBs ($pg\ m^{-3}$)	ΣPCNs ($pg\ m^{-3}$)
1	Feb. 20/21	N	448	3	15	20 000	472	112
2	" 21	D	339	0	34	39 900	359	23
3	" 21/22	N	398	0	60	34 400	294	41
4	" 22	D	337	0	162	102 100	621	87
5	" 22/23	N	445	2	75	48 800	485	92
6	" 23	D	329	4	83	93 000	506	175
7	" 23/24	N	421	0	25	18 100	247	43
8	" 24	D	348	2	34	62 400	208	37
9	" 24/25	N	448	0	41	49 000	316	44
10	" 25	D	325	4	69	41 900	279	24
11	" 25/26	N	425	0	37	25 700	174	28
12	" 26	D	314	0	58	21 400	143	57
13	" 28	D	323	0	123	200 300	588	378
14	" 28/29	N	395	0	87	46 300	282	68
15	Mar. 1	D	320	0	87	65 300	273	87

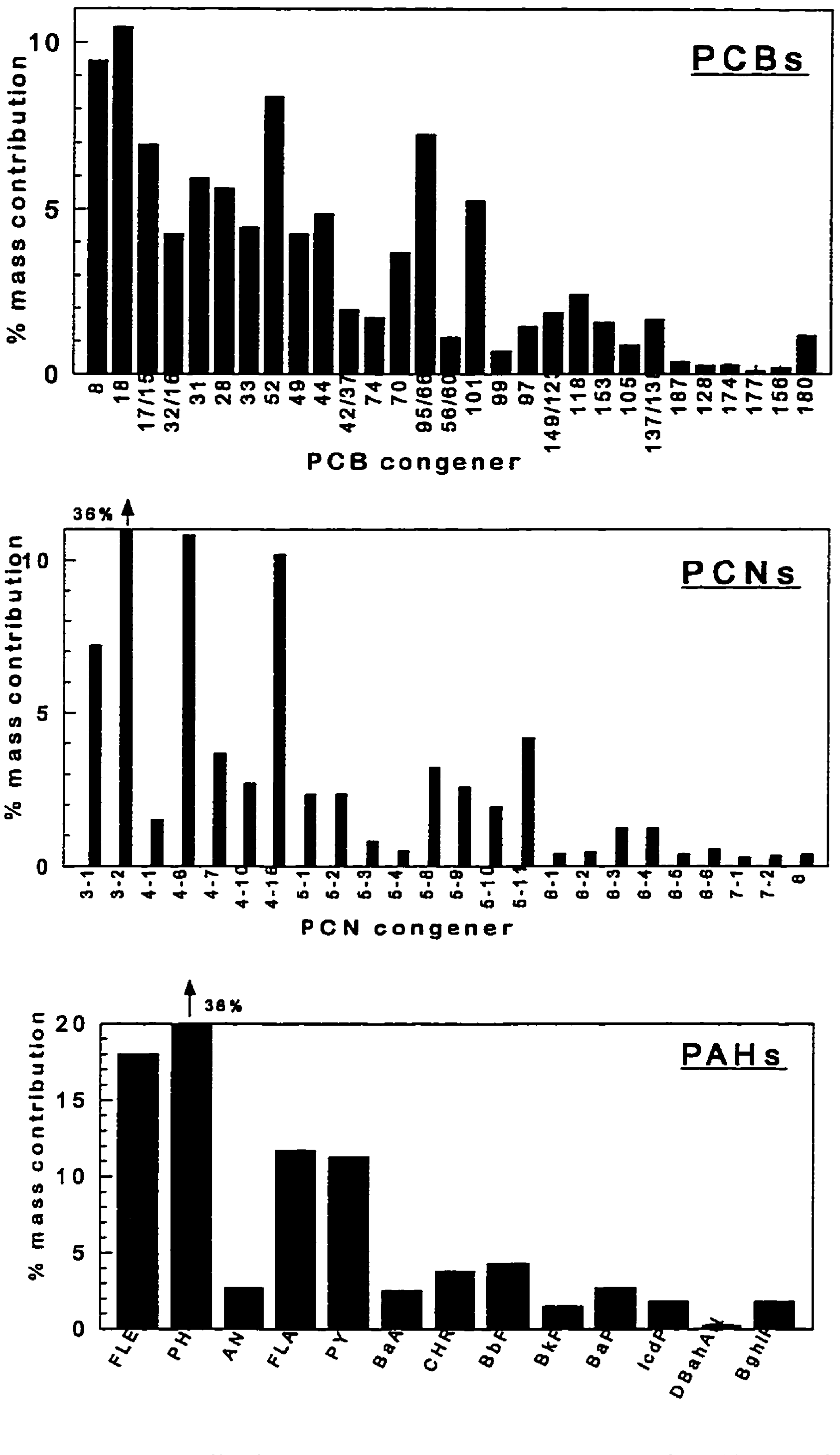

Figure 1. Mass percent contributions of PAHs, PCBs, and PCNs in Chicago air. (PAHs: FE=fluorene, PH=phenanthrene, AN=anthracene, FLA=fluoranthene, PY=pyrene, BaA=benz(a)anthracene, CHR=chrysene, BbF=benzo(b)fluoranthene, BkF=benzo(k)fluoranthene, BaP=benzo(a)pyrene, IcdP=indeno(1,2,3,cd)pyrene, DBahAN=dibenz(ah)anthracene, BghiP=benzo(ghi)perylene.

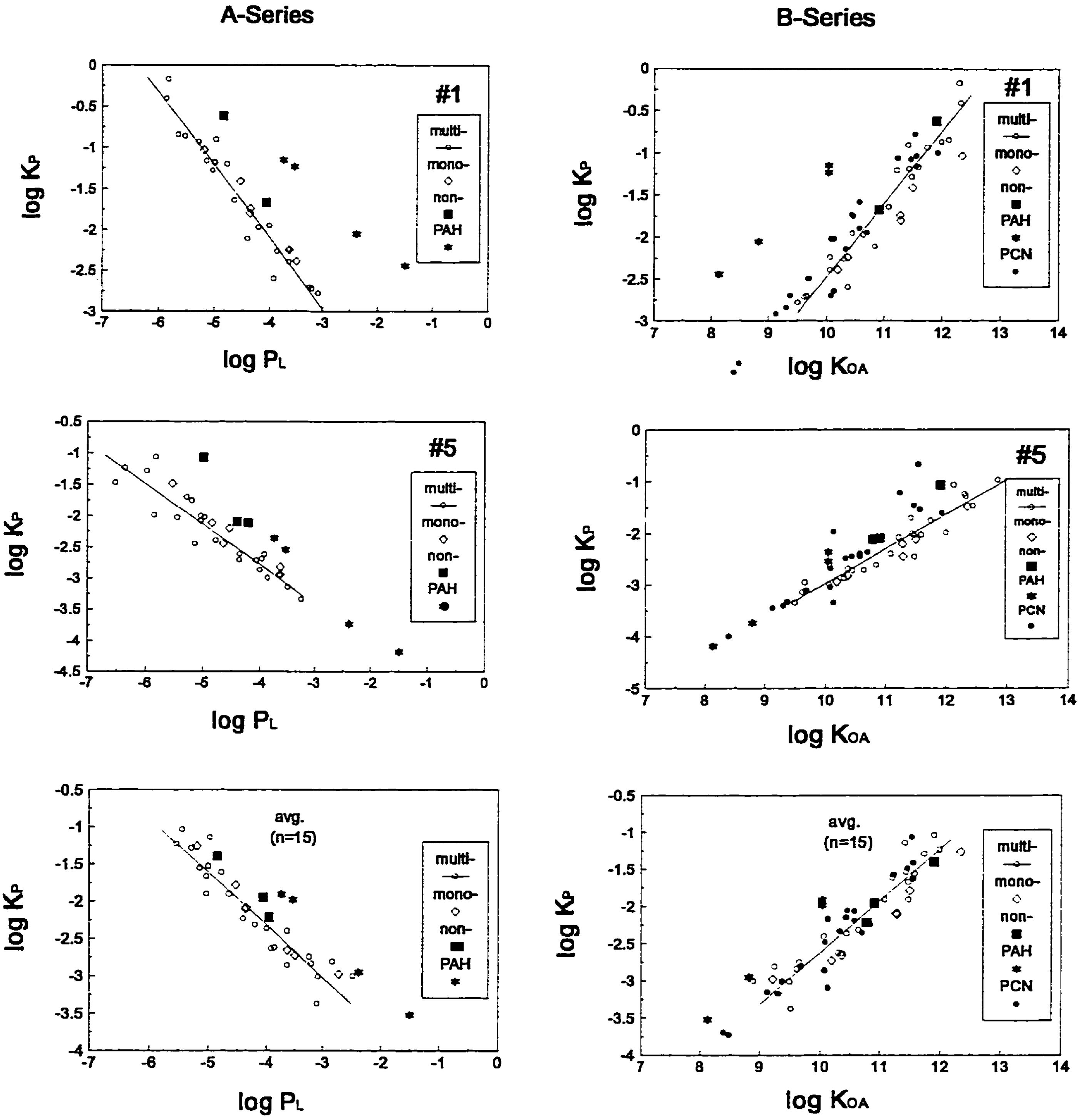

Figure 2. Log-log plots of K_P against a) p^{o}_{L} (Pa) and b.) K_{OA} in Chicago air samples for PAHs (FE, PH, FLA and PY), multi-ortho PCBs, mono-ortho PCBs, non-ortho PCBs, and PCNs (K_{OA} only). Samples 1 and 5 are examples which show large and moderate enrichment of PAHs over PCBs. Note that differences in partitioning between the multi- and non-ortho PCBs are minimized in the latter plot. Regression lines are for multi-ortho points.

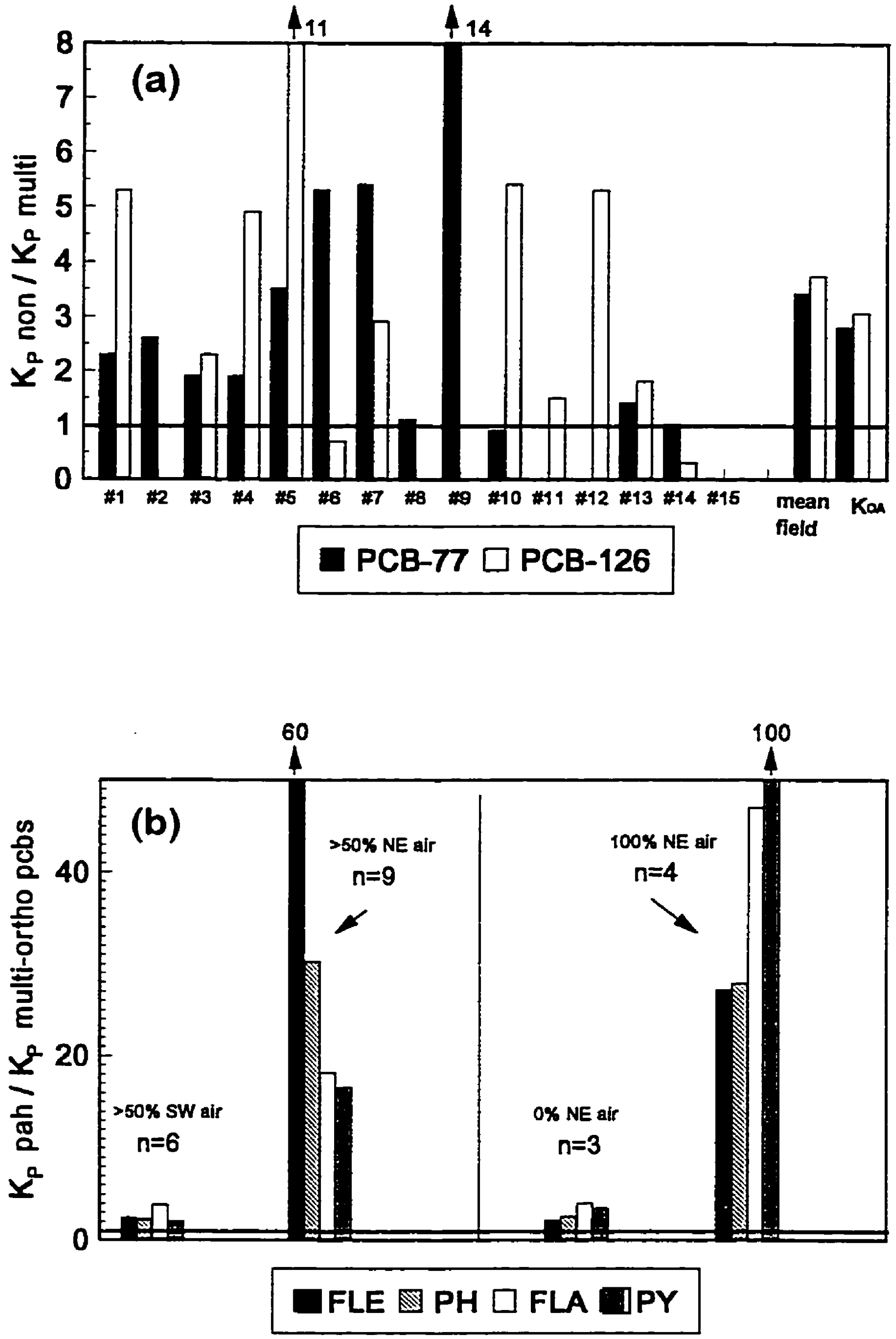

Figure 3. Particle/gas partition coefficient enrichment factors in Chicago air samples for a) PCBs (EF = $K_{P\,(non\text{-}ortho)}$ / $K_{P\,(multi\text{-}ortho)}$) and b) PAHs (EF = $K_{P\,(PAH)}$ / $K_{P\,(multi\text{-}ortho)}$). Note the differences in EF values for PAHs depending on aerosol source region - N-E sector (315° to 135°) air versus S-W sector (135° to 315°) air.

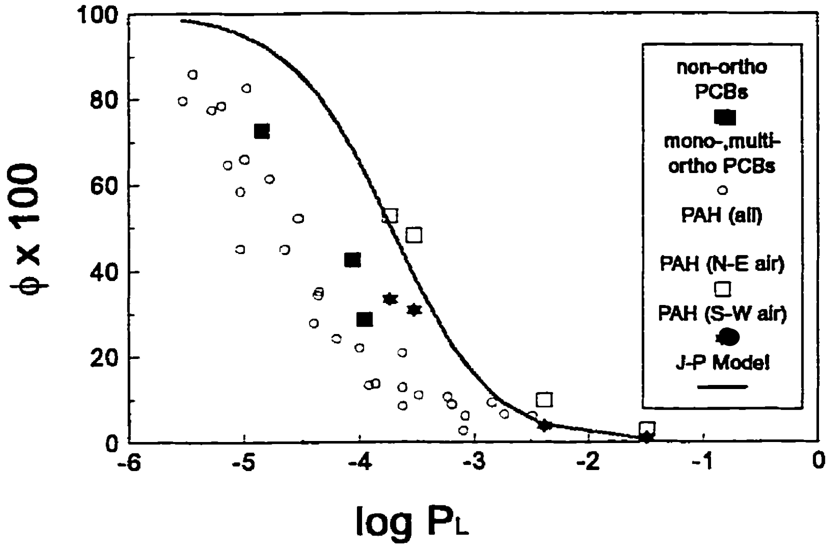

Figure 4. Junge-Pankow adsorption model of particulate fractions (φ × 100) for PAHs and PCBs as a function of vapor pressure, p^{o}_{L} (Pa).

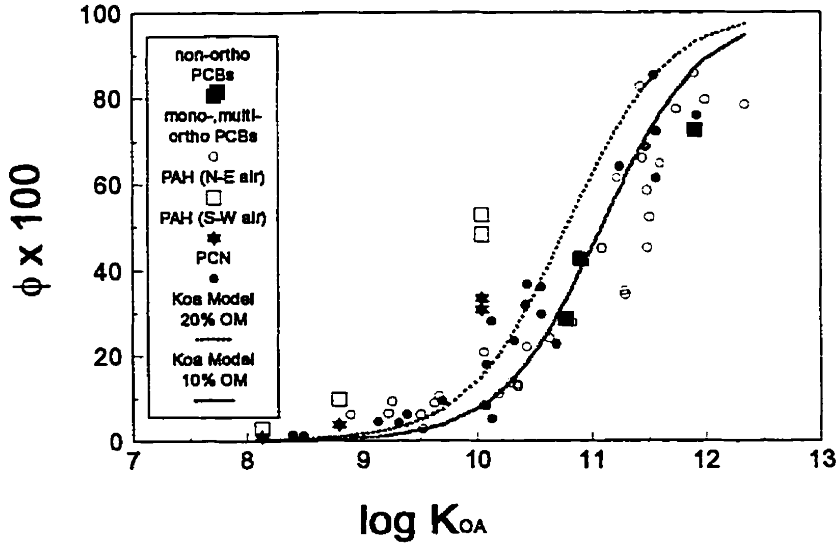

Figure 5. Absorption model of particulate fractions for PAHs and PCBs as a function of K_{OA} for an aerosol containing 10% and 20% organic matter.

Paper IV: Polychlorinated Naphthalenes In Urban Air

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Abstract

Air samples were collected at an urban site (Chicago, IL) and a semi-urban location (Downsview, Ontario) in February and March, 1995 to measure atmospheric concentrations and particle/gas partitioning of polychlorinated naphthalenes (PCN). PCNs were quantified by gas chromatography - negative ion mass spectrometry (GC-NIMS) against Halowax 1014, a commercial mixture of PCN compounds. GC-flame ionization responses were used to assign mass percent contributions to congeners in Halowax 1014. The reliability of this method was checked using pure compounds and was within ±20% of the true value for 5 out of 6 congeners tested. Mean atmospheric concentrations (ΣPCN) at the urban and semi-urban site were 68 pg/m^3 (n=14) and 17 pg/m^3 (n=2) respectively. Several bioaccumulating PCNs which have "dioxin-like" toxicity similar to coplanar PCBs were quantified. The tetrachlorodibenzodioxin (TCDD) toxicity contribution of one of these these PCNs in Chicago air was estimated to outweigh the contributions of some of the coplanar PCBs. The fraction of PCNs on particles exhibited a stepwise increase with homolog group. A need for relevant physicochemical data for this group of compounds was identified.

Introduction

Recently there has been increasing interest towards levels of polychlorinated naphthalenes (PCNs) in the environment (Falandysz and Rappe, 1996; Falandysz et al., 1996; Dörr, et al., 1996; Asplund et al., 1994b; Järnberg et al., 1993). PCNs, like their polychlorinated biphenyl (PCB) counterparts, have ideal chemical properties and thermal stability which promoted their usage in the electrical industry. Their most important applications include dielectric fluids in transformers and capacitors, cable insulation, wood preservation, engine oil additives, electroplating masking compounds and feedstocks for dye production (Crookes and Howe, 1993). They are also released from waste incineration processes (Oehme et al., 1987) and occur as by-products in technical PCB formulations (Järnberg et al., 1993) although the latter are believed to account for less than 1% of their total production. Global production of PCNs is estimated to be at least 10% of total PCB production (Beland and Greer, 1973). Halowax, produced by Koppers Co. U.S.A., was one of the major PCN products and comprised of several technical grades containing varying percentages of chlorine. Brinkman and de Kok (1980) estimated that 320 tons was produced in the U.S. in 1978. Although U.S. production of PCNs ceased in 1980, they are still found in new electrical equipment and it has been proposed that landfilled items containing PCNs are currently a major emission source (Crookes and Howe, 1993).

Today, PCNs are as widespread as PCBs and are reported in various environmental compartments and in biological samples from remote areas like the Arctic (Asplund et al., 1990). Erickson et al. (1978) reported air concentrations as high as 1400 ng/m^3 near a manufacturing site and 33 ng/m^3 near suspected user sites. Sediments collected in the Trenton Channel of the Detroit River revealed ΣPCN concentrations up to 61 000 ng/g (dry weight of sediment) with notable levels of octachloronaphthalene (Furlong et al., 1988). Analysis of sewage sludge in Sweden indicated that PCNs are of the same magnitude as PCBs and DDT compounds (Nylund et al., 1992).

Of the 75 possible PCN congeners, several have dioxin-like activity and have been assigned tetrachlorodibenzodioxin (TCDD) toxic equivalency factors (TEF) which are similar in magnitude to the coplanar PCBs (Hanberg et al., 1990). In particular, two hexachloronaphthalenes, PCN-66 & 67, are strongly bioaccumulating (Asplund et al., 1994b) and account for 0.3-13% of the TCDD equivalents in fish from Swedish lakes (Järnberg et al., 1993). Jansson et al. (1984) found levels of PCN in Swedish freshwater biota between 3 and 62 ng/g lipid and Tarhanen et al. (1989) reported levels of 4 to 85 ng/g in salmon and white-tailed eagle from the Baltic Sea. Consumption of contaminated fish is considered to be an important entry route for humans. High high levels of penta- and hexachloronaphthalenes in human blood plasma have been correlated to fish intake (Asplund et al., 1994a). Williams et al. (1993) detected penta- and hexachloronaphthalene congeners in human adipose tissue from various regions of Ontario, Canada. Recently, Falandysz and Rappe (1996) measured bioaccumulation of PCNs in the pelagic food chain in the Baltic Sea. They speculated that long-range atmospheric transport and deposition is an important route for PCNs entering this region.

The abundance in the environment, toxicity and continued use provides an incentive to investigate levels of PCNs in the environment. It is only recently that a select number of individual congeners have been synthesized or isolated from mixtures (Auger et al., 1993; Haglund and Bergman, 1989; Jakobsson et al., 1992) and the lack of useful physical-chemical data for this group of chemicals makes fate-modelling by traditional means difficult. This paper reports atmospheric levels and particle/gas distributions of PCN in Chicago and Toronto collected from February and March, 1995. A method for quantifying individual PCN congeners based on their percentages in Halowax 1014 is described.

Experimental

Collection of Air Samples

Air samples (15) were collected in Chicago approximately 2 km inland from the shore of Lake Michigan on the roof of Farr Hall, Illinois Institute of Technology (IIT), in February/March 1995. Two samples were also taken at the Atmospheric Environment Service (AES) headquarters, located in Downsview, a semi-urban region about 25 km north of metropolitan Toronto, in March 1995. A high volume sampling train consisting of double glass fibre filters (20 × 25 cm, Gelman A/E) followed by two polyurethane foam plugs was used. Procedures for preparing sampling media have been previously reported (Billings and Bidleman, 1980). Chicago samples were taken over 12 h day or night periods to avoid diurnal temperature variations and thereby minimize filtration artifacts. Meteorological data were provided by the Illinois State Water Survey monitoring stations at Farr Hall and Indiana Dunes National Lakeshore near the southern tip of Lake Michigan. Toronto samples were collected over 72-h periods. Collection information is summarized in Table 1.

A separate sampling train consisting of a single glass fibre filter and two polyurethane foam plugs was used for total suspended particulate concentration determinations (TSP, μg particles / m^3 air). The polyurethane foam plugs were included so that the air flow rates for TSP determinations and air samples were of similar magnitude. The filters were equilibrated in a constant humidity chamber for 48 h at 20 °C over a saturated sodium chloride solution before and after sampling. This ensured that any changes in filter mass were only attributed to particulate matter and not to differences in water content of the filters.

Analytical Methods

Air samples were analyzed for several compounds including PCNs, PCBs, and polycyclic aromatic hydrocarbons (PAHs). Results for PCBs and PAHs are presented elsewhere (Harner and Bidleman, 1997). Polyurethane foam plugs were Soxhlet extracted overnight with petroleum ether or hexane and filters were extracted for the same time period using dichloromethane. After volume reduction to 2 mL and transfer to isooctane the samples were fractionated on a column containing 3 g silicic acid (3% added water) topped with 2 g neutral alumina (6% added water) and 1 cm anhydrous granular sodium sulfate. The column was prewashed with 25 mL dichloromethane followed by 25 mL petroleum ether. The sample was applied, PCNs/PCBs were eluted in the first fraction (F1) with 20 mL petroleum ether and the PAHs were eluted in the second fraction (F2) with 20 mL dichloromethane. Both fractions were reduced into isooctane by blowing down with a stream of nitrogen.

After an additional cleanup by shaking with 18M sulfuric acid, F1 was reduced to 0.5 mL and further fractionated on a mini-column containing AX-21 activated carbon mixed 1:20 with silicic acid prepared as described by Falconer et al. (1995). The carbon-silicic acid mix (100 mg) was sandwiched between 50-mg layers of silicic acid in a disposable pasteur pipet containing a small plug of glass wool at the lower end. The column was prewashed with 5 mL toluene followed by 5 mL 30% dichloromethane in cyclohexane. The first fraction (F1-1) was eluted with 5 mL 30% dichloromethane in cyclohexane and contained the multi- and mono- ortho PCBs. The second fraction (F1-2) was eluted with 5 mL toluene and contained the PCNs and non-ortho (coplanar) PCBs. Both fractions were reduced to 0.2-0.4 mL and F1-1 was transferred to isooctane.

Analysis

To quantify the PCNs on a congener basis, it was necessary to determine their mass percent contributions in Halowax 1014, a mixture containing mainly 4-7 chlorinated naphthalenes (Imagawa, 1993). A standard of this PCN mixture was obtained from EPA - Research Triangle Park, NC. Mass percent contributions were determined by gas chromatography (Hewlett-Packard 5890 Plus) with flame ionization detection (GC-FID) which was assumed to respond to the carbon skeleton of the PCN molecule. Peaks were separated on a 60 m DB-5 MS column (J&W Scientific, 0.25 mm i.d., 0.25 µm film thickness) operated with hydrogen carrier gas at 50 cm/s. Sample injections (1 µL) were splitless with split opened after 0.5 minutes. The temperature program was 90 °C for 0.5 min., 10 °C/min to 160 °C, 2 °C/min to 250 °C with the flame ionization detector at 300 °C and the injector at 250 °C. A series of n-alkanes in the C16-C26 range was used as standards to calibrate the flame ionization detector response. To account for injector discrimination of compounds having different molecular weights, PCN congener areas were normalized to the response of an n-alkane with similar retention time. Mass percent contributions were then assigned based on these relative peak areas and the molecular weights of the congeners. The percent mass contribution (m_i %) of peak (congener) i is given by,

$$m_i \% = 100(A_i)(M_i) / \sum_{i=1}^{n} (A_i)(M_i) \qquad (1)$$

where A_i is the area of peak i, M_i is the molecular weight of compound i, and n is the number of peaks integrated. The term $\sum_{i=1}^{n} (A_i)(M_i)$ represents the sum of (area × molecular weight) for all of the congener peaks in Halowax 1014.

PCNs in fraction F1-2 were analyzed by gas chromatography - negative ion mass spectrometry (GC-NIMS) on a Hewlett Packard 5890 GC - 5989B MS Engine operated in the negative ion mode with methane at a nominal pressure of 1.0 Torr. Ions monitored in selected ion mode were (target, qualifier) 3-Cl: 232, 230; 4-Cl: 266, 264; 5-Cl: 300, 298; 6-Cl: 334, 332; 7-Cl: 368, 366; 8-Cl: 404, 402. The criterion for acceptance was a target/qualifier ion ratio within ±20% of the standard. PCB-103 was used as the internal standard (ions monitored were 291, 289). The same GC-operating conditions were used as in the flame ionization analysis except that a 30m DB5-MS column was used with helium as the carrier gas. Other operating temperatures were: transfer line 250°C, ion source 150°C and quadropole 100°C.

Results and Discussion

Composition of Halowax 1014

Although there are several common Halowax mixtures, the congener profile in air was most similar to the composition of Halowax 1014. The FID chromatogram of Halowax 1014 is shown in Figure 1 where peaks are labelled according to various schemes used in the literature (Järnberg et al, 1993, Wiedmann and Ballschmiter, 1993). IUPAC congener numbers and structures are also shown for peaks which have been identified in the literature (Wiedmann and Ballschmiter, 1993, Imagawa et al., 1993, Falandysz et al., 1996). Table 2 lists the identified structures and mass percent contributions for the major peaks and homolog groups. Some discrepancies exists between homolog mass percent contributions determined in this work and measurements made by Wiedmann and Ballschmiter (1993). This may be attributable to variations in batches of the Halowax 1014 technical mixture.

Pure PCN compounds were obtained from several sources. Congeners 1,2,4,7-TeCN (CN-34), 1,2,3,5,7-PeCN (CN-52) were obtained from Larodan AB (Malmö, Sweden); 1,2,3,4,6,7- / 1,2,3,5,6,7-HxCN (CN-66/67), 1,2,4,5,6,8-HxCN (CN-71) and 1,2,3,4,5,6,7-HeptaCN (CN-73) came from Åke Bergman and Eva Jakobsson (Department of Environmental Chemistry, Stockholm University, Stockholm, Sweden); 1,2,3,4,5,6,7,8-OctaCN (CN-75) was purchased from Ultra Scientific (Hope, Rhode Island).

The accuracy of the mass percent composition of Halowax 1014 (Table 2) was checked by quantifying a solution of these six pure congeners by GC-NIMS against the same peaks in Halowax 1014. Accuracy ratios, calculated as found/actual concentrations, were as follows: (CN-34) 1.20 ± 0.03; (CN-52) 1.87 ± 0.03; (CN-66/67) 0.78 ± 0.02; (CN-71) 0.93 ± 0.03; (CN-73) 0.84 ± 0.04; (CN-75) 0.79 ± 0.05. Accuracy ratios were within ±20% for five out of the six congeners. The deviation for peak 5-1 may be due to an underlying peak (CN-60) in the Halowax 1014 mixture as identified by Imagawa et al., 1993. Overestimation would occur if the GC-NIMS response factor for CN-60 were less than for CN-52.

Quality Control

The analytical procedure for isolating and determining PCNs involved several fractionation columns and volume reduction steps. In order to account for procedural losses, four polyurethane foam plugs were spiked in the field with a Halowax 1014 standard and treated as samples. Spike recoveries ranged from approximately 50% for 3-4 chlorinated homologs to 65-70% for the 6-8 chlorinated homologs with good reproducibility (±10%). A duplicate set of laboratory spike tests was performed at a later date which supported the field spike recovery values. Results for air samples were corrected for recovery factors.

Field blanks of polyurethane foam were also analyzed and showed no detectable PCNs. Limit of detection values (L.O.D.) were calculated based on the area of the smallest noise peak which could be integrated. On this basis the L.O.D. is estimated to be 10 pg or approximately 0.025 pg/m^3 for each congener.

Air Samples

Fourteen of the fifteen Chicago air samples showed ΣPCN in the range 24-175 pg/m^3 with an average value of 68 pg/m^3. One outlier, which was likely due to a local source, had a value of 469 pg/m^3; during this sampling period trash was burned at a demolition site about 500 m to the north with an odor of smoke noticeable on the roof of Farr Hall. Levels of PCNs in the two Downsview samples were lower at 12 and 22 pg/m^3, which may reflect fewer emission sources near this semi-urban site. These results are in good agreement with data by Dörr et al. (1996) who recently reported ΣPCN=60 pg/m^3 in urban air in Augsburg, Germany and ΣPCN=24 pg/m^3 at a rural background station. Average levels of ΣPCB in Chicago and Downsview for these samples were 329 and 383 pg/m^3 (Harner and Bidleman, 1997). The average ΣPCN/ΣPCB ratios were 0.21 in Chicago (excluding one outlier) and 0.044 in Downsview.

Meteorological data collected on the roof of Farr Hall and at Indiana Dunes (south of Chicago) were used to assign a mean wind direction to the fifteen Chicago air samples. Figure 2 (which excludes the outlier) is a plot of PCN air concentration versus the percent of time that the air was coming from the urban sector, defined as the region 135° to 360° with respect to the sampling location. The plot shows that PCN levels in air are relatively constant with a suggestion of a slight increase when the wind blows from the urban sector. However, it may be argued that wind coming from the direction of Lake Michigan (0° to 135°) is not much different from "urban sector air" since it passes over at least 2 km of urban district before arriving at the roof of Farr Hall. Figure 3, which correlates ΣPCN with ΣPCB (Harner and Bidleman, 1997) for 14 Chicago air samples (outlier was omitted from regression), shows that PCN and PCB concentrations tend to co-vary, which is likely indicative of similar source/emission regions for these compounds.

It is interesting to examine the proportion of the dioxin-like PCNs in the air samples. Levels (pg/m^3, excluding one outlier) of PCN-42 (4-1), PCN-52+60 (5-1), and PCN-66+67 (6-1) were 0.3-3.01, 0.04-2.8 and <0.03-1.0; the mean values were 1.06 ± 0.69, 1.44 ± 0.73, and 0.32 ± 0.36 respectively. These levels are about an order of magnitude greater than mean concentrations of coplanar PCBs; PCB-77=0.43, PCB-126=0.061, and PCB-169 <0.030 pg/m^3 (Harner and Bidleman, 1997). Hanberg et al. (1990) reports TCDD toxic equivalence factors for PCNs and coplanar PCBs {i.e. 0.001 (PCB-77), 0.2 (PCB-126), 0.007 (PCB-169) and 0.003 (6-1, presumably PCN-66+67)}. Based on these values and the respective concentrations of these compounds in Chicago air, it is estimated that the TCDD toxicity of PCN-66+67 is 2-5 times greater than the values for PCB-77 and PCB-169 and represents approximately 8% of the toxicity attributable to PCB-126. The contribution of the bioaccumulating PCNs would be higher if PCN-42 and PCN-52 were included but TCDD toxic equivalence factors have not been assigned for these compounds.

Figure 4 shows the average percent mass contribution for the fifteen Chicago samples with the greatest proportion attributed to the 3 to 5 chlorinated homologs. Peak 3-2 (1,4,6-trichloronaphthalene) alone accounts for approximately 37% of the total. This is substantially greater than its mass contribution in Halowax 1014 of 5.9% (Table 2). The 6 to 8 chlorinated homologs have minor inputs and combined account for less than 10% of ΣPCNs.

Particle/Gas Partitioning

PCNs are present in the gas phase and attached to particles. Figure 5 displays GC-NIMS chromatograms of the PCNs found on the front polyurethane foam plug and front filter. A clear distinction can be seen for the partitioning behavior among the different PCN homologs. At ambient temperatures of 0 to +4°C in Chicago, the lighter (3 and 4 chlorinated) congeners are predominently in the gas phase and the heavier (7-8) chlorinated congeners show a higher proportion on aerosols. This particular sample (#6) showed a high proportion of octachloronaphthalene relative to its abundance in Halowax 1014. It is likely that other Halowax technical mixtures, such as 1051 which contain mainly 7- and 8-chlorinated congeners, are also important sources of PCNs to the atmosphere. The 5-6 chlorinated homologs are split between these phases. Particulate percentages range from 1.5-2% for the 3-Cl homolog to as high as 94% for octachloronaphthalene for samples collected over the temperature range 0 to +4 °C. A shift to higher gas-phase percentages is expected to occur at higher temperatures. It would be desireable to correlate particle/gas distributions against a physicochemical parameter such as subcooled liquid vapor pressure, p^{o}_{L}, or octanol-air partition coefficient. This would allow predictions of particle/gas partitioning behavior at different temperatures and would be especially useful for modelling purposes. However, these properties have not been reported for PCNs.

Conclusions

Average levels of ΣPCN in urban air averaged about 68 pg/m^3 for Chicago and 17 pg/m^3 for Toronto. Although these concentrations are approximately an order of magnitude lower than typical ΣPCB values for urban centers the levels of the bioaccumulating, dioxin-like PCNs exceed levels of coplanar PCBs in urban air. PCNs are therefore an important class of pollutants which merits further study. Especially needed are congener-specific physicochemical property data, to compare the particle/gas partitioning of PCNs with other semivolatile compounds such as PCBs and PAHs.

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Table 1. Collection data and ΣPCNs in air.

sample	date 1995	day (D) or night (N)	m^3 air	mean temp (°C)	TSP (μg/m^3)	ΣPCNs (pg/m^3)
Chicago samples:						
1	Feb. 20/21	N	448	3	15	112
2	" 21	D	339	0	34	23
3	" 21/22	N	398	0	60	41
4	" 22	D	337	0	162	87
5	" 22/23	N	445	2	75	92
6	" 23	D	329	4	83	175
7	" 23/24	N	421	0	25	43
8	" 24	D	348	2	34	37
9	" 24/25	N	448	0	41	44
10	" 25	D	325	4	69	24
11	" 25/26	N	425	0	37	28
12	" 26	D	314	0	58	57
13	" 28	D	323	0	123	378
14	" 28/29	N	395	0	87	68
15	Mar. 1	D	320	0	87	87
Toronto samples:						
1	Mar. 17-20	D/N	2249	5	not measured	12
2	" 20-23	D/N	2288	5	not measured	22

Table 2: Mass percent contribution assignments for PCNs in Halowax 1014. (GC-FID chromatogram using DB-5MS column)

peak		congener	mass	homolog contribution	
(a)	(b)	(c)	(%)	(this study)	(d)
Dichloronaphthalenes				0.9	0.3
2-1		CN-5 (1,4)	0.85		
Trichloronaphthalenes				9.9	2.8
3-1	3a)	CN-19 (1,3,5)	0.58		
3-2	3b)	CN-24 (1,4,6) CN-14 (1,2,4)	5.87		
3-5			0.36		
3-6			0.16		
3-7			0.30		
3-10			2.65		
Tetrachloronaphthalenes				14.0	18.2
4-1	(4a)	CN-42 (1,3,5,7)	0.31		
4-6	(4b)	CN-33 (1,2,4,6) CN-34 (1,2,4,7) CN-37 (1,2,5,7)	3.32		
4-7	(4c)	CN-47 (1,4,6,7)	1.26		
4-8		CN-36 (1,2,5,6)	0.40		
4-10	(4d)	CN-28 (1,2,3,5) CN-43 (1,3,5,8)	1.27		
4-14	(4f)	CN-32 (1,2,4,5)	0.32		
4-15	(4g)	CN-35 (1,2,4,8)	1.48		
4-16	(4h)	CN-38 (1,2,5,8)	3.78		
4-18		CN-46 (1,4,5,8)	1.90		

Table 2. continued

peak (a)	(b)	congener (c)	mass (%)		homolog contribution (this study)	(d)
<u>Pentachloronaphthalenes</u>					33.9	46.8
5-1	(5a)	CN-52 (1,2,3,5,7) CN-60 (1,2,4,6,7)	3.57			
5-2	(5b)	CN-58 (1,2,4,5,7)	0.32			
5-3	(5c)	CN-61 (1,2,4,6,8)	3.78			
5-4	(5d)	CN-50 (1,2,3,4,6)	0.97			
5-8	(5e)	CN-57 (1,2,4,5,6)	5.57			
5-9	(5f)	CN-62 (1,2,4,7,8)	6.46			
5-10	(5g)	CN-53 (1,2,3,5,8)	4.81			
5-11	(5h)	CN-59 (1,2,4,5,8)	8.41			
<u>Hexachloronaphthalenes</u>					32.4	23
6-1	(6a)	CN-66 (1,2,3,4,6,7) CN-67 (1,2,3,5,6,7)	0.89			
6-2	(6b)	CN-64 (1,2,3,4,5,7) CN-68 (1,2,3,5,6,8)	3.00			
6-3	(6c)	CN-69 (1,2,3,5,7,8)	7.08			
6-4	(6d)	CN-71 (1,2,4,5,6,8) CN-72 (1,2,4,5,7,8)	13.3			
6-5	(6e)	CN-63 (1,2,3,4,5,6)	3.30			
6-6	(6f)	CN-65 (1,2,3,4,5,8)	4.87			
<u>Heptachloronaphthalenes</u>					4.8	1.6
7-1	(7a)	CN-73 (1,2,3,4,5,6,7)	0.92			
7-2	(7b)	CN-74 (1,2,3,4,5,6,8)	3.90			
<u>Octachloronaphthalene</u>					0.1	6.6
8	(8)	CN-75 (1,2,3,4,5,6,7,8)	0.13			
				Total:	96%	99.3%

(a) labelling scheme used in this work. (b) labelling used in Järnberg et al., 1993.

(c) peaks identified using information from Wiedmann and Ballschmiter, 1993, Imagawa et al., 1993 and Falandysz et al., 1996.

(d) homolog mass percent contributions from Wiedmann and Ballschmiter, 1993.

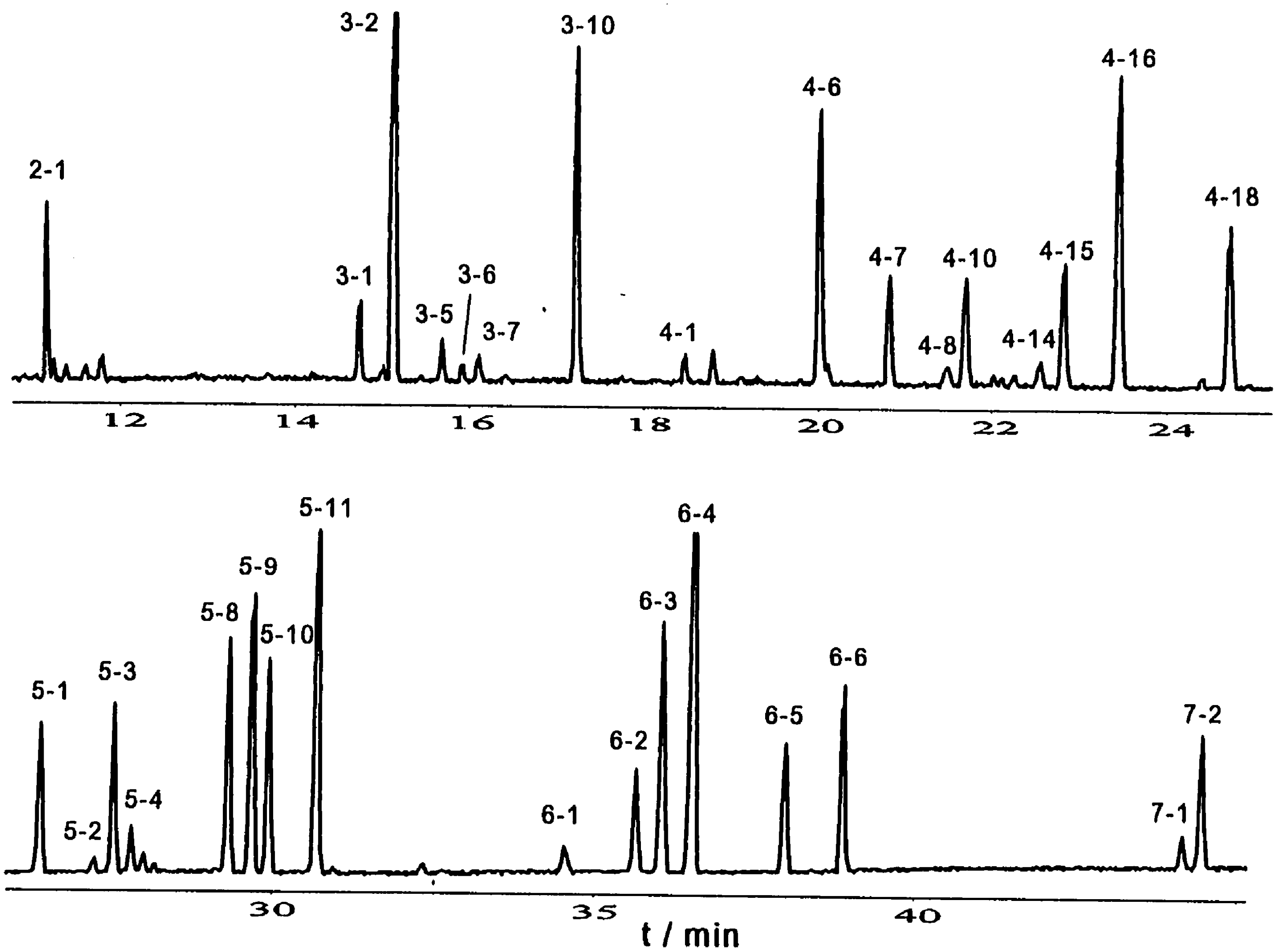

Figure 1 GC-FID chromatogram of Halowax 1014.

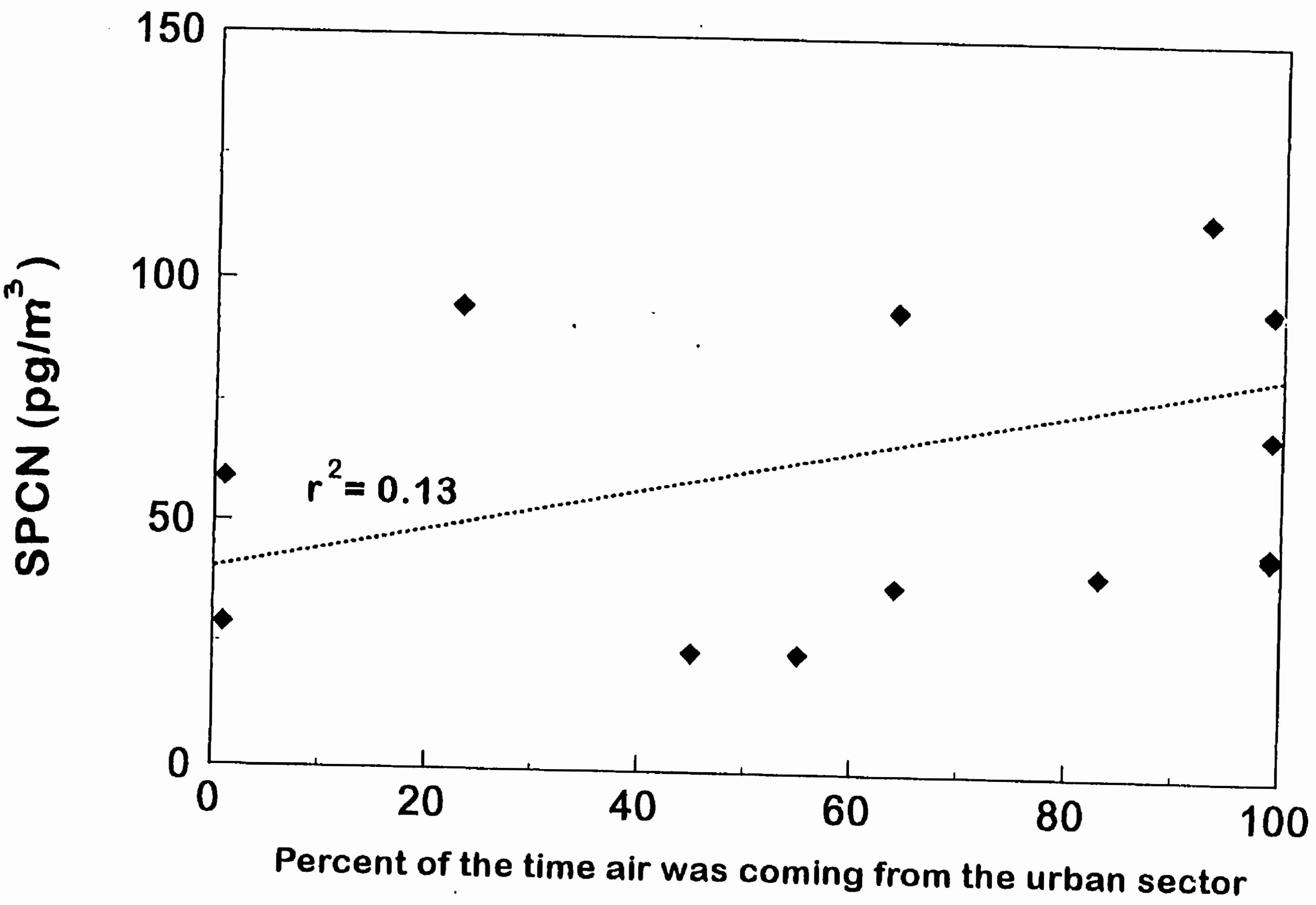

Figure 2 Variation of PCN air concentrations in Chicago with the percent of the time that the wind was blowing from the urban sector.

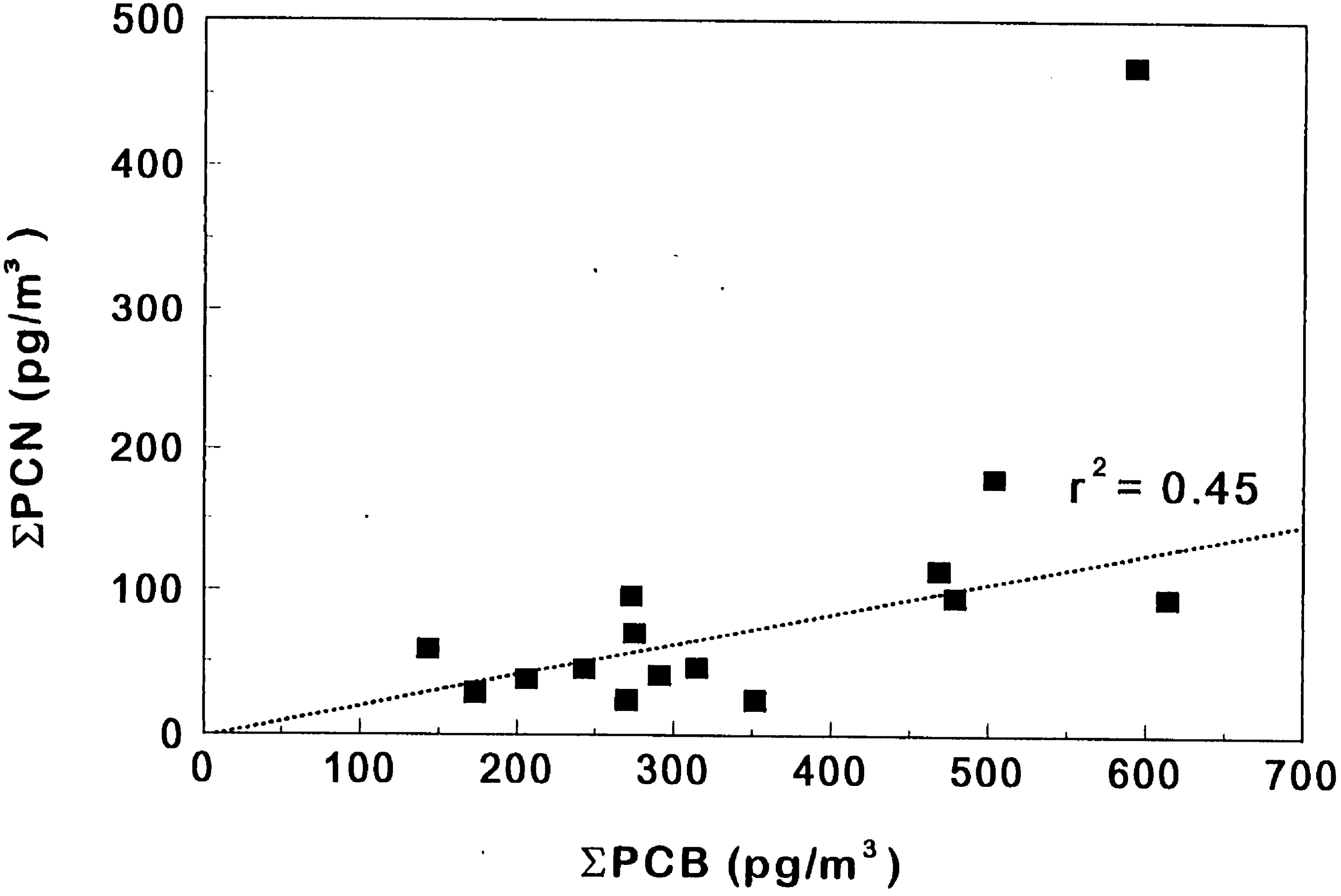

Figure 3 Correlation of levels of PCN and PCB in Chicago air. (The high PCN point was omitted from the regression.)

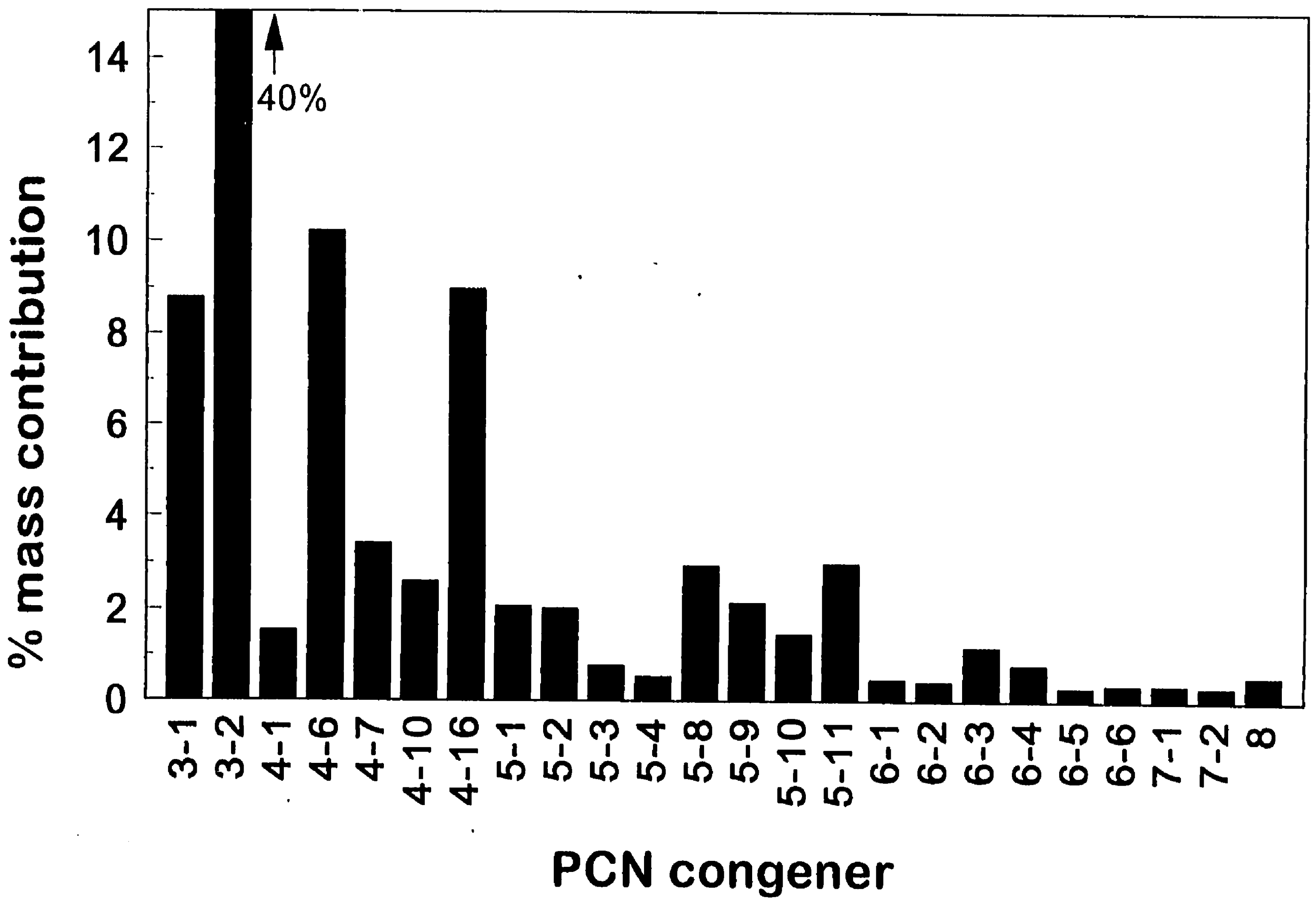

Figure 4 Average mass percent contribution of PCN congeners in Chicago air.

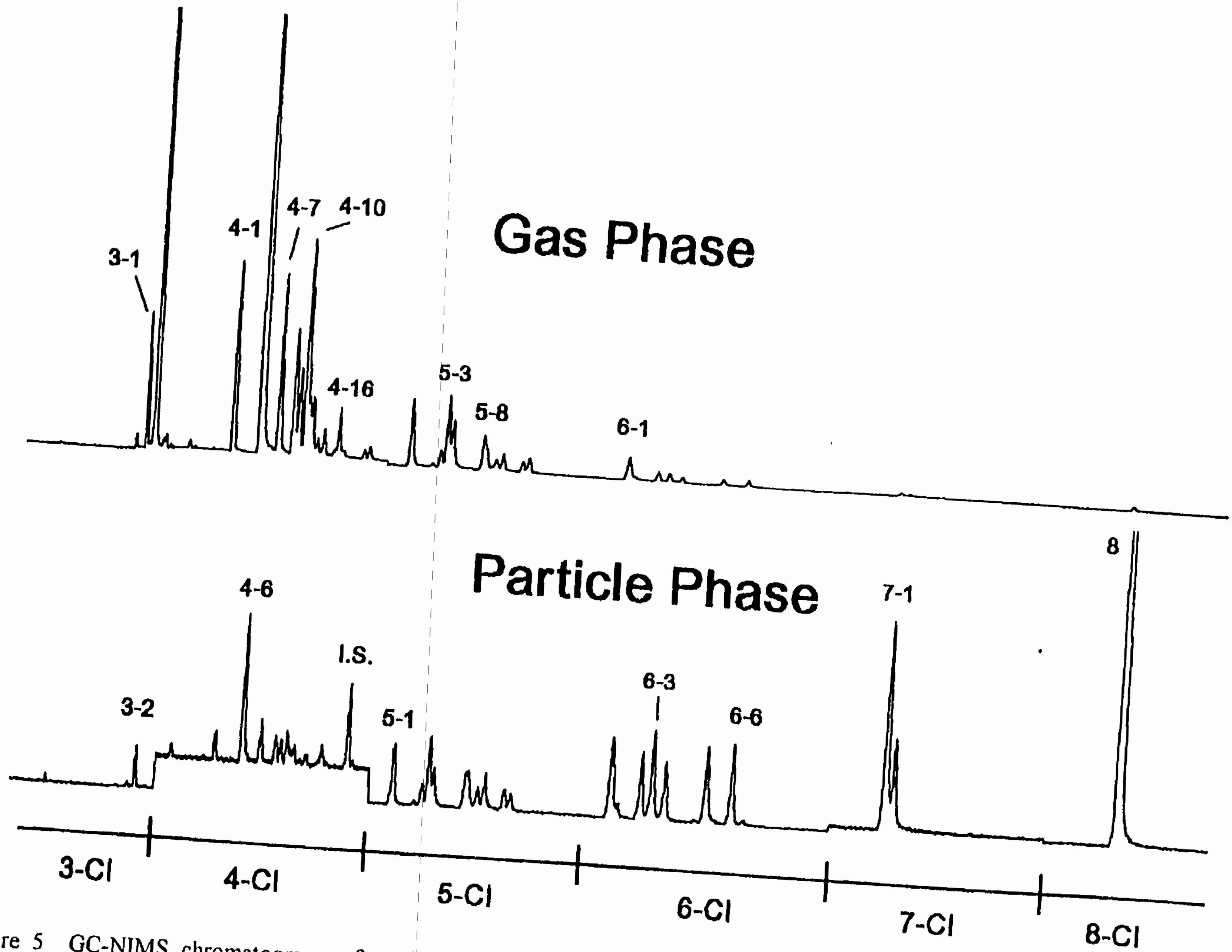

Figure 5 GC-NIMS chromatograms of particulate and gaseous PCNs in Chicago air (#6). Major peaks are marked on the chromatogram for reference (I.S.= internal standard)

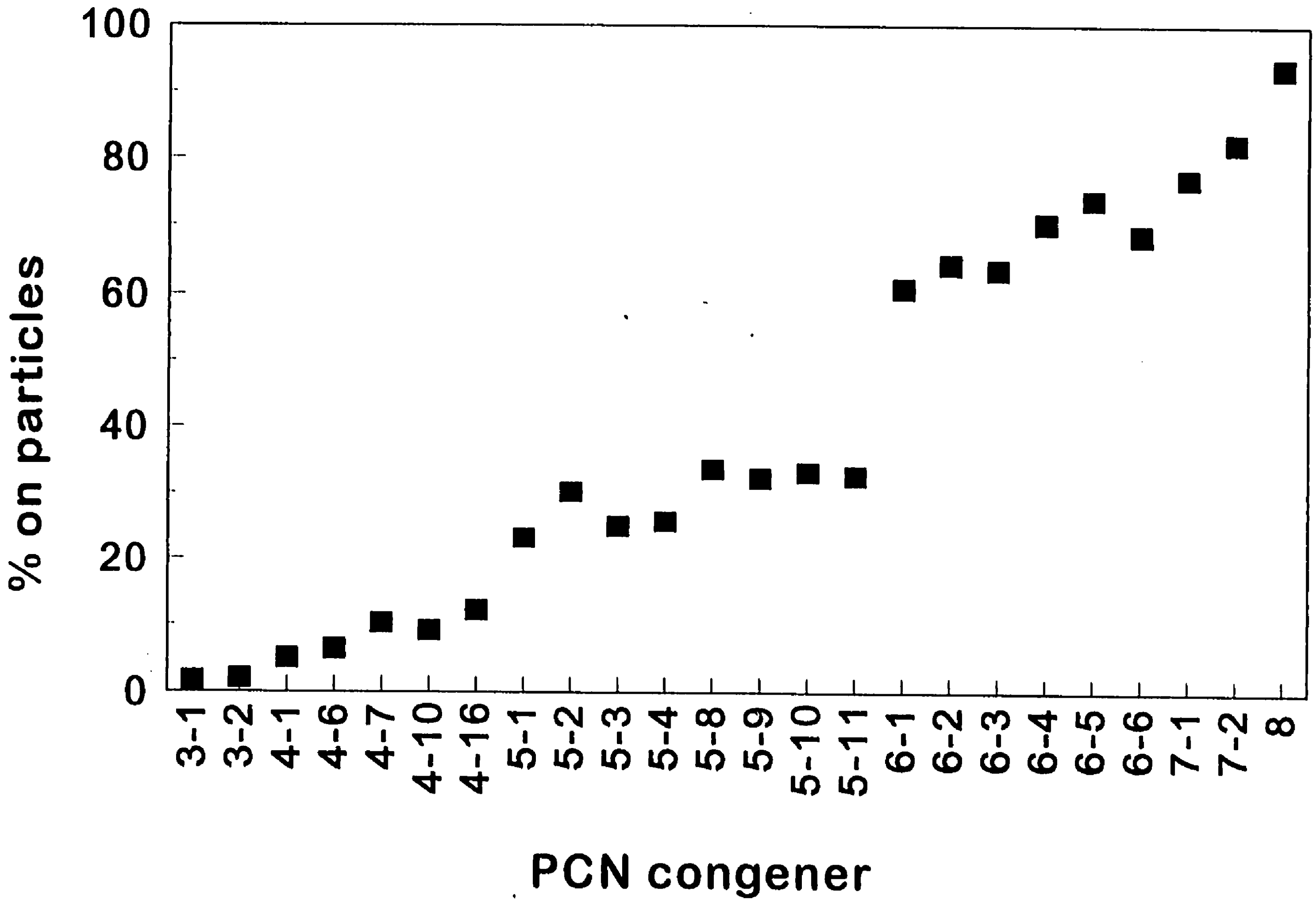

Figure 6 Percent of individual PCN congeners on particles in Chicago air (average for all samples).

PAPER V: POLYCHLORINATED NAPHTHALENES AND COPLANAR POLYCHLORINATED BIPHENYLS IN ARCTIC AIR

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Abstract

This paper reports the first measured concentrations of PCNs and coplanar PCBs in arctic air. The data represent bulked air samples from the Barents Sea (n=2), north eastern Arctic Ocean (n=12), and two land-based monitoring stations at Alert, Canada (n=5) and Dunai, Island in eastern Siberia, Russia (n=3). Average values for ΣPCN (pg m^{-3}) were 3-38 for shipboard samples and 0.5-8 for land-based stations, and were dominated by the 3-Cl and 4-Cl homologs which accounted for 90-95% of the total mass. Concentrations (fg m^{-3}) of coplanar PCBs were 3-40 (PCB-77) and 0.3-4 (PCB-126) - about an order of magnitude lower than in Chicago air. High concentrations of PCB-77 and PCB-126 were observed in the Barents Sea - 470 and 6.8 (fg m^{-3}) respectively. The 2,3,7,8-TCDD toxicity of the air samples was assessed in terms of the TEQ (dioxin toxic equivalents) contribution of mono-ortho PCB-105 and non-ortho (coplanar) PCBs (congeners-77, -126) and the contribution of the dioxin-like PCNs for which TEFs (toxic equivalent factors) have been determined. The results show a significant TEQ contribution of PCNs and it is concluded that further investigation of this compound class is merited.

Introduction

Polychlorinated naphthalenes (PCNs) are widespread environmental pollutants which have been quantified in a range of environmental media (Järnberg et al, 1993, Falandysz et al., 1996) including arctic biota (Koistinen et al., 1989, Asplund et al., 1990). The ubiquitous nature of PCNs is of concern because of their dioxin-like toxicity, which is of similar magnitude to some of the coplanar PCBs (Hanberg et al, 1990). Although the use of PCNs has declined in the past few decades, they are not prohibited in most countries and still occur in many PCB-like applications such as capacitor fluids, engine oil additives, and electrical insulators (Crookes and Howe, 1993). PCNs have also been found in incinerator emissions (Oehme et al., 1987), are detected as contaminants in commercial PCB fluids (Haglund et al., 1993), and have recently been quantified in air (Dörr et al., 1996, Harner and Bidleman, 1997). PCNs were aldo identified in air samples from N. Sweden, but not quantified (Järnberg et al., 1997).

Polychlorinated biphenyls (PCBs) are also a concern in the Arctic environment. Unlike the PCNs, levels of PCBs in arctic air (Stern et al., 1997) and biota (Weis and Muir, 1997; Muir et al., 1988) have been fairly well monitored, especially in the past decade. However, levels of coplanar PCBs, the most toxic of the PCBs, have not been reported in air. Coplanar PCBs have no ortho-substituted chlorines and are structurally similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin. They represent a small percent of the total PCB mass and often co-elute with more abundant congeners. Consequently, the analysis of coplanar PCBs often requires special fractionation procedures (Schwartz et al., 1993).

This paper summarizes atmospheric levels of PCNs and coplanar PCBs over the Eastern Arctic Ocean and at two land-based arctic monitoring stations (Alert, NWT-Canada and Dunai Island, Russia). Results are compared with urban data on the basis of average concentrations, congener profiles, and relative toxicity contributions.

Experimental Methods

Eastern Arctic Ocean

In the summer of 1995, the Swedish icebreaker Oden embarked on a three month scientific expedition to the Barents Sea and North Eastern Arctic Ocean (Fig. 1-cruise track). A total of 34 air samples was collected using a high volume train consisting of a glass fiber filter (GFF) followed by two polyurethane foam plugs (PUF). Flow rates were approximately 0.4 m^3 min^{-1}. Collection dates and other information are summarized in Table 1.

Previous studies with persistent organic pollutants (POPs) in the arctic have shown that most of the chemical mass is associated with the gas phase, especially during summer months. Therefore, only the PUF plug values were used to assess air concentrations. PUF plugs were soxhlet extracted using petroleum ether and volume was reduced to 2 mL by rotary evaporation and nitrogen blow-down. Extracts were fractionated on a column of silicic acid overlaid with neutral alumina. PCNs and PCBs were eluted in fraction F1 with 30 mL petroleum ether. Fraction F2, which was not analyzed in this study, was eluted with 25 mL dichloromethane and contained polycyclic aromatic hydrocarbons and most organochlorine pesticides. To increase detection, several samples were bulked in groups of 2-4 giving a total of 14 representative air samples. The F1 portions were further fractionated on a mini carbon column to separate the mono- and non-ortho PCBs from the multi-ortho congeners. This column consisted of AX-21 activated carbon mixed 1:20 with silicic acid prepared as described by Falconer et al. (1995). The first fraction (F1-1) was eluted with 5 mL 30% dichloromethane in cyclohexane and contained the multi-ortho and a portion of the mono-ortho PCBs. The second fraction (F1-2) was eluted 5 mL of toluene and contained the PCNs, non-ortho PCBs and the remainder of the mono-ortho congeners. PCB-103 was added as an internal standard and samples were analyzed by gas chromatography negative ion mass spectrometry (GC-NIMS) on a Hewlett Packard 5890 - MS Engine using a 30 m DB-5MS column (0.25 mm i.d., 0.25 µm film, J&W Scientific). For peaks to qualify, the ion ratio (target/qualifier) had to be within 20% of the standard. PCNs were quantified against Halowax 1014, a commercial mixture of 2-Cl to 8-Cl PCNs. PCBs were quantified against a mixture of non-ortho and mono-ortho PCBs. The details of the sample extraction and clean-up methods and the GC-MS procedure are presented elsewhere (Harner and Bidleman, 1997, Harner and Bidleman, submitted).

Prior to soxhlet extraction, PUF plugs were fortified with a surrogate mixture containing $^{13}C_{12}$ PCB - congeners 81, 77, 126, 169. Surrogate recoveries were used to correct for PCB losses. To correct for PCN losses, four clean PUFs were spiked with Halowax 1014 and treated as samples.

Alert and Dunai

The stations at Alert and Dunai have been monitoring air concentrations of persistent organic pollutants since 1992 as part of the Northern Contaminants Program initiated by the federal Department of Indian Affairs and Northern Development, Canada. The Alert station (N60.2, W134.1) is located on Ellesmere Island and the Russian station is located on Dunai Island in eastern Siberia (N74.6, E124.3).

At both locations, weekly air samples were collected at a flow rate of approximately 1.1 m^3 min^{-1} using a high volume train consisting of a 20 cm diameter glass fiber filter followed by two 20 cm diameter, 4 cm thick PUF plugs. Each weekly sample represented an air volume of about 11 400 m^3. Monthly PUF blanks were collected by handling a clean PUF as a sample but not drawing air through it. More details regarding sample collection, preparation and analysis are presented elsewhere (Stern et al., 1997, Fellin et al., 1996) .

PUF plugs and filters were soxhlet extracted using a 1:1 mixture of hexane and dichloromethane. After drying over anhydrous sodium sulfate and volume reduction to 20 mL, half of the extract was archived. For this study, we were able to obtain a limited set of archived weekly PUF and GFF extracts representing approximately 2500 m^3 (Alert) and

3000 m^3 (Dunai) air; five samples from Alert for months June, July, August, 1993 and January, April, 1994 and three samples from Dunai for months June, July, August, 1993. GFF extracts were analyzed for the July, 1993 and January, 1994 Alert samples and for the July, 1993 sample from Dunai Island.

All extracts were fortified with $^{13}C_{12}$-PCBs and analyzed by the same method described for the eastern arctic samples.

Chicago

Air samples were collected in February-March, 1995 on the roof of Farr Hall, a five story building on the campus of the Illinois Institute of Technology, which is located just south of downtown Chicago and approximately 2 km inland from Lake Michigan. This work was part of a study to investigate concentrations and particle/gas partitioning of PCBs, PAHs, and PCNs in urban air (Harner and Bidleman, 1997; Harner and Bidleman, submitted). Sample volumes were approximately 400 m^3. Details regarding sampling and analytical information are presented elsewhere (Harner and Bidleman, 1997).

Results and Discussion

Quality Control

In the treatment of the Barents Sea and N. E. arctic air samples, five back PUFs were analyzed to assign blank levels. Limit of detection (L.O.D.) values were calculated as mean blank+(3×SD). When quantifying samples by GC-NIMS, peaks had to meet two criteria to qualify. The first criteria was that the ion ratio (target ion: qualifier ion) had to be within ± 20% of the value for the standard. Secondly, the sample peaks were required to exceed the L.O.D.. For the Alert and Dunai samples, peaks qualified if they exceeded the single blank value. Qualified analytes were blank corrected and adjusted using recovery factors.

Mean recoveries of surrogate $^{13}C_{12}$-PCB in the Eastern Arctic / Alert, and Dunai samples were: $^{13}C_{12}$-PCB81, 72% / 76%; $^{13}C_{12}$-PCB77, 78% / 79%; $^{13}C_{12}$-PCB126, 80% / 74%; $^{13}C_{12}$-PCB169, 95% / 76% and $^{13}C_{12}$-PCB105, 13% / 43%. The value for PCB-105 is not a true recovery but the percent which eluted in carbon column fraction F1-2 - this was the fraction used for quantification. Unlike the coplanar PCBs which elute entirely in F1-2, PCB-105 is split between F1-1 and F1-2, mostly eluting in F1-1. For PCNs, recoveries ranged from 35% for the volatile 3-Cl congeners to 95% for the higher molecular weight 6- and 7-Cl homologs. L.O.D. values for individual PCN congeners in the Eastern Arctic samples ranged from 3-680 fg m^{-3}. L.O.D. values for the coplanar PCBs and PCB-105 (fg m^{-3}) were lower: PCB-81, 1.4; PCB-77, 1.5; PCB-126, 0.3; PCB-169, 0.4 and PCB-105, 0.90.

PCNs in Air

Concentrations of PCNs at each of the sampling sites are summarized in Table 1. Average concentrations of ΣPCN (pg m^{-3}) were 38 and 9 for the Barents Sea and north east Arctic Ocean samples respectively. Values at the monitoring stations were: Alert - 3.7 (n=5) and Dunai Island - 1.0 (n=3) (pg m^{-3}). These levels are approximately an order of magnitude lower than values reported in urban areas. The average winter (February-March, 1995) concentration of PCNs in Chicago was 68 pg m^{-3} (Harner and Bidleman, 1997) and the yearly average for Augsburg , Germany was 60 pg m^{-3} (Dörr et al., 1996).

Figure 2 shows GC-NIMS chromatograms for Halowax 1014 and a PUF sample from Alert. Peaks are labeled according to a scheme adopted by Harner and Bidleman (1997) where the first number designates the homolog group and the second number is the elution order within the homolog. The PCN pattern in the sample and standard are well matched with the sample showing significant enrichment of the lower molecular weight congeners and depletion of the higher molecular weight congeners relative to Halowax 1014. This is further demonstrated in Figure 3 which compares congener mass profiles for the land-based Arctic sites and the Chicago samples with mass contributions in Halowax 1014.

The Arctic and Chicago samples exhibit a greater proportion of the less chlorinated congeners compared to the standard. This fractionation is also suggested by Figure 1 which shows the average homolog mass distribution at the sampling sites. The 3-Cl and 4-Cl congeners account for approximately 80% of the total mass in Chicago and are enriched to 90-95% of the total mass in the arctic samples. This may be due to preferential volatilization of the lighter PCN congeners. i.e. global fractionation (Wania and Mackay, 1996). An alternate explanation may involve differences in source signatures. Halowax 1001 and 1099 accounted for 65% of the market share of Halowax sales (Crookes and Howe, 1993) and are dominated by 3-Cl (40%) and 4-Cl (40%) congeners. In Halowax 1014 the contributions are smaller - 3-Cl (14%) and 4-Cl (34%) (Harner and Bidleman, 1997).

Before any definitive statements can be made regarding PCN transport and global distribution, more studies are required to investigate PCN partitioning in the atmosphere as well as other environmental media. A good starting point is to look at the particle/gas partitioning of PCNs in air. Particle-gas partitioning is an important factor in the transport of chemicals away from sources and in their deposition from the atmosphere. Absorption of chemicals to particles can be described using the octanol-air partition coefficient, K_{OA} (Finizio et al., 1997, Harner and Bidleman, submitted), which has been recently measured for PCN congeners as a function of temperature (Harner and Bidleman, 1998). Figure 4 is a log-log plot of F/A versus K_{OA} for a January, 1994 air sample from Alert. F and A represent the particle-phase and gas-phase concentrations (pg m^{-3} air). The good correlation supports the use K_{OA} as a partitioning descriptor for PCNs.

PCBs in Air

Concentrations of total PCBs (approximately 100 congeners) were taken from Stern et al. (1997) and are summarized in Table 1 for the five Alert and three Dunai samples. Average ΣPCB (pg m^{-3}) were 37.6 ± 22.5 and 29.9 ± 2.7 respectively. ΣPCB were not determined for the north east Arctic Ocean samples. On average, ΣPCB were approximately 5-30 times greater than ΣPCN in arctic samples and 5-6 greater in Chicago samples (Harner and Bidleman, 1997a, Table 1).

Levels of coplanar PCBs, congeners 77 and 126, are summarized in Table 2. Values for congeners 81 and 169 were excluded since most samples were at or below detection limits and ion ratios were not satisfactory. The mass percentage contributions of congeners 77 and 126 have been reported in Aroclor mixtures 1242 and 1254 (Schwartz et al., 1993) and Clophen mixtures (Haglund et al., 1993). Figure 5 shows that, except for the Barents Sea samples (n=2), the mass contribution of the coplanar PCBs in air is within the range reported for technical mixtures. It should be noted that ΣPCB values were not determined for Arctic Ocean samples. Mass percentages for the coplanar PCBs were derived by assuming a ΣPCB value of 34 pg m^{-3}, the average found at Alert and Dunai (Table 1).

Implications regarding Toxicity

Because of their shape and size, some coplanar PCBs (and a few mono- and di-ortho congeners) and PCNs exhibit 2,3,7,8-tetrachlorodibenzodioxin (TCDD) toxicity. Toxic equivalent factors (TEFs) have been determined for PCBs (Ahlborg et al, 1994) and several 6-7 chlorinated PCN congeners (Hanberg et al, 1990). By calculating TCDD toxic equivalents (TEQs), it is possible to compare dioxin-like toxicity of different compounds on a common scale. TEQs are calculated by multiplying the air concentration of the particular compound by its TEF value. Table 2 and Figure 6 summarize the air concentrations and TEQ values for PCBs 77 and 126 and several dioxin-like PCNs at the sample locations. Although it is not coplanar, PCB-105 (a mono-ortho) was also included in the comparison. Despite its lower TEF value, this congener is abundant in air, resulting in a substantial TEQ contribution. In all cases however, the highest TEQ contribution is attributed to the coplanar PCBs, mostly congener 126 (Table 2). The Dunai site has an increased contribution of PCB-105. A previous study (Stern et al., 1997) found enrichment in the 5-Cl and 6-Cl mono-ortho PCBs at this site. The PCNs also make an important contribution - accounting for ~20% of the TEQ at the four arctic sites and 40% in Chicago.

Conclusions

Polychlorinated naphthalenes (PCNs) and non-/mono-ortho PCBs have been quantified in arctic air samples. Results indicate that PCNs contribute significantly to the dioxin-like toxicity in air - a problem which has already been identified in urban samples. A recent study has shown that approximately 14% of the TCDD toxicity measured in plasma in an Inuit population from Nunavik (arctic Quebec) is attributed to non-ortho PCBs. This contribution is slightly higher (20%) in southern Quebec (Ayotte et al., 1997). More work is merited to investigate concentrations of coplanar PCBs and PCNs in arctic samples, since these compounds may have significant human and animal toxicities.

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Table 1. Sampling information and concentrations of total PCNs and PCBs.

Sample	date	lat./long. (initial)	lat/long. (final)	(m^3) air volume	($pg\ m^{-3}$) ΣPCN^a	ΣPCB^b
Barents Sea						
air#1	96-07-18/19	N71, 8’/ E21, 35’	N73, 34’/E24, 60’	945		
air#2	96-07-19/21	N73, 34’/ E25, 1’	N73, 47’/ E25, 40’	1258	28.8	NA
air#3	96-07-21/22	N73, 52’/ E25, 60’	N78, 25’/ E56, 10’	659		
air#4	96-07-22/23	N77, 5’/ E41, 15’	N78, 25’/ E56, 10’	710		
air#5	96-07-23/24	N78, 25’/ E56, 60’	N80, 18’/ E65, 43’	623	46.7	NA
				mean	37.8	NA
North East Arctic Ocean						
air#6	96-07-24/25	N80, 59’/ E67, 42’	N81, 44’/ E65, 53’	846		
air#7	96-07-25/26	N81, 46’/ E65, 39’	N82, 49’/ E65, 39’	767		
air#8	96-07-26/27	N82, 53’/ E65, 37’	N83, 50’/ E66, 56’	1096	10.6	NA
air#9	96-.07-28/29	N84, 48’/ E71, 41’	N85, 22’/ E71, 41’	891		
air#10	96-07-29/30	N85, 23’/ E71, 40’	N85, 34’/ E72, 18’	876		
air#11	96-07-30/01	N85, 40’/ E72, 52’	N86, 20’/ E74, 15’	1221	13.9	NA
air#12	96-08-01/02	N86, 55’/ E86, 50’	N87, 3’/ E123, 8’	709		
air#13	96-08-03/04	N87, 1’/ E129, 50’	N86, 23’/ E142, 12’	855	11.6	NA
air13-2	96-08-23	N87, 9’/ E144, 48’	N87, 4’/ E142, 17’	777		
air13-3	96-08-23/24	N87, 4’/ E142, 17’	N86, 29’/ E130, 6’	771		
air13-4	96-08-24/25	N86, 29’/ E130, 6’	N86, 27’/ E130, 57’	1168		
air#14	96-08-25/26	N86, 27’/ E130, 57’	N85, 26’/ E137, 20’	835	8.1	NA
air#15	96-08-29/30	N85, 24’/ E152, 17’	N85, 31’/ E155, 3’	1015		
air#16	96-08-30/31	N85, 31’/ E155, 3’	N85, 33’/ E156, 35’	1232		
air#17	96-08-31/01	N85, 33’/ E156, 37’	N85, 40’/ E160, 22’	669	12.6	NA
air#18	96-09-02/03	N86, 57’/ E152, 54’	N87, 37’/ E146, 47’	929		
air#19	96-09-03/04	N87, 37’/ E146, 47’	N87, 37’/ E158, 28’	956		
air#20	96-09-04/05	N87, 37’/ E158, 28’	N87, 10’/ E169, 13’	984	5.4	NA
air#21	96-09-07/08	N88, 36’/ E179, 38’	N88, 52’/ E179, 58’	768		
air#22	96-09-08/09	N88, 59’/ E179, 59’	N89, 54’/ E156, 9’	930		
air#23	96-09-10/12	N89, 51’/ E51, 11	N87, 60’/ E23, 19’	1265	4.7	NA
air#24	96-09-12/13	N87, 60’/ E23, 19’	N86, 30’/ E19, 33’	1306		
air#25	96-09-13/14	N86, 25’/ E19, 1’	N85, 31’/ E12, 30’	1030		
air#26	96-09-14/15	N85, 31’/ E12, 30’	N85, 33’/ E10, 55’	873	7.0	NA

Table 1. (continued)

air#27	96-09-15/16	N85, 33’/ E10, 55’	N84, 37’/ E15, 40’	931		
air#28	96-09-16/17	N84, 33’/ E15, 37’	N84, 2’/ E11, 18’	767		
air#29	96-09-17/18	N84, 1’/ E11, 11’	N82, 41’/ E13, 19’	989	13.3	NA
air#30	96-09-21/22	N78, 15’/ E15, 39’	N74, 37’/ E14, 34’	883	6.8	NA
air#31	96-09-22/23	N74, 29’/ E14, 37’	N71, 4’/ E15, 51’	770		
air#32	96-09-23/24	N70, 42’/ E15, 58’	N67, 29’/ E12, 54’	797		
air#33	96-09-24/25	N67, 29’/ E12, 54’	N63, 23’/ E6, 19’	793	3.0	NA
air#34	96-09-25/26	N63, 23’/ E6, 18’	------------	680	8.4	NA
				mean	8.8	NA
				(SD)	(3.6)	
Alert’93/94						
January-PUF					2.6	57.3
April-PUF					0.99	29.1
June-PUF					8.0	9.9
July-PUF					2.9	64.1
August-PUF					4.1	27.8
July-GFF					0.1	
				mean[c]	3.7	37.6
				(SD)	(2.6)	(22.5)
Dunai’93						
June-PUF					1.3	30.7
July-PUF					0.46	32.2
August-PUF					1.1	26.9
July-GFF					0.1	
				mean[c]	0.95	29.9
				(SD)	(0.44)	(2.7)
Chicago’95					68	350
Augsburg ‘92/’93[d]					60	NR

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[a] ΣPCN represent PUF values for bulked Eastern Arctic samples.

[b] ΣPCB values for Alert and Dunai from Stern et al. (1997); Chicago values from Harner and Bidleman, 1997 and Harner and Bidleman (submitted); ΣPCB in air over Eastern Arctic Ocean not yet determined.

[c] mean of PUF values; NA = not analyzed; NR=not reported.

[d] average of nine-month monitoring data from seven stations (Dorr et al.,1996).

Table 2. Air concentrations and TEQs for of dioxin-like PCBs and PCNs in Arctic and urban air.

	concentration (fg m^{-3})							ΣTEQs (fg TEQ m^{-3})		
	PCN				1-ortho PCBs	0-ortho				
Location	CN-66/67	CN-69	CN-63	CN-73	-105	-77	-126	PCNs	1-ortho	0-ortho
Barents Sea										
air#1,2	54.2	390	170	51.6	375	166	5.0			
air#3,4,5	2.8	<LOD	<LOD	<LOD	1178	773	8.5			
mean^{a}	28.5	154	63.8	10.4	776	470	6.8	0.527	0.078	0.91
North East Arctic Ocean										
air#6,7,8	<LOD	<LOD	<LOD	<LOD	NA	39.3	1.0			
air#9,10,11	19.2	<LOD	48.6	16.1	NA	29.3	1.7			
air#12,13	33.9	203	90.1	24.8	NA	35.7	0.9			
air#13-2to14	<LOD	<LOD	<LOD	<LOD	261	20.2	2.3			
air#15,16,17	<LOD	<LOD	<LOD	<LOD	87.2	34.9	1.2			
air#18,19,20	31.6	182	77.0	<LOD	38.1	13.9	1.0			
air#21,22,23	<LOD	<LOD	<LOD	<LOD	57.5	17.2	1.0			
air#24,25,26	<LOD	<LOD	<LOD	<LOD	47.3	16.7	0.7			
air#27,28,29	34.5	196	85.0	27.9	41.5	14.3	0.3			
air#30	<LOD	<LOD	<LOD	<LOD	NA	NA	NA			
air#31,32,33	<LOD	<LOD	<LOD	<LOD	NA	NA	NA			
air#34	<LOD	139	60.6	12.4	NA	NA	NA			
mean^{a}	6.4	9.9	0.8	<LOD	88.7	24.6	1.1	0.034	0.0089	0.111

Table 2. (continued)

Alert '93/94										
January	1.4	1.8	0.87	ND	23.1	2.84	ND			
April	3.5	1.7	6.9	ND	31.3	3.1	ND			
June	5.4	43.6	20.3	ND	61.1	8.0	2.1			
July	22.4	33.8	21.5	ND	133	36.8	12.2			
August	ND	3.3	2.1	ND	70.8	12.7	3.1			
mean	8.2	16.8	10.3	ND	63.9	12.7	3.6*	0.071	0.0064	0.36
Dunai '93										
June	0.66	2.4	1.6	ND	595	41.8	4.2			
July	ND	0.85	ND	ND	616	39.6	2.9			
August	ND	5.7	3.7	ND	381	19.8	1.1			
mean	0.29*	2.98	5.4*	ND	531	33.7	2.7	0.017	0.053	0.29
Chicago '95										
mean (n=15)	370	810	210	250	3270	420	63	3.4	0.33	6.51

ND= not detected; NA=not analyzed; * used instrument detection limit value (0.2 fg m^{-3}) for ND when calculating average.
[a] Alert and Dunai PCB data for mono-ortho and SPCB taken from Stern et al., ES&T, 1997, 31, 3619-3628.
CN-66/67=1,2,3,4,6,7/1,2,3,5,6,7; CN-69=1,2,3,5,7,8; CN-63=1,2,3,4,5,6; CN-73=1,2,3,4,5,6,7
TEF values (PCNs) from Hanberg et al. (1990): CN-66/67=0.002, CN-69=0.002, CN-63=0.002, CN-73=0.003.
TEF values (PCBs) from Ahlborg et al. (1994): PCB-77=0.0005, PCB-126=0.1, PCB-105=0.0001.

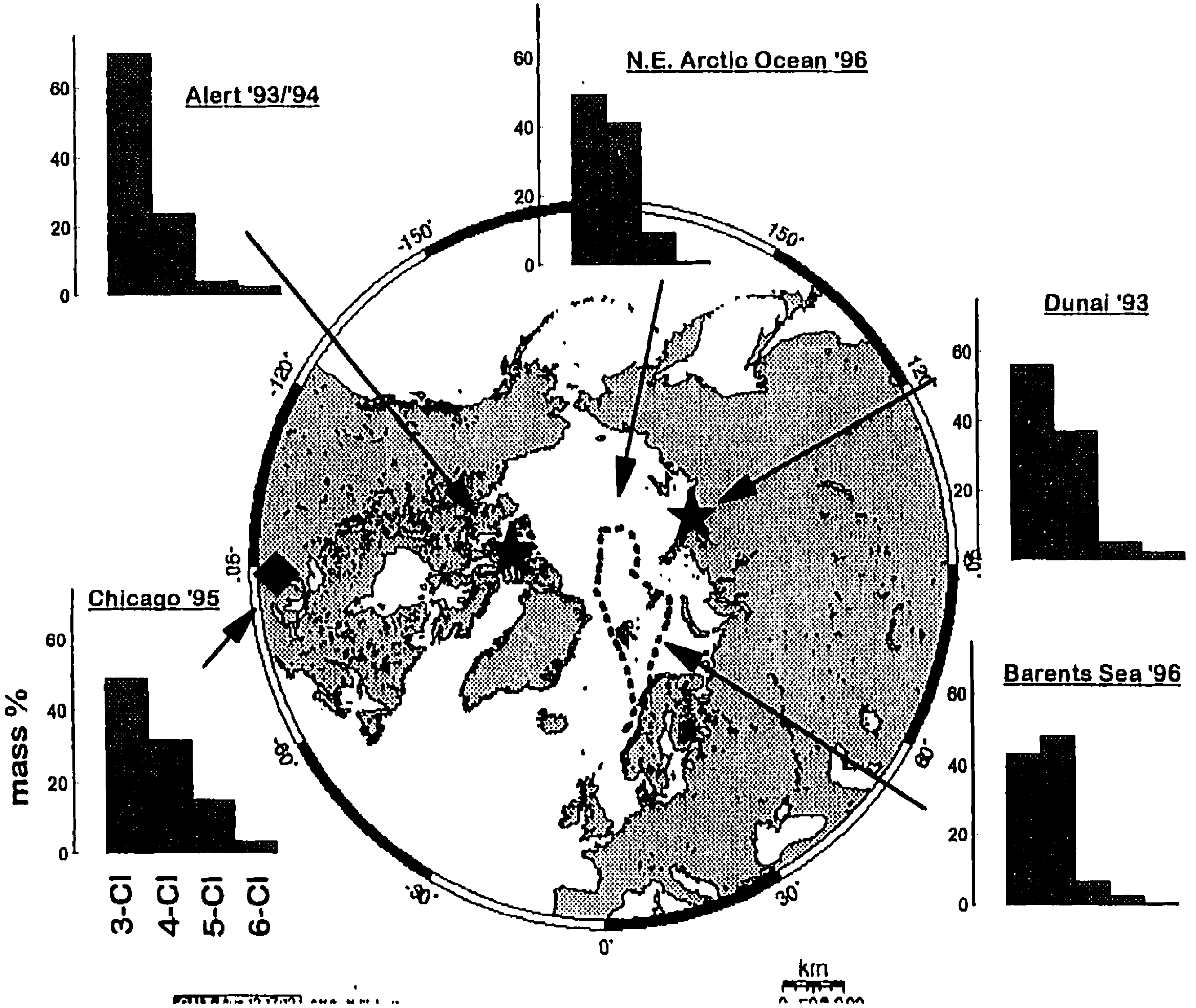


Figure 1. Map showing PCN homolog profiles at the various sampling locations. Dotted line represents the cruise track for the Oden 1996 cruise - Barents Sea and N.E. Arctic Ocean samples.

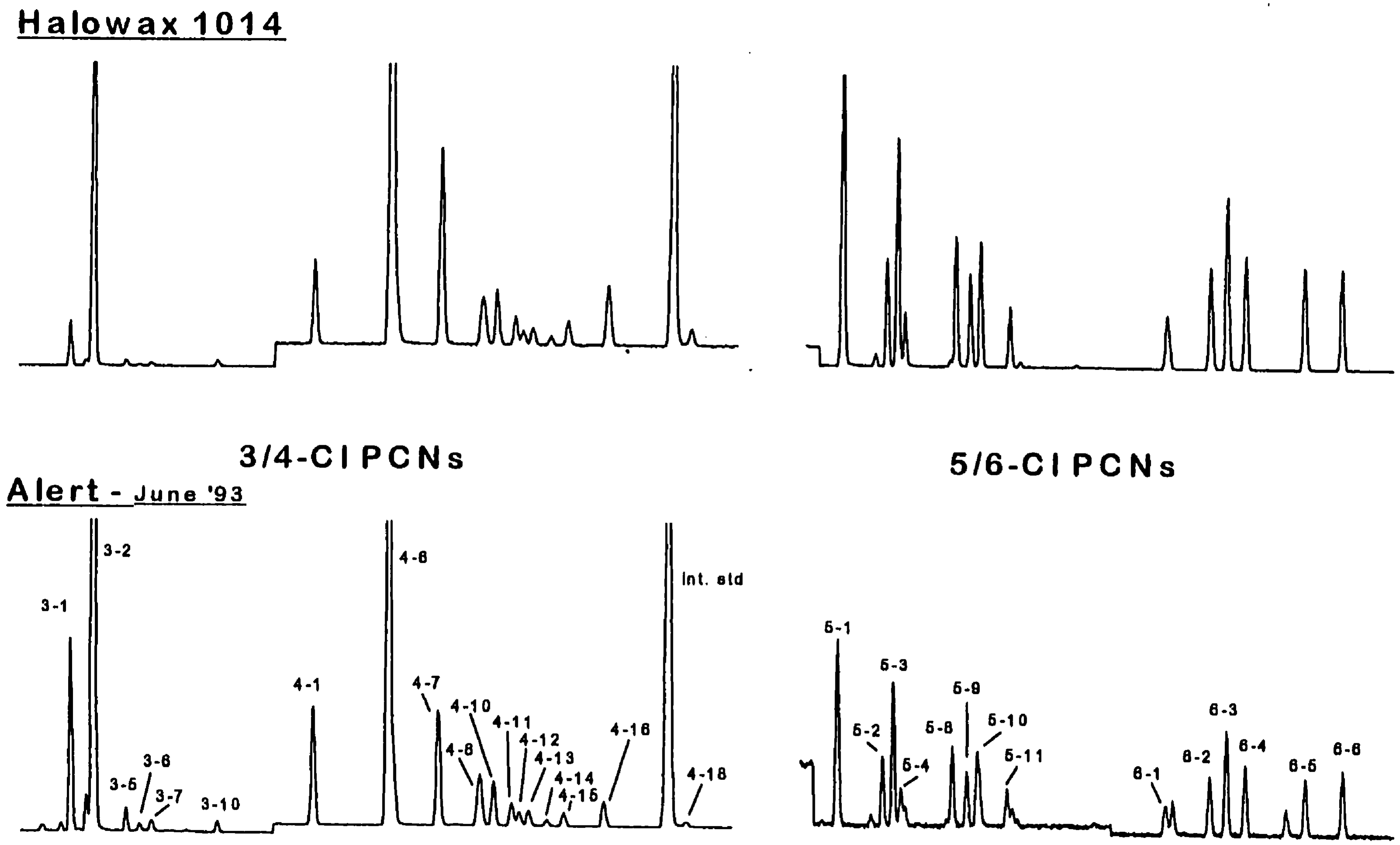
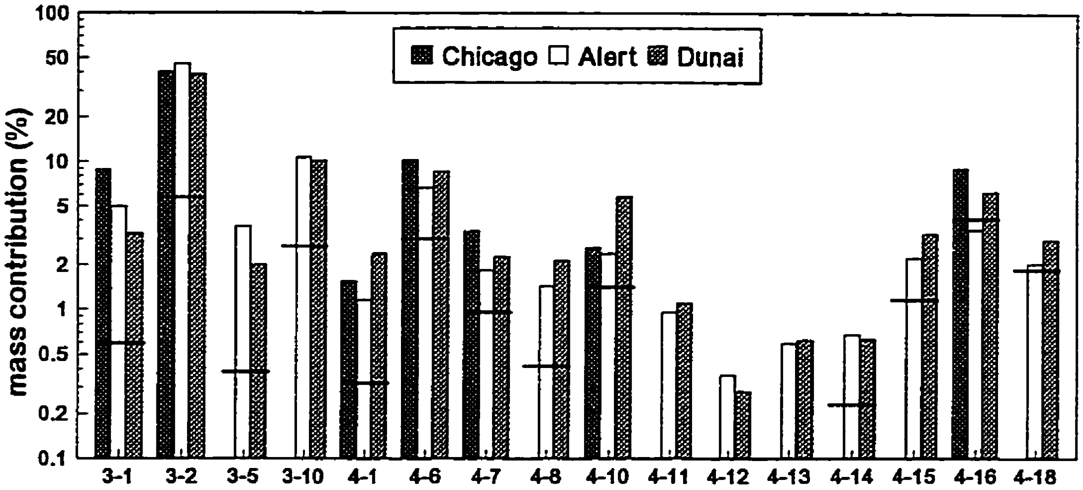


Figure 2. GC-NIMS chromatograms of technical PCN standard (Halowax 1014) and an air sample from Alert. The 5/6-Cl section of the chromatogram in the Alert sample is magnified by a factor of ten. Peak labelling and identification is presented in Harner and Bidleman (1997).



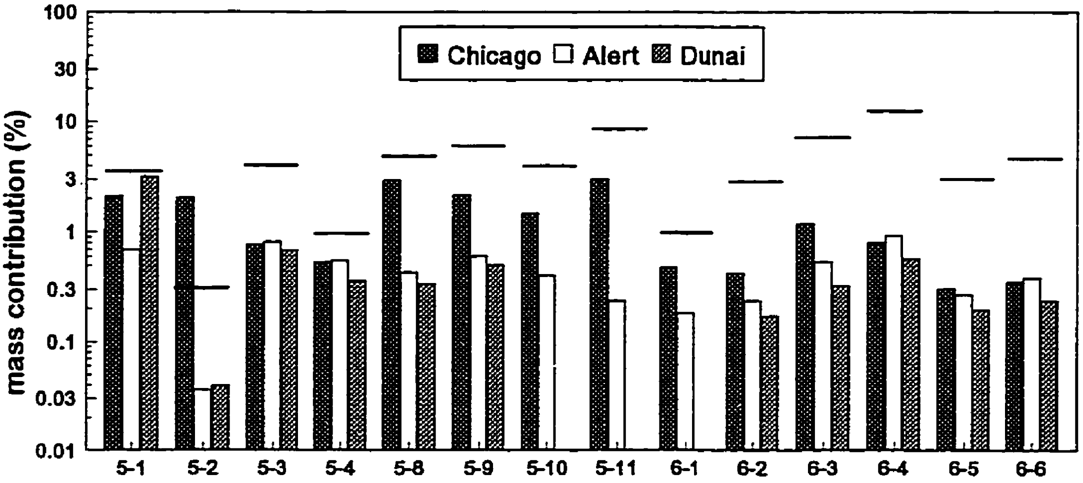


Figure 3. Mass distribution of PCN congeners at the sample locations. Dashed lines represent mass contributions in Halowax 1014 (Harner and Bidleman, 1997).

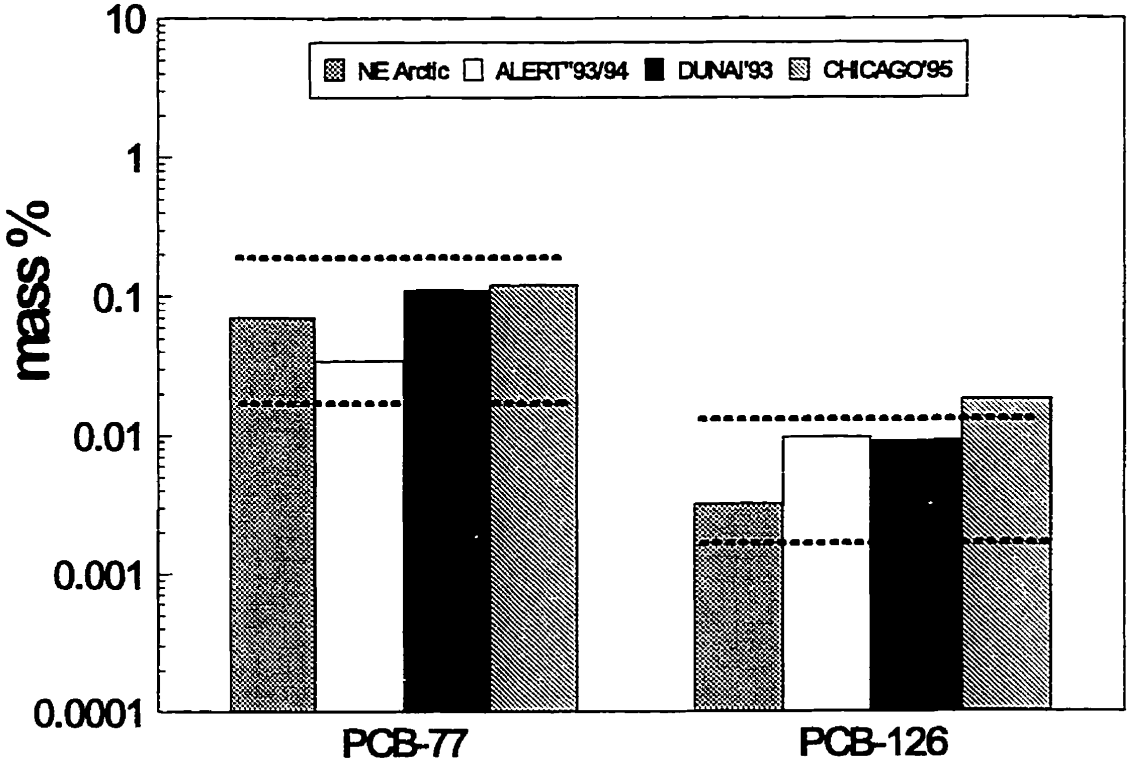


Figure 4. Mass distribution for coplanar PCBs at the sample locations. Dashed lines represent upper and lower mass contributions in technical PCB formulations (Schwartz et al., 1993; Haglund et al., 1993).

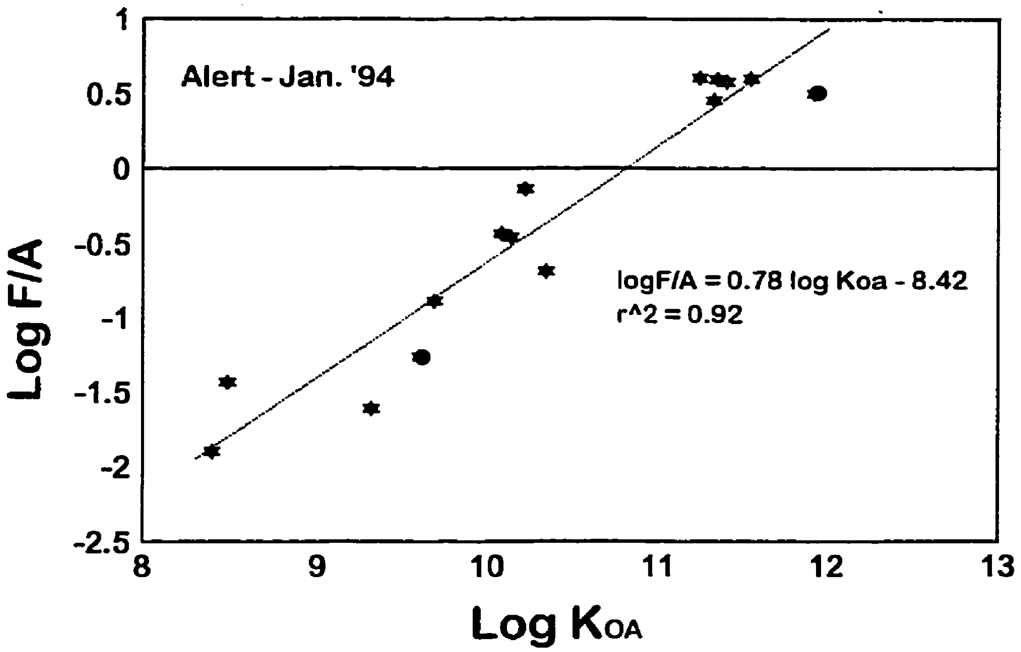


Figure 5. Particle/gas partitioning of PCNs at Alert (January, 1994).

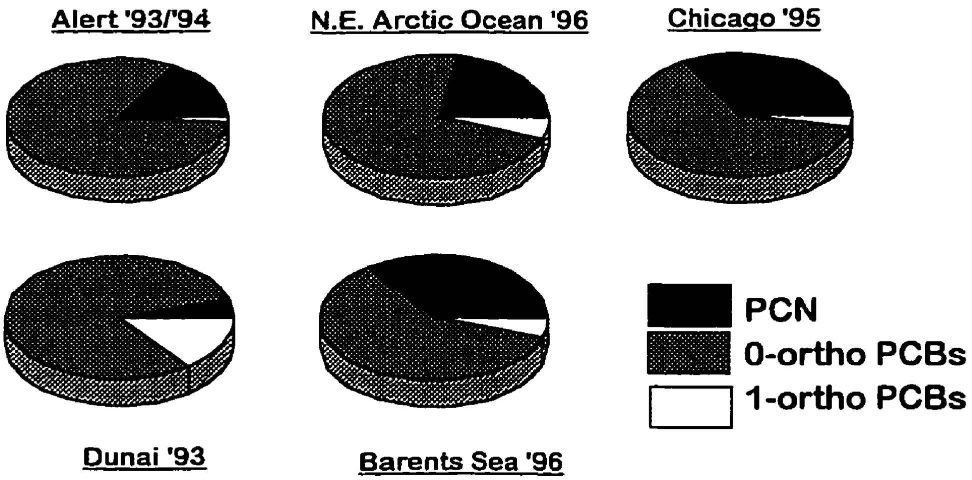


Figure 6. Percent TCDD TEQ contributions of PCNs, coplanar PCBs (congeners 77 and 126), and mono-ortho PCB-105 in air samples from arctic and urban air.

Paper VI: Organochlorine Contamination of the Canadian Arctic and Speculations On Future Trends

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Abstract: Emission of organochlorine chemicals in urban, agricultural and industrial regions of the world has resulted in a substantial influx to the Canadian Arctic. By the process of long-range atmospheric transport and what has been referred to as "global distillation" many chemicals are transported from warm, source areas to cold, polar regions. Organochlorines are detected in Arctic air, water, and snow, with substantial accumulations in animals, marine mammals, and humans. This has led to concern regarding health effects to native people who consume traditional foods. Speculations on future trends of organochlorines in the Arctic is presented and related to global warming effects and the physical chemistry of the compounds of interest. It is conceivable that high levels of certain contaminants in the Arctic environment may persist for decades despite recent reductions in global emissions.

1. Introduction

To those who have never seen it, the Canadian Arctic is envisioned as a pristine sanctuary which supports unique marine and animal life and inhabits populations of indigenous people. These people represent the earliest established culture in the Americas and have adjusted to the environment and molded their way of life according to the resources available to them. Seal, caribou, narwhal and fish are just some examples of their common staple foods. Heart disease and other Western, diet-related ailments are uncommon.

In the past several decades however, there has been increasing concern regarding the observed influx of organochlorine (OC) contaminants, pollution aerosols, and other anthropogenic toxins. In 1977, in response to the discovery of unexpectedly large amounts of pollution aerosol in certain parts of the Arctic, the first symposium on Arctic aerosols was held in Lillestrøm, Norway at the Norwegian Institute for Air Research (N.I.L.U.). In 1980, a second symposium on Arctic air chemistry was held at the Graduate School of Oceanography at the University of Rhode Island in Narragansett, RI. (Rahn and Heidam, 1981). This is where the first questions were asked; questions regarding the sources of these compounds, the mechanisms of their movement to polar regions, their influence on the ecosystem, and their persistence spawned the thinking that directed research efforts in the years ahead.

Today, almost two decades later, we have a clearer picture of Arctic pollution. A spectrum of toxic and potentially toxic organochlorines is detected in all compartments of the freshwater and marine ecosystems (Muir et al., 1992, Thomas et al., 1992, Barrie et al., 1992). Polychlorinated biphenyls (PCBs) and a variety of pesticides such as DDT, hexachlorocyclohexane (HCH), chlordane, and toxaphene top the priority lists and are found in significant quantities in animal tissues including marine mammals (Norstrom and Muir, 1994) which are an important component of native diets. This has triggered concern regarding health risks associated with human consumption of these foods (Kinloch et al., 1992). Those at the top of the food chain - seal, polar bear, and humans are most at risk. Besides eliciting toxic effects many of these compounds have implications for reproduction and hence species continuity (The Washington Post, 1994, Patlak, 1996). To complicate things further some behave synergistically and increase the toxicity of other compounds. Although there is still much to learn about the threat posed by these chemicals, it is evident that OC chemicals will continue to stress the arctic ecosystem for many more years with unknown consequences.

This paper summarizes the current state of knowledge and answers some of the questions posed at the first arctic meetings regarding sources, pathways, and levels in the ecosystem. However, now that this phenomenon is understood with a comfortable level of confidence and arctic monitoring programs are continuing, other questions and speculations arise regarding future trends. Will the use of persistent OCs continue and by whom? What are the implications of global climate change for OC contaminants in the Canadian Arctic? Lastly, what is the fate of the arctic ecosystem - will it become more or less contaminated?

2. The Arctic Environment

A good starting point for a discussion of issues related to contaminant effects in the Arctic is a description of the environment itself. Knowledge of factors such as climate, geography, and food chain structure and type are helpful in understanding the fate and effects of OC contaminants in this region.

Geography/Climate

The Canadian Arctic and sub-Arctic regions cover an immense area (3.38×10^6 km^2) ranging from the Beaufort Sea in the West to Baffin Bay and Davis Strait in the East (Barrie et al., 1992). The north-south boundaries are Ellesmere Island and Hudson's Bay. Mountain ranges such as those of Ellesmere, Devon, and Baffin islands are geographic barriers which result in drastic differences in climate among polar regions, and contribute to the uniqueness of the terrestrial, freshwater, and marine environments. North of the Canadian Archipelago, a collection of islands and straits, is the open Arctic Ocean which is divided into two main basins - the Eurasian and the Canadian (Figure 1). The MacKenzie river is the only freshwater source for the ocean on the Canadian side and contributes approximately 16% of the total freshwater inflow. The remainder comes from Russia (Barrie et al., 1992). Precipitation in the Arctic is low, averaging about 100-150 mm, most of which occurs in the summer. The arctic region is essentially a polar desert. Sea ice acts as a cap for the ocean most of the year and limits air-water exchange of contaminants but it can also serve as a transport route to the arctic. Chemicals which are deposited to the ice surface can be carried great distances before being released to the atmosphere or water column (Pfirman et al., 1992).

The Arctic is often called a region of extremes. Winter months are characterized by continuous darkness and temperatures can drop to as low as -50 °C. Conversely, in the summer there is continuous sunlight and temperatures at the pole average near 0 °C and are warmer inland (Maxwell, 1992). Cold temperatures in the Arctic are a result of several factors. First, the low angle of the sun with respect to the earth results in polar regions receiving on average about 40% less radiation than tropical regions. The albedo effect caused by ice cover amplifies this by reflecting 80-90% of the incoming radiation back to the atmosphere. Some of this heat loss is compensated for by an influx of warm oceanic currents primarily from the North Atlantic (Sugden, 1992). The unequal heating of the globe combined with the rotation of the earth play an important role in atmospheric circulation.

Atmospheric/Oceanic Circulation

Air patterns play an important role in the movement of contaminants in and out of the Arctic region. In the winter the strong Siberian anticyclone introduces air from the Eurasian continent which then exits over North America. This pattern is reversed somewhat in summer and there is a net north-south movement of air to Eurasia. Warmer summer temperatures also result in episodic influxes of north Pacific and North Atlantic air (Barrie et al., 1992).

The arctic ocean consists of 3 main layers. The first is called the polar mixed layer (0-50 m) and contains cold, low density water. The next layer (50-200 m) is referred to as a pynocline, in which density increases with depth. It also isolates the polar mixed layer from deeper water. Together, these form the arctic layers and it is estimated that the residence time (the time required for this volume of water to be replaced) is on the order of 14-30 years (Barrie et al., 1992). Underneath the arctic layers (200-800 m) is a layer of warm, saline, Atlantic water. Water flows into the Arctic through the Atlantic route (80%) and the Bering Strait (20%) and outflow is primarily to the Atlantic ocean. Ocean currents serve as another important transport route moving contaminants from warmer waters to the Arctic Ocean (Schlosser et al., 1995).

Arctic Wildlife

The arctic supports terrestrial, marine, and freshwater ecosystems. The terrestrial systems include animals such as the wolverine, arctic fox, mountain hare, and the Porcupine Caribou herd which is one of the largest herds of wild animals left in the world. The polar bear is considered both a terrestrial and marine animal and spends much of its time on the icepack hunting seal. The marine ecosystem includes a variety of whales (beluga, fin, humpback, narwhal), seals (harbour, ringed) and fish as well as communities of algae and plankton living under the ice (Remmert, 1980). Fish are also abundant in freshwater lakes. Generally speaking, marine food chains are simple: phytoplankton-zooplankton-fish-seal-polar bear or phytoplankton-zooplankton-whale.

The arctic ecosystem is an important breeding ground for approximately 6 million seabirds or 3/4 of the birds in N. America (ICBP, 1984), 40% of beluga whales and 85 % of narwhals. Thus contamination of the Arctic can profoundly effect wildlife on a continental scale. Arctic marine mammals have increased burdens of OC contaminants because of their high lipid contents, low metabolism, and long lives (Norstrom and Muir, 1994). These contaminants tend to partition into lipid-rich media such as fat and are biomagnified through the food chain. The longest lived animals at the top of the food chain (seal, polar bear, humans) are most susceptible to this risk.

Arctic wildlife can also be described as being extremely adaptable. Populations often undergo cycles which range from a few years to decades. Several factors affect populations dynamics including climate conditions, food supply, disease, and presence of predators. With this constant variability it is difficult to attribute declining populations to contaminant effects.

Indigenous People

The first settlers in arctic Canada migrated from Siberia some 4000 years ago and spread across the continent to Greenland and constituted what is known today as the Dorset culture. Over the next few thousand years these people were divided into sub-cultures due to geographical and food-source constraints. Some of the sub-cultures depended on whaling, others like those in the eastern Arctic began ice hunting of seals and invented the igloo. For other cultures the hunting of herd animals such as caribou gained greater importance. In the tenth century A.D. the Thule culture swept across this region. In the centuries that followed many changes occurred - sub cultures arose and populations migrated. When Europeans reached the Canadian Arctic, the Inuit population was about 50,000 (Sugden, 1992). This contact led to further changes - new tools and new ways of thinking.

Today isolated communities of indigenous people inhabit the Arctic, with average settlement sizes of a few hundred people. Approximately 15,000 Inuit live in the Northwest Territories (1/3 of the population are Inuit), 4 000 inhabit northern Quebec, and another 1,000 in Labrador. Native people are able to preserve their ties to their ancestral culture through their food. Foods such as seal, whale, fish and caribou have been traditional for thousands of years providing a solid source of nutritional and energy value. For example retinol, which occurs in whale and seal blubber, plays an essential role in visual acuity and helps protect the lungs against respiratory infection and prevents colon cancer. These foods are also important sources of omega-3 fatty acids which are known to protect against cardiovascular disease and enhance the functioning of the immune system (Kinloch et al., 1992).

Contamination of the Arctic environment has raised questions regarding health risks associated with continued intake of traditional foods. Fetuses and infants who are breastfeeding from mothers who have been contaminated though their diet are most at risk (Hild, 1995). It may become necessary to introduce market type foods. Such measures would have drastic effects on these communities (Kinloch et al., 1992). Not only would they lose the nutritional benefits of their native food but they would also be deprived of their way of life and their identity.

3. Organochlorine Chemicals In The Canadian Arctic

Organochlorine chemicals are one of many classes of compounds contaminating the arctic environment. Other important contributors include polycyclic aromatic hydrocarbons (PAHs), metals (mercury, cadmium, lead), acids (sulfur oxides and nitrogen oxides), and radionuclides (Barrie et al., 1992). Several OCs which are measured in arctic media are of concern due to their toxicity, persistence, and ability to bioaccumulate in the food chain. These include industrial chemicals such as PCBs, chlorobenzenes, and a range of chlorinated pesticides such as DDT, HCH, chlordane, and toxaphene. These compounds tend to have high chemical and biological stability and show enhanced partitioning into lipid media such as animal tissue.

Production and usage of many of these chemicals have declined significantly in recent years as a result of restrictions on productions and use in industrialized countries (Li et al., 1996, Voldner and Li, 1995). However, for most of these chemicals significant quantities have already been released and continue to cycle in the global system while they slowly migrate to their polar sinks.

Priority Chemicals: Sources

PCBs exist as a mixture of 209 congeners and have been produced since the 1930s reaching peak levels in the US in 1970 at 40 000 t. Because of their favorable thermal and chemical properties PCBs have been used extensively in industry as dielectric fluids in transformers and capacitors. Total US production between 1930 and 1975 is estimated to be about 600 000 t although in 1971 new usage in OECD countries was limited to transformers. However, 10 000 - 15 000 t continued to be exported from Europe to non-OECD countries until 1983 (Barrie et al., 1992). Although production of PCBs has now ceased in OECD countries, there is still little information regarding usage in other industrialized countries such as the former Soviet Union, India, and Mexico. This is an important group of chemicals which has high potential for bioaccumulation in the food chain and many congeners are known to exhibit "dioxin-like" toxicities (Ahlborg et al., 1994, Barrie et al., 1992).

The emission route for chemicals into the environment differs significantly depending on their use. PCBs were used in electrical equipment such as transformers and capacitors since the 1970s, and before that as plasticizers and hydraulic fluids. Their main route to the environment is through leaks in equipment and emission from landfills. Pesticides are released during spraying of fields. This distinction gives them a "head start" in attaining considerable concentrations in air which facilitates their transport away from source regions.

DDT is an important agricultural pesticide which tends to bioaccumulate heavily in marine and terrestrial organisms. It also has metabolites DDE and DDD which have similar persistence and toxicity. Since its first production in 1945, 1.5 million tonnes of DDT have been produced globally. Banned in Canada and the US in the 1970s, it continues to be produced and used in some countries in Asia, Africa, Central America, and South America primarily for control of malaria and other insect-borne pathogens. Besides these current emission sources it is also believed that previously treated soils release considerable amounts of DDT and DDE into the air by volatilization (Barrie et al., 1992, Voldner and Li, 1994).

Technical HCH is one of the more volatile classes of pesticides. It is a mixture of several isomers: alpha (α-HCH) 55-70%, beta (β-HCH) 5-14%, gamma (γ-HCH) 10-18%, delta (δ-HCH) 6-10% and other impurities, ~5%. Use of the technical mixture was banned in Canada and the US in the 1970; however the active isomer, γ-HCH which is also known as lindane, is still used. Li et al. (1996) estimate that global useage of α-HCH and γ-HCH in 1980 was 28 000 t and 11 900 t respectively, and 20 400 t and 8 400 t in 1990. It is estimated that 6 x 10^4 t were used in the mid-to-late 1970s in Asia and China which are considered to be heavy users (Barrie et al., 1992, Voldner and Li, 1994).

Chlordane is another multicomponent mixture. Major constituents include trans- and cis-chlordane, trans- and cis-nonachlor, and heptachlor. Metabolites which are carcinogenic and accumulated in the food chain include heptachlorepoxide, photoheptachlor and oxychlordane (Norstrom and Muir, 1994). Approximately 0.25 million tonnes of chlordane were used in the US between 1945-1988; usage in Canada and the US was restricted in the 1970s with the exception of termite control purposes (Barrie et al., 1992).

Toxaphene, is an insecticidal mixture of hundreds of chlorinated bornanes. It is estimated that 6.7 x 10^5 t were applied globally between 1970-1993. Toxaphene is now banned in most industrialized countries but like DDT, it continues to be released from previously contaminated soils (Voldner and Li, 1994).

Pathways

The means by which contaminants are transported to the Arctic is an interesting area of research which involves an understanding of many physical and chemical processes. Chemical properties such as vapor pressure, Henry's Law Constant (HLC), aqueous solubility, octanol-water partition coefficient (K_{OW}), and octanol-air partition coefficient (K_{OA}) are important determinants of chemical behavior in the environment. These properties help to identify compounds which have a high bioaccumulation potential and others which have high volatilities and hence lend themselves to transport in the atmosphere. Environmental factors such as presence of aerosols, atmospheric and oceanic circulation, and the effect of temperature are also important in the movement of organochlorine compounds in the environment. It is not surprising that global models of contaminant transport and fate are usually quite complicated. The following sections will describe several important aspects of contaminant circulation which have been shown to be especially important in the transport of organochlorines to polar regions.

Episodic air transport

Long-range atmospheric transport is recognized as an important process by which chemicals in southern source regions are transported to and deposited in arctic regions. In this phenomenon air is transported great distances in a relatively short period of time. As the air cools, contaminants undergo a decrease in volatility and partition more strongly to particles and are then deposited. Falling snow is believed to be an important scavenger of OCs in the atmosphere (Patton et al., 1991, Hoff et al., 1995).

Oehme (1991) and Oehme and Ottar (1984) attributed high levels of contaminants in the Arctic to long-range transport from southern sources in Europe. In field studies in 1982-1984 they utilized back trajectory data for air to link episodes of high levels of PCBs and HCH in the arctic atmosphere to long-range transport episodes from Europe and the Soviet Union. An important aspect of this research involved confirming that the air being measured during these episodes was in fact "new" air and not aged air which had been cycling in the Arctic. Aged air was distinguished from "new" air by examining the ratio of α-HCH to γ-HCH. Oehme believes that the γ isomer is photochemically transformed to α and hence new air typically has α:γ ratios of 5-10:1 whereas aged air has ratios which are greater than 20:1. However, Iwata et al. (1993b) question this theory and attribute differences in the α:γ to differences in the air-sea exchange of these two isomers.

Canada has a long-term program for monitoring persistent organic pollutants in the Arctic. The Alert monitoring station was the first functioning site, with sample collection beginning in 1992. Preliminary results for the HCHs show that concentrations average about 60 pg/m^3 for both the summer and winter months with little seasonal variation. The main sources are believed to be long-range transport from distant source regions and gas-exchange with the surface ocean (Fellin et al., 1996). The Canadian results are in good agreement with values recently reported by Oehme et al. (1996) which also show a lack of seasonality for the HCHs in northern Norway.

Global distillation

Besides episodic long-range transport there are numerous other processes and interactions involved in contaminant transport to the Arctic. Contaminants are continually cycled in the environment (Figure 2) between air, water, soil and vegetation. The extent and direction of partitioning depends both on the physical and chemical properties of the compounds and environmental parameters.

The net effect as described by Wania and Mackay (1993, 1996) is that compounds tend to volatilize into air in warmer climates and then condense onto particles, soil, vegetation and water when temperatures decrease. As temperatures rise again, this cycle repeats itself and compounds migrate northwards in a series of short hops. This is often referred to as the "grasshopper effect" (Wania and Mackay, 1996). Thus contaminants gradually move from warm source regions to colder "sinks". Wania and Mackay use this process to explain their observations that chemicals are globally fractionated based on their volatility (Figure 3). Very volatile chemicals, such as the chlorofluorocarbons (CFCs) become well mixed in the global atmosphere with no apparent fractionation. Less volatile compounds, HCH and the lower chlorinated PCBs for example, have intermediate volatilities and hence are latitudinally fractionated, where the more volatile compounds (in this group) are able to attain higher concentrations in northern latitudes relative to the less volatile compounds. The last group contains contaminants such as DDT and the higher chlorinated PCBs.

These compounds have low volatilities, are unable to attain high atmospheric levels and are generally deposited near their source.

Vapor pressure (p^{o}_{L} , Pa) and the octanol-air partition coefficient (K_{OA}) are key indicators of a compound's potential to be transported by the atmosphere. Vapor pressure is a measure of a compound's volatility whereas K_{OA} describes it's equilibrium partitioning between octanol and air. Octanol is a surrogate for environmental lipids such as waxes and lipids in vegetation, organic carbon in soil, and oily surfaces on aerosols. Thus, a lipophilic compound of low volatility will have a high K_{OA} and a low p^{o}_{L}.

Table 1 relates p^{o}_{L} and K_{OA} values to potential for atmospheric transport for different classes of compounds. At +30°C, compounds such as PCB-3, hexachlorobenzene, and α-HCH have relatively low K_{OA} values and high vapor pressures. Hence, they readily partition into the atmosphere and have high atmospheric transport potentials. At -10 °C however, these same compounds are only moderately transportable. Their vapor pressure decreases by approximately two orders of magnitude and K_{OA} increases by the same factor. Under cold temperatures they are more likely to partition or condense onto aerosols, soil, vegetation, water and other surfaces.

This overall process by which compounds move to more northern climates is called "global fractionation" or "cold condensation". It is often described by analogy with gas chromatography in which the earth's soil, vegetation, and oceans represent the stationary phase and the atmosphere is the mobile phase (Risebrough, 1990, Wania and Mackay, 1996). Contaminants are transported through the global chromatographic column following a warm to cold temperature gradient. The partitioning of the compounds between the air and the stationary phases and the effect of temperature govern how far from the source the chemicals will migrate and how long it will take for this to occur.

The "global distillation" model approaches this migration from a fugacity standpoint. A chemical's fugacity essentially describes its escaping tendency from a certain media. More specifically it refers to a chemical's partial pressure (Pa) and is related to concentration by,

$$f_x = C_x/Z_x$$

where C_x ($mol.m^{-3}$) is the concentration of the compound in compartment x. and Z_x ($mol.m^{-3}.Pa^{-1}$) is the compound's fugacity capacity in compartment x (Mackay, 1991). A Z-value is a measure of a compartment's capacity for a chemical. For example, organochlorines which are lipophilic compounds have very large Z-values in lipid phases such as soil organic carbon, waxes in vegetation, organic films on atmospheric aerosols, and fat in animal tissues and are thus able to partition strongly into these compartments. This is also the basis for high levels of these compounds bioaccumulating in the food chain. Z-values in air and water are considerably smaller.

Wania and Mackay (1994) indicate that it is likely that some compounds have already achieved their peak concentrations in the arctic. Removal processes such as degradation, transformation and sedimentation are occurring at rates which exceed the influx rates of these chemicals. Other compounds, however, especially stable OCs, are still cycling in the environment and gradually migrating to their ultimate polar sinks. The maximum levels of these compounds in the arctic ecosystem may only be realized in the years ahead.

This is currently one of the most important aspects of contaminant transport to the Arctic; knowing and understanding which compounds are now achieving peak concentrations and which are likely to do so in the future. The answer lies in the balance between migration of contaminants from existing reservoirs in soil, water, and vegetation versus the decline in global usage. Compartmental models are useful tools for resolving these questions and can be employed to predict future trends based on a range of assumed global emission and climate scenarios.

Role of oceans

The atmosphere-ocean exchange of contaminants is also important in the transport of contaminants to colder climates. Most of the earth's surface is covered by oceans which act as huge repositories for atmospherically deposited compounds (Duce et al., 1991). In addition, many industrial and urban centres which are emission sources for chemicals such as PCBs are located near the sea. Similarly, agricultural areas where pesticides are applied often consist of a watershed which drains into streams and rivers which then flow into the sea. For many compounds, their journey to the Arctic begins in the ocean.

Iwata et al. (1993) studied the role of oceans in the global distribution of persistent OC chemicals. They report concentrations in air and surface water from samples collected in several oceans on 5 cruise routes during the period April 1989 to August 1990. The exchange of chemical across the air-water interface is controlled by the Henry's Law Constant (HLC) which describes the equilibrium partitioning of a chemical between air and water. Essentially it is a ratio of the compound's vapor pressure (Pa) over its aqueous solubility ($\mathrm{mol.m^{-3}}$). HLC ($\mathrm{Pa.m^{3}.mol^{-1}}$) has a strong temperature dependence and partitioning of a chemical into water is favored at lower temperatures. Iwata indicates that it is this temperature-dependent partitioning that causes chemicals with higher HLCs and high vapor pressures to be transported and deposited in the cold oceans.

Figures 4 and 5 (from Iwata et al., 1993) compare surface water and air concentrations for HCH and DDT. High air concentrations are indicative of sources while high surface water concentrations identify sinks. The figure shows that in 1989-1990 HCHs were primarily released from east Asia and India but were accumulating in the northern oceans. Due to its high volatility HCH is able to be atmospherically transported to colder oceans where it is deposited and becomes less volatile due to the temperature dependence of HLC. DDT on the other hand is less volatile and hence less transportable. Consequently surface water concentrations are highest near source regions.

Iwata also found that compounds with high HLC and high vapor pressures were enriched in northern samples. This supports the global distillation hypothesis which implies that compounds will become latitudinally fractionated based on their volatility.

Haze aerosols

In winter and spring of each year there is an influx of pollution aerosols into the arctic atmosphere. The light scattering properties of these particles result in a thick haze and it is this property which gives these aerosols their name. Sulfate is the main constituent and can be derived from three sources: anthropogenic, marine biogenic, or from sea salt. During the haze season it is estimated that more than 75% of sulfate is due to anthropogenic sources - mostly a result of fossil fuel and other combustion sources. Particle diameters range from 0.1 μm to 10 μm and the finer particles contain mostly sulfuric acid. Other constituents include anthropogenic metals, nitrogen oxides, black carbon, PAHs, and a variety of hydrocarbons (Barrie, 1996).

The main source regions for haze aerosols have been identified as Asia and Europe. Programs which monitor aerosols and sulfate have been ongoing in the Canadian Arctic since 1980. Results show consistent seasonal variations with maximum levels in January-April and minimums in June-September. A comparison of total sulfate concentrations in the past 14 years indicates no yearly changes (Barrie, 1996).

Sulfur aerosols play an important role in moderating the earth's radiation budget and possibly climate. Aerosols are good cloud condensation nuclei and are believed to initiate cloud formation. Because clouds reflect incoming solar radiation and hence decrease the warming of the earth, aerosols are believed to moderate global warming. It has recently been postulated (Barrie, 1996) that in the Arctic, sulfur aerosols counteract global warming by another mechanism. By initiating cloud formation and precipitation these aerosols cause a dehydration of the arctic atmosphere. Water vapor is an ideal greenhouse gas and due to its absence in the atmosphere, less solar radiation is absorbed and global warming is lower than expected.

In relation to OC contamination of the arctic however, the most important aspect of aerosols is in their role as a transport medium. Combustion aerosols are typically rich in organic matter and consequently have high Z-values (capacities) for lipophilic compounds. They serve as an ideal medium into which gas-phase OCs can partition when temperatures decrease. The OCs are then deposited as the particles settle.

Levels In The Arctic Environment

In the past two decades monitoring programs in the arctic have revealed that many of these priority pollutants are widespread and fairly uniform in arctic air, water, and snow/ice. Levels in air tend to respond fairly rapidly to changes in emissions hence many monitoring programs follow seasonal and yearly changes in atmospheric concentrations. Snow and ice also play an important role in contaminant fate. Atmospheric OC may be deposited to snow and ice and eventually end up in water or soil during snow-melt season.

The sea serves as both an important pathway for OCs to the arctic and a very large sink for OCs deposited from the air. By measuring contaminant concentrations in the water column and in the air above the water, it is possible to estimate the magnitude and direction of air-water gas exchange (Bidleman et al., 1995). Such calculations are instructive because they provide chemical inventories which estimate the loading or contaminant flux into arctic waters. Contaminant levels in arctic seas and freshwater lakes are perhaps the most noteworthy because they represent the critical link to the food chain. Bioaccumulation in aquatic food chains results in substantially greater contamination in marine mammals compared to the terrestrial food chain.

Recently, Muir et al. (1992) and Norstrom and Muir (1994) presented a thorough summary of contaminant levels in the Canadian arctic. Figure 6 compares the distribution of various organochlorines in arctic media (air, snow, water) and marine food chain. The most hydrophobic (or lipophilic) compounds such as DDT, PCBs, chlordanes, and toxaphene (also called chlorobornanes or CHBs) strongly partition into animal tissues and constitute a significant partition of the organochlorine burden in these animals. Due to their low vapor pressure and aqueous solubility, they are unable to achieve high levels in air or water. Compounds such as HCH and hexachlorobenzene (HCB) are more volatile and are the most abundant OCs in arctic air. HCH is also the most abundant organochlorine in arctic water due to its moderate water solubility.

High levels of organochlorine contaminants in arctic animals threatens their immune function (Swart et al., 1994), reproductive viability, and general health. It also poses a substantial health risk to indigenous populations who consume large amounts of traditional foods such as ringed seal, beluga and narwhal meat, and muktuk (blubber) (Cameron and Weiss, 1993). Kinloch et al. (1992) report that in Broughton Island (N.W.T.) 12% of women and 22% of men exceed established PCB intake levels. It is not surprising therefore that high concentrations of organochlorines are found in breast milk from Inuit women at levels of concern for children who are nursing (Dewailly et al., 1993).

The next steps in investigating ecosystem health effects is to observe those at the top of the food chain who are receiving the highest doses. Studies in Canada have recently been initiated (Dewailly et al., 1993) to study neurological conditions and infectious diseases in children to determine the link between health and pollution in these communities. However, this type of research is expensive and requires large sample populations to be statistically significant. Carl Hild (1995) perhaps summarizes the situation most accurately by saying, “arctic species, including humans, have become the canary in the mine of global pollution”.

4. Future Trends

Future Sources and Transport of Organochlorines to the Arctic

In the past few decades persistent OC contaminants have been either banned or deregistered in industrialized countries but are continued to be used in less developed countries. Voldner and Li (1995) report continued use of pesticides such as toxaphene, DDT, and HCH in several countries in South America, Central America, Africa, and Asia. For instance there is continued use of toxaphene in Mexico and usage of technical HCH in India has increased from 21 570 t/yr in 1980 to 28 400 t/yr in 1990 (Li et al., 1996). In essence there has been a geographical transition in the use of toxic contaminants from more developed countries to less developed countries usually in or near tropical regions (Iwata et al., 1993). Warmer temperatures in these source regions promote volatilization and ultimately atmospheric transport to colder climates.

There is some debate however, over the relative contribution of these new sources to the total emission of pesticides on a global scale (Wania and Mackay, 1996). It is also possible that emissions from previously contaminated soils in more developed countries may be important. The United States was one of the heaviest users of toxaphene and DDT with total usage estimated to exceed 100,000 metric tonnes in each chemical. Much of this was applied to soils in the southern "cotton belt" regions. Due to slow rates of degradation it is likely that a significant portion is still present. In 1992, Hoff et al. (1995) used 5-day air back trajectories to demonstrate that organochlorine pesticides ending up in the Great Lakes passed over potential source regions in the southern United States. However, trajectory data are not always conclusive and it is possible that the true sources are beyond the 5-day limit of these trajectories or even in a region much closer to the Great Lakes.

In summary, although overall emissions of organochlorine chemicals has decreased there is expected to be continued use in less developed countries over the next decade at least. Coupled with this is a constant cycling of old sources in the global environment, especially re-emission from previously contaminated soils in regions where pesticides were heavily used.

Aerosols

In the last decade considerable research has gone into monitoring levels of sulfate haze aerosols in arctic Canada. These aerosols are shown to originate in eastern Europe and

Asia and are effective at scavenging and transporting trace contaminants including organochlorines to the Arctic. Although global combustion in general has risen due to population growth and increased biomass burning, there has been no evidence to suggest increased particle loading to the Canadian Arctic (Barrie, 1996). This may be due partly to the use of cleaner combustion fuels. On this basis it is likely that aerosol loading to the arctic will not change significantly and hence aerosols will continue to be an important, yet not increasing, contaminant source for this region. IPCC (1995) however, predicts significant increases in global aerosol emissions in the next 50 years. This is also expected to dampen global warming and increase precipitation

Global Warming Effects

In the past 100 years global mean, surface temperature has increased by about 0.3 to 0.6 °C and may rise by another 2 °C by the year 2100. This is based on best estimates of levels of greenhouse gases and aerosol emissions (IPCC, 1995).

Global warming in the 21st century is expected to increase air temperatures with greatest increases occurring at the poles. The temperature gradient between the equator and the poles drives the global distillation effect and makes polar regions efficient sinks for chemicals. In the absence of this temperature gradient there will be some redistribution of chemicals on a global scale. Warmer air temperatures in the Arctic may result in decreased ice cover and the release of previously trapped chemicals. However, it is also possible that it may lead to increased snowfall and an accumulation of the ice-pack. The minimization of the equatorial-polar temperature gradient will also result in diminished equatorial-polar atmospheric circulation resulting in stagnant air masses. Hence, episodic long-range transport will be less efficient.

Some of these consequences which may have important impacts on organochlorine behaviour and fate include the following. First, the ocean will serve as an important heat reservoir resulting in increased ocean temperatures, possible reductions in ice cover and increases in sea levels, and alterations in ocean currents. Air-water gas exchange is important in the migration of contaminants to polar regions. Warmer temperatures in the tropical and temperate oceans will increase volatilization of chemicals and enhance their transport to colder regions (Iwata et al., 1993). This assumes however, that air temperatures remain relatively constant.

There are also numerous secondary effects which are less obvious. For instance it is believed that global warming will lead to the spread of malaria and other airborne pathogens to previously unexposed populations (Martin and Lefebvre, 1995). Controlling the migration of mosquitos and other parasites may require renewed use of DDT and other chemicals to avoid public health disasters. Already, a few developing countries which once banned DDT, have started using it again due to renewed outbreaks of malaria (Thompson, 1990).

Although global warming is sure to have many direct and indirect effects on OC fate in arctic regions, the magnitude and even direction of these future trends is still very speculative.

Apparent Decline of Organochlorines in the Arctic Ecosystem

Although levels of persistent OC contaminants have certainly declined in source regions as a result of decreased emissions, there is very little data which support reduced levels in polar sink regions such as the Canadian Arctic. This is partly explained by the fact that cold temperatures result in greater stability and hence longer lifetimes and the chemicals are less likely to be degraded or volatilized. Hence even if all inputs to the arctic ceased, levels of contaminants would only decline at a very slow rate.

HCH is one of the few persistent OC chemicals which has shown a decline in the Arctic. Levels in air over the Bering and Chukchi seas off the coast of Alaska have decreased from 800 pg/m^3 in the late 1970s and early 1980s to less than 200 pg/m^3 in 1992-1993. However, levels in the seas have remained relatively constant at about 2-3 ng/L (Jantunen and Bidleman, 1995). By comparing air and water concentrations for two different time periods Jantunen and Bidleman have shown that the net flux of α-HCH has reversed from net deposition in 1988 to net volatilization in 1993. Once a sink for HCHs, the arctic ocean is now behaving as a source to the atmosphere. It is estimated that 8.1 kt is contained in the upper 200 m of the arctic ocean. Re-emissions from this large reservoir will likely dampen reductions in arctic atmospheric levels which would otherwise result from decreased global emissions.

Although atmospheric levels of HCH and other chemicals in the Canadian arctic are declining, there is little temporal data to suggest that the more persistent chemicals are also declining, especially in the food chain. A comparison of PCBs, HCH, and chlordane levels in Polar Bear from Baffin Bay in 1969 and 1983/4 shows factor of 2-4 increases over this time period. Only DDT levels decreased by about 20% (Norstrom and Muir, 1994). Despite reductions in atmospheric emission (Loganathan, 1994) contaminants continue to bioaccumulate in the food chain. Levels in marine mammals are expected to respond to decreased levels in the environment with a delay period which may last several generations. Besides entry through the food chain a large load of persistent contaminants is passed on through mother's milk during nursing.

The "Secondary Pulse"- a hypothesis

It has already been discussed that the two main pathways for contaminant movement from source regions to polar regions is atmospheric transport and global distillation. Atmospheric transport is a fast, episodic process which can transport an air parcel across great distances with minimal degradation in a matter of days. Global distillation on the other hand is a more gradual process which may occur over many years. Therefore, many chemicals cycle in the environment for years before settling in cold regions in a secondary "pulse". Compounds will be degraded to varying degrees before coming to rest in polar regions depending on the time scale of this migration.

This raises an important question - *"if transport of contaminants to the arctic is occurring by two processes on two different time scales is it possible that reductions in the arctic* *environment may also occur on two different time scales?"*. In other words, the recent reductions in arctic levels for many of these contaminants may be due to a significant reduction in atmospheric transport due to reduced emissions. Observation of these recent reductions might lead one to believe that this trend will continue as long as new emissions are kept to a minimum. But this excludes the global distillation effect. For many persistent chemicals a significant portion of their total global production is still cycling in the environment and the full impact of these old sources in polar regions may occur sometime in the future.

Figure 7 is taken from Wania and Mackay (1994) where they demonstrate with their global distillation model that a unit discharge of monochlorobiphenyl, γ-HCH, HCB, and DDT in the northern tropical zone takes at least 25 years to achieve maximum levels in the Arctic. It is conceivable therefore, that a large portion of previously emitted organochlorines has not yet reached the Arctic. Depending on the magnitude, a secondary pulse of these compounds will retard the decline of contaminant levels in the ecosystem or even result in renewed high concentrations for some compounds.

This hypothesis is demonstrated in Figures 8a and 8b, which describe total levels in the arctic environment resulting from contributions from atmospheric transport and global distillation for two classes of compounds. This is a simple, illustrative plot which does not distinguish between levels in air, water, snow or biota. The first case (Figure 8a) corresponds to one of the more volatile OC contaminants such as HCH which are less persistent in the environment relative to some of the other OC chemicals. In this illustration levels of HCH in the arctic ecosystem are governed primarily by episodic long-range transport and reflect emissions in source regions which peaked in the late 1960s and early 1970s. The global distillation contribution is likely to be less significant for HCH since a significant portion of HCH would degrade over the time scale (i.e. approximately 15-25 years) required for this migration to occur.

The second case (Figure 8b) corresponds to less volatile compounds which tend to be more resistant to degradation (e.g. higher chlorinated PCBs, DDT). For these compounds the cumulative global distillation effect is significant because they are able to persist as they migrate to cold regions. Figure 8b depicts a situation where there is a temporary decline c.1980-1990 in total levels due to lower emissions and consequently a reduced contribution from episodic transport. At this point in time, the global distillation contribution begins to dominate and total levels in the arctic environment may increase again (as depicted in the figure) or this may simply cause a reduction in the rate of decline of these contaminants. The global distillation contribution is large for some classes of compounds because it represents the cumulative effect for all undegraded emissions in the last 50-60 years.

Although the hypothesis of a delayed secondary pulse is a simplification which does not represent absolute magnitudes, it is an extrapolation based on accepted theory of contaminant fate and transport.

In summary, despite efforts to reduce new emissions it is likely that levels of organochlorine contaminants will persist in the Canadian arctic for at least several decades. Contaminants already present in this ecosystem have extremely long lifetimes and the global reservoir of old sources is continually migrating towards the poles. Although arctic mammals and native people have tolerated these toxins so far, there is already evidence that prolonged exposure may result in immunological and reproductive effects (Ayotte, 1994).

5. Conclusion

Global emissions of persistent, toxic chemicals over the past several decades has transformed the Canadian Arctic from a region once referred to as pristine to one which is occasionaly described as a "toxic soup". The uniqueness of the environment is threatened. The health of marine mammals such as whales, seals, and Polar Bears is at risk and problems associated with immunological or reproductive difficulties are imminent. The human population is also at risk. Because they rely on contaminated foods as the main source of their diet many indigenous people have significantly higher levels of toxic organochlorines in their tissues than people living in temperate regions.

Despite reductions in emissions of persistent OC chemicals in recent years, high levels of contaminants in the arctic ecosystem are expected to persist for several decades due to continued inputs through global distillation of previously emitted chemicals. Although the push for future reductions in emissions will certainly help to reduce inputs to the Canadian Arctic, there are consequences which need to be considered. For instance, some organizations claim that if DDT had not been banned 20 years ago, millions of lives would have been saved (Loganathan and Kannan, 1994). This is one instance where the cost associated with preventing the use of a persistent OC chemical may have outweighed the benefits.

Since the first symposium in arctic air chemistry in 1980, there have been many advances in the study of organochlorine contamination of the Arctic, many of which were summarized in this paper. This has evolved as a complex, global-scale issue. A successful resolution to this problem is still ahead and will require a vast spectrum of scientific and social considerations.

Acknowledgements

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Table 1: Log K_{OA} and p^o_L values at +30°C and -10 °C for selected compounds with varying degrees of atmospheric transport potential.

Compound	+30 °C			-10 °C		
	[a,b] log K_{OA}	[c,d] p^o_L (Pa)	atmospheric transport potential	log K_{OA}	p^o_L (Pa)	atmospheric transport potential
hexachlorobenzene	6.66	0.194	high	8.63	0.00316	moderate
PCB-3 (mono-Cl)	6.63	1.44		8.37	0.0256	
α-HCH		0.35			0.006	
PCB-29 (tri-Cl)	7.74	0.07	moderate	9.65	0.0007	low
PCB-49 (tetra-Cl)	8.18	0.028		10.18	0.0002	
p,p'-DDT	9.85	0.00092	low	11.83	3.3 e-6	very low
PCB-180 (hepta-Cl)	10.27	0.00025		12.54	7.2 e-7	

a. Harner and Mackay, 1995.

b. Harner and Bidleman, 1996

c. Falconer and Bidleman, 1994.

d. Hinckley et al., 1990.

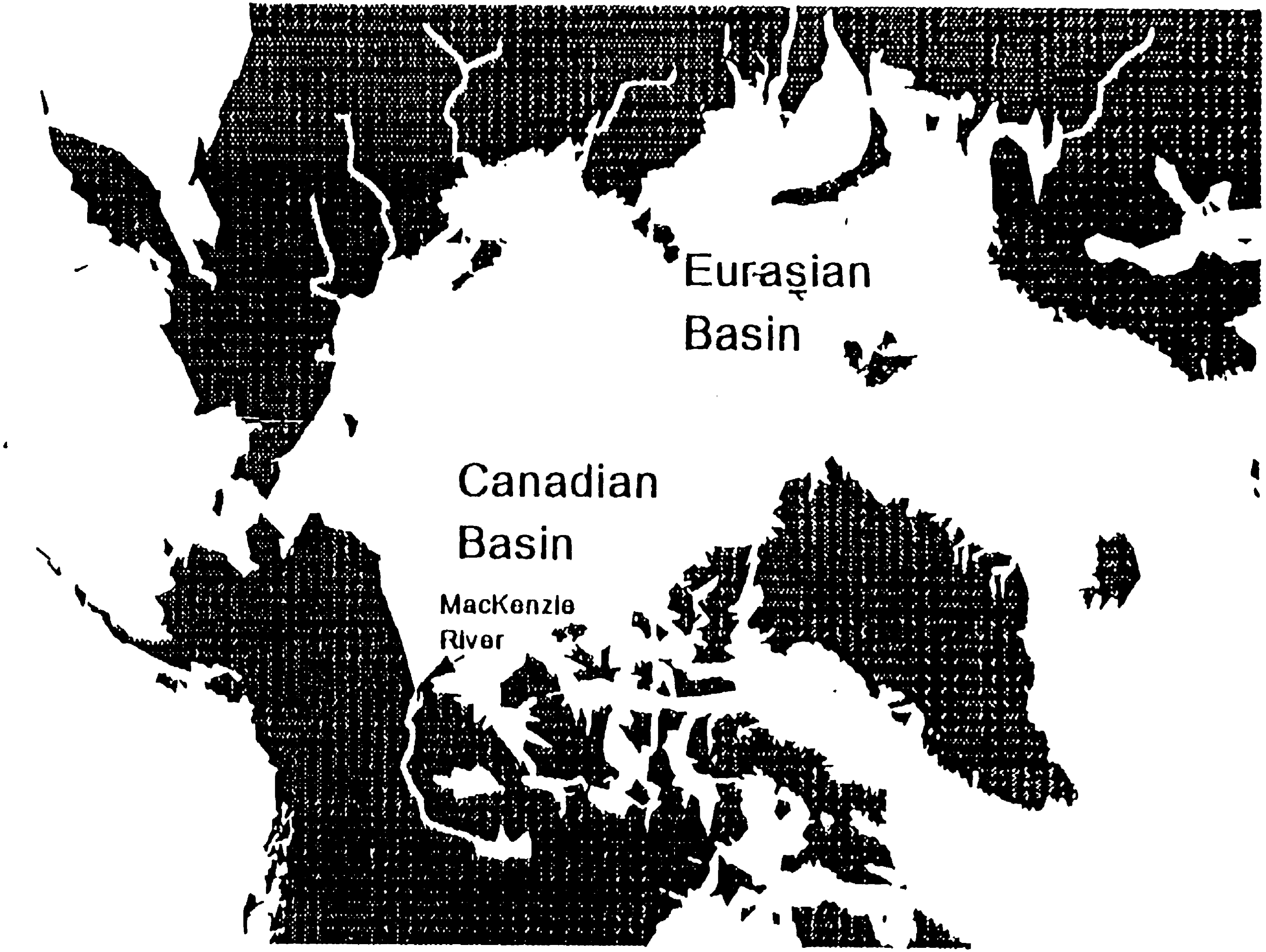


Figure 1. Schematic showing the MacKenzie River and the major basins in the Arctic Ocean.

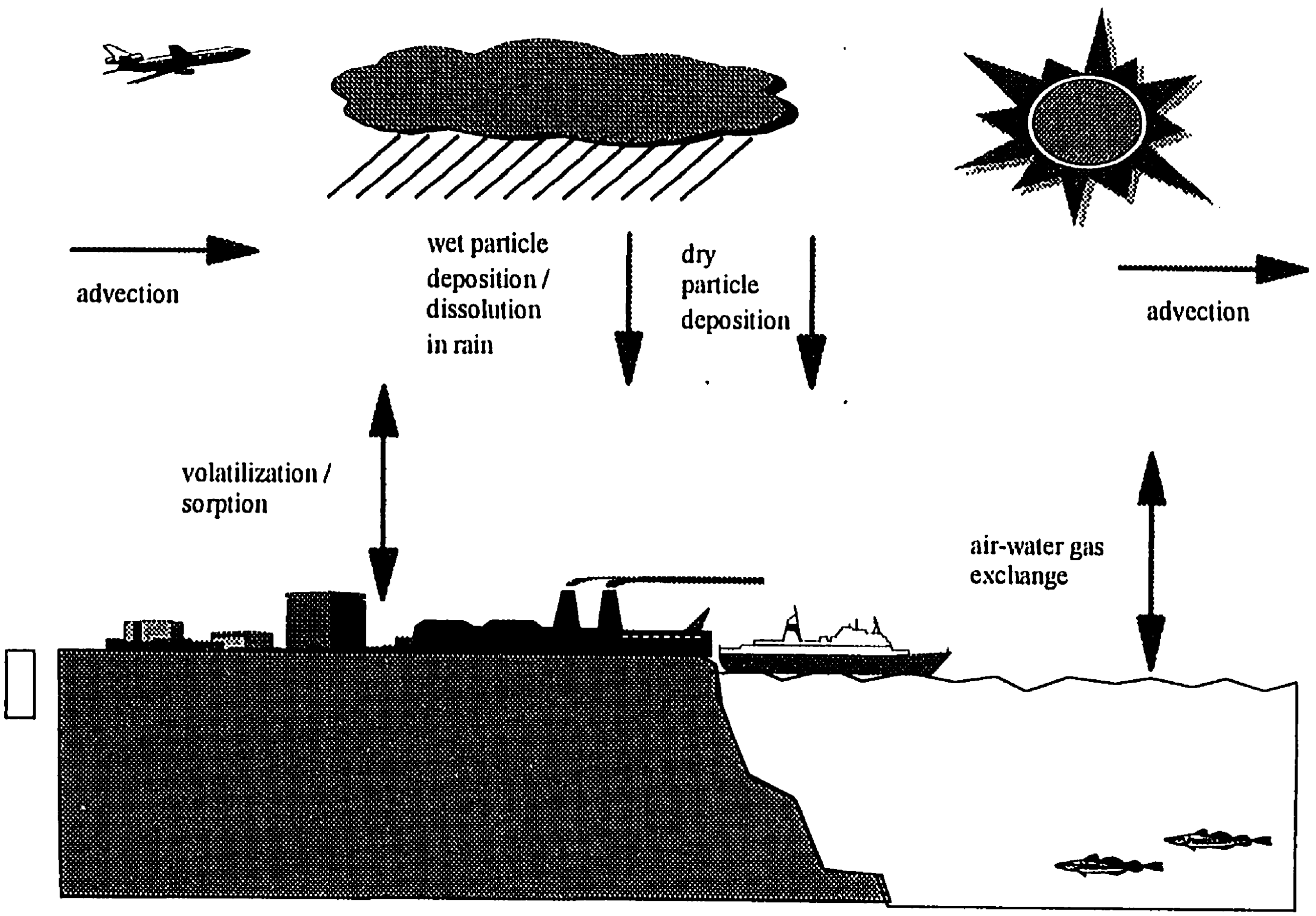


Figure 2. Processes affecting the fate and behavior of organochlorines in the environment.

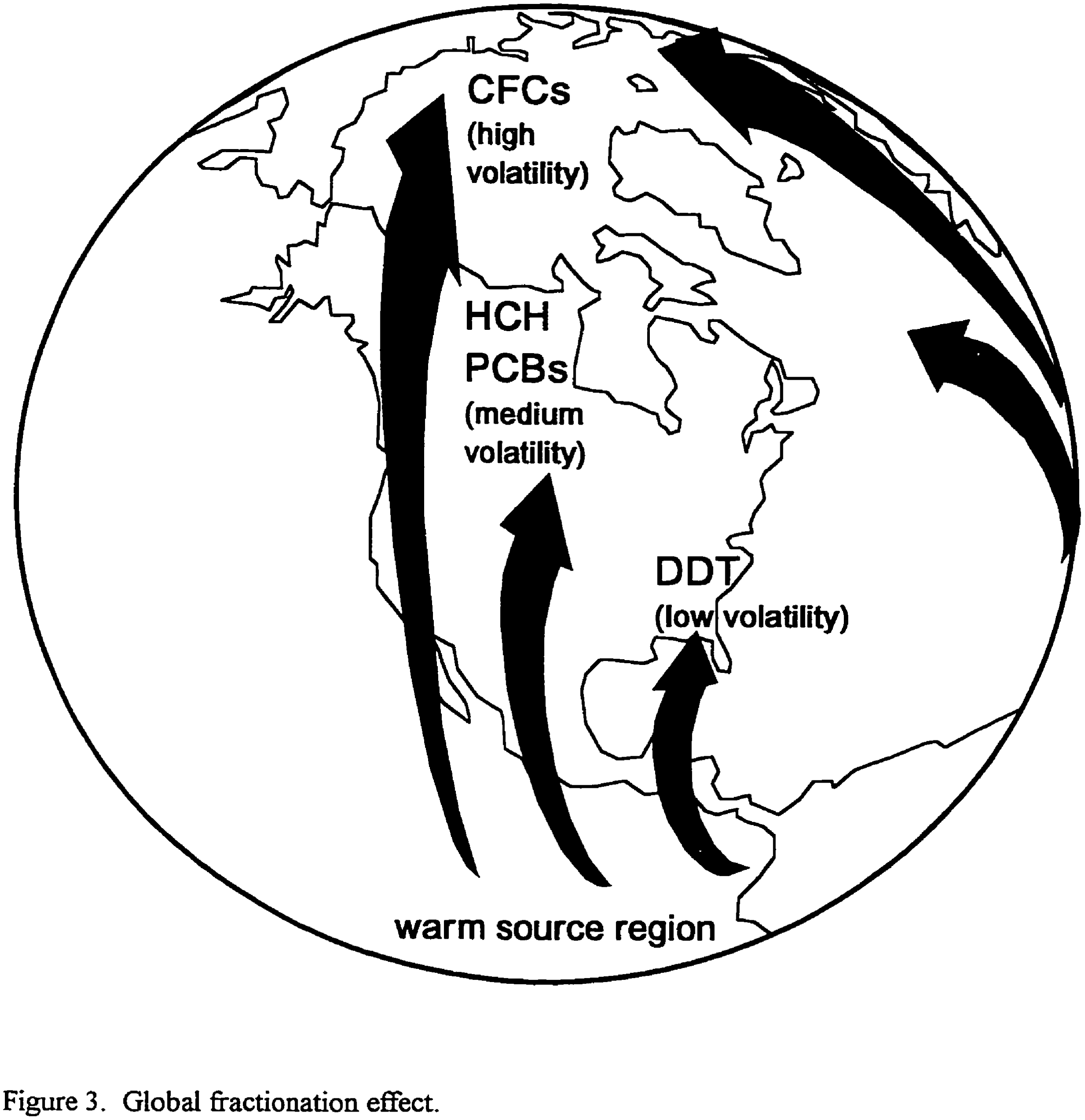


Figure 3. Global fractionation effect.

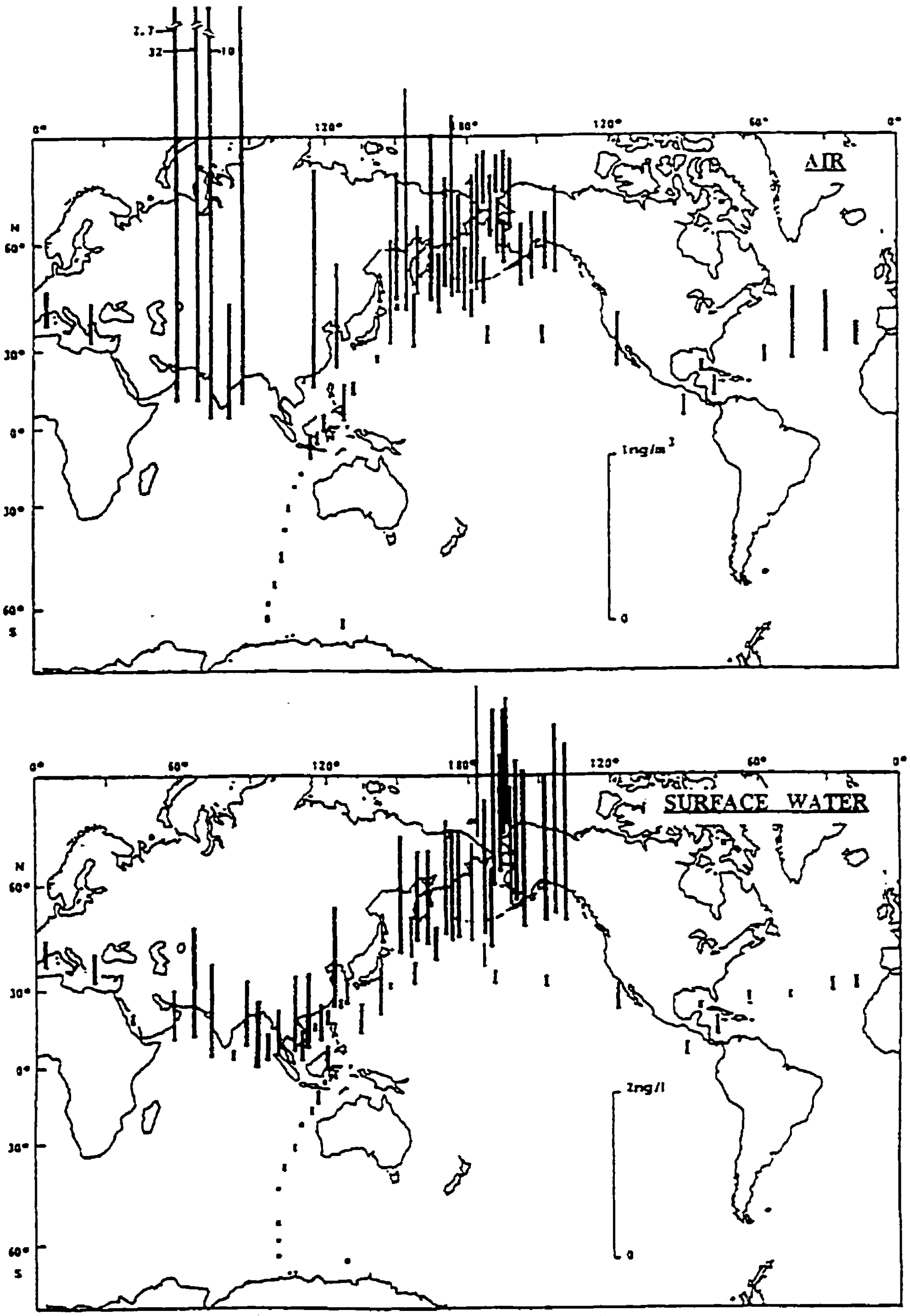


Figure 4. Distribution of HCH (sum of α- and γ- isomers) concentrations in air and surface seawater (Iwata et al., 1993).

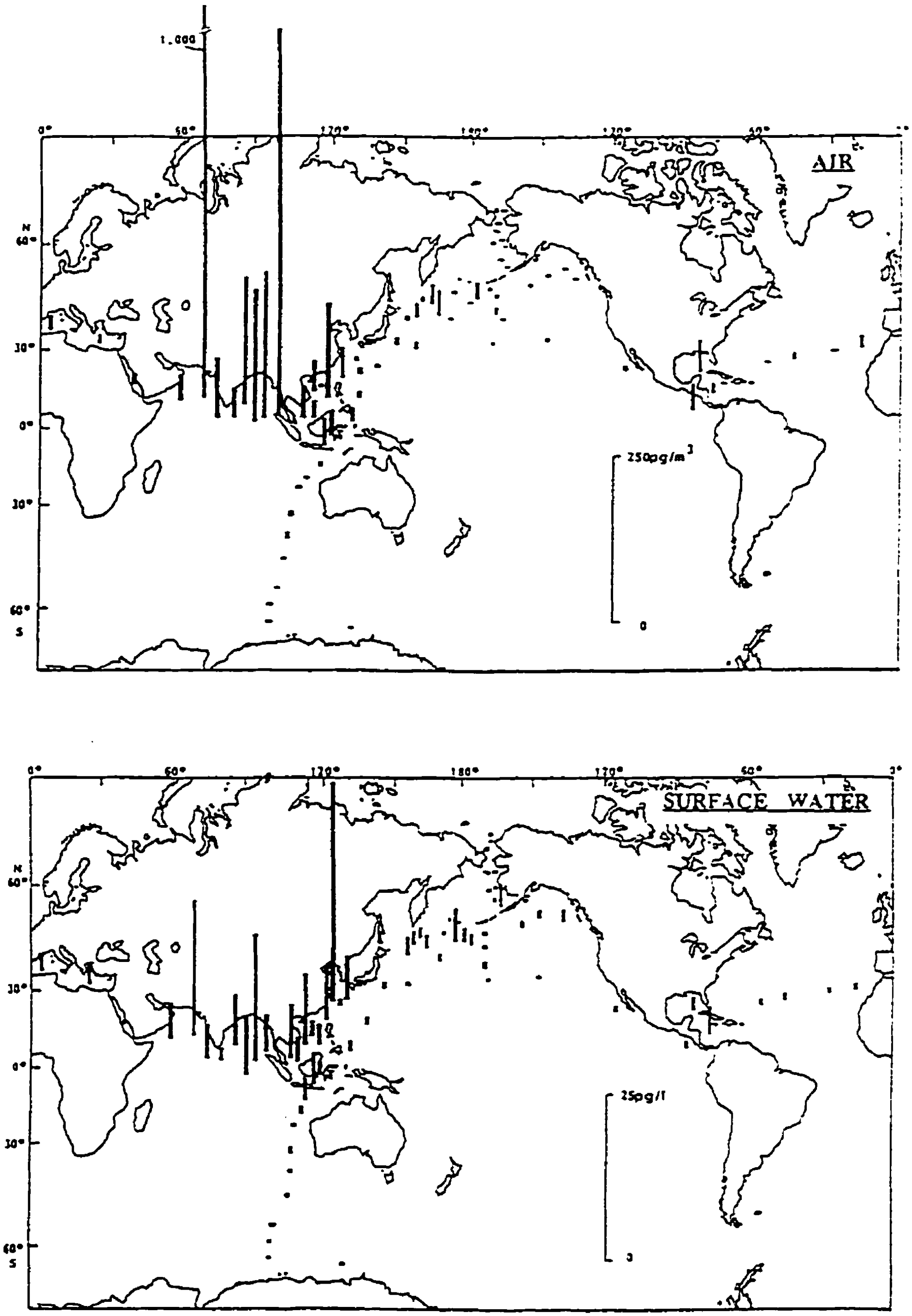


Figure 5. Distribution of DDT (sum of p,p'-DDE and p,p'-DDT) concentrations in air and surface seawater (Iwata et al., 1993).

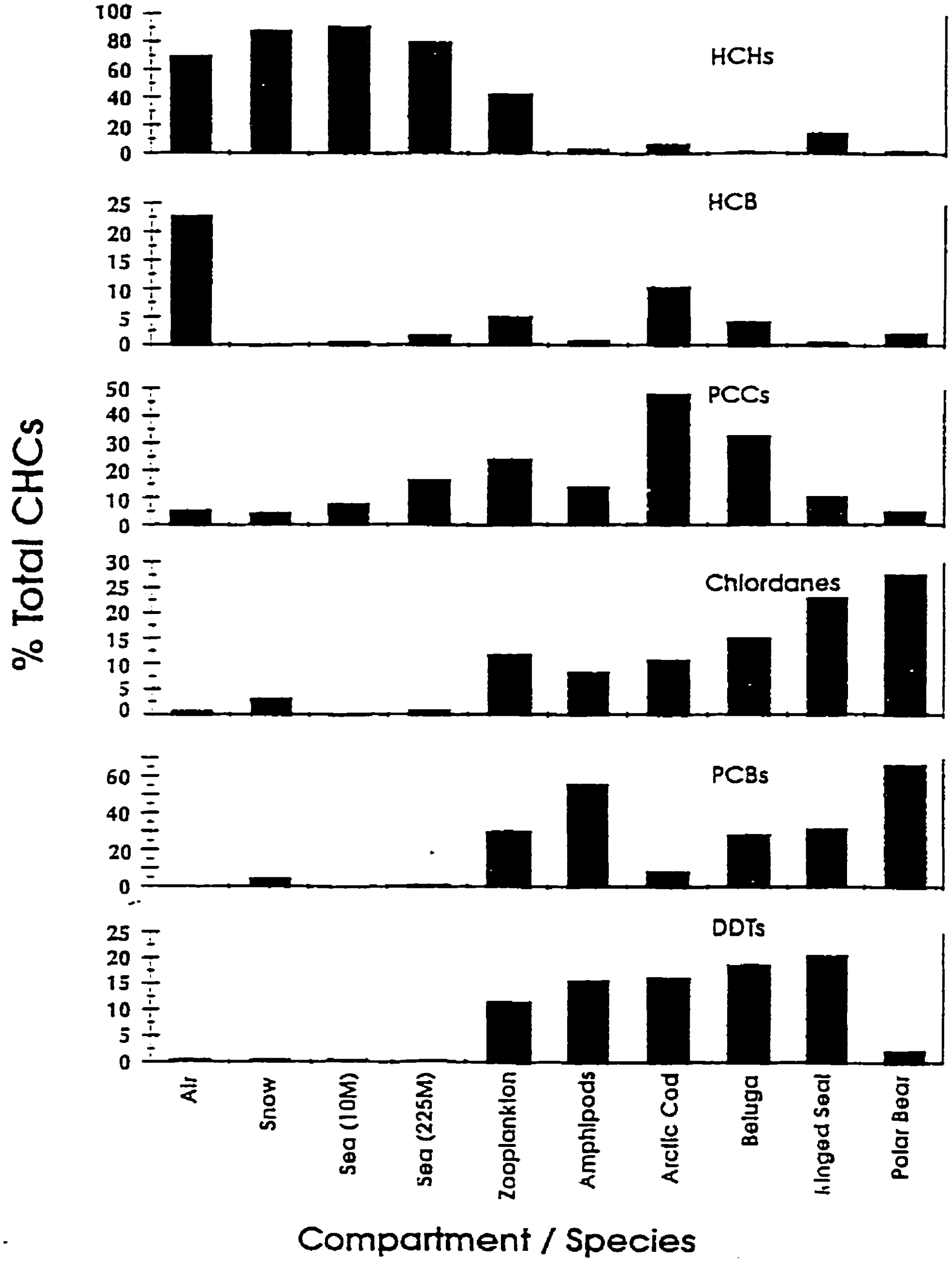


Figure 6. Distribution of organochlorine contaminants in Arctic media and marine food chain (Norstrom and Muir, 1994).

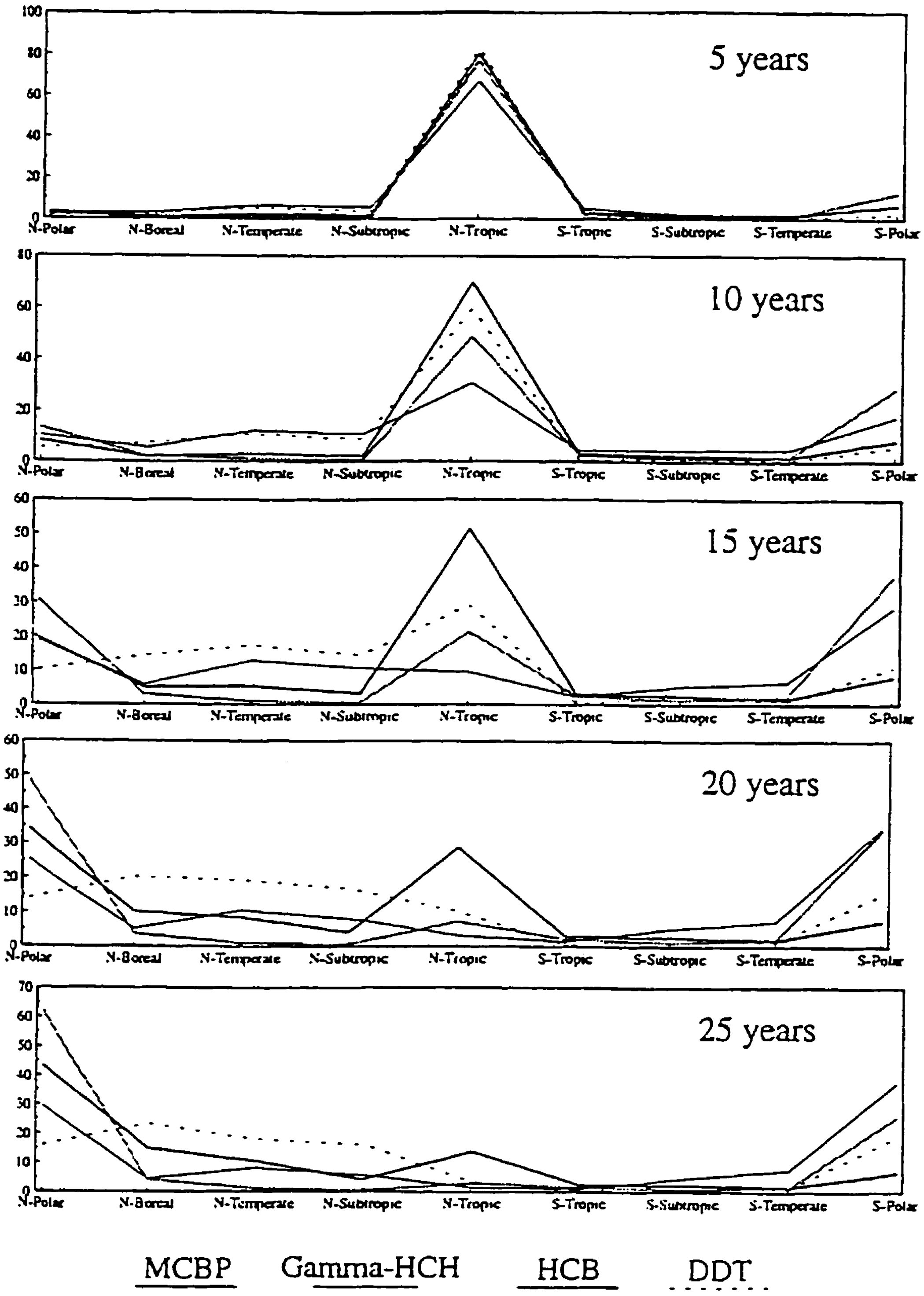


Figure 7. Percentage distribution of monochlorobiphenyl, DDT, HCB, and γ-HCH among nine clamatic zones at various points in time after a full unit discharge into the northern tropical zone (Wania and Mackay, 1994).

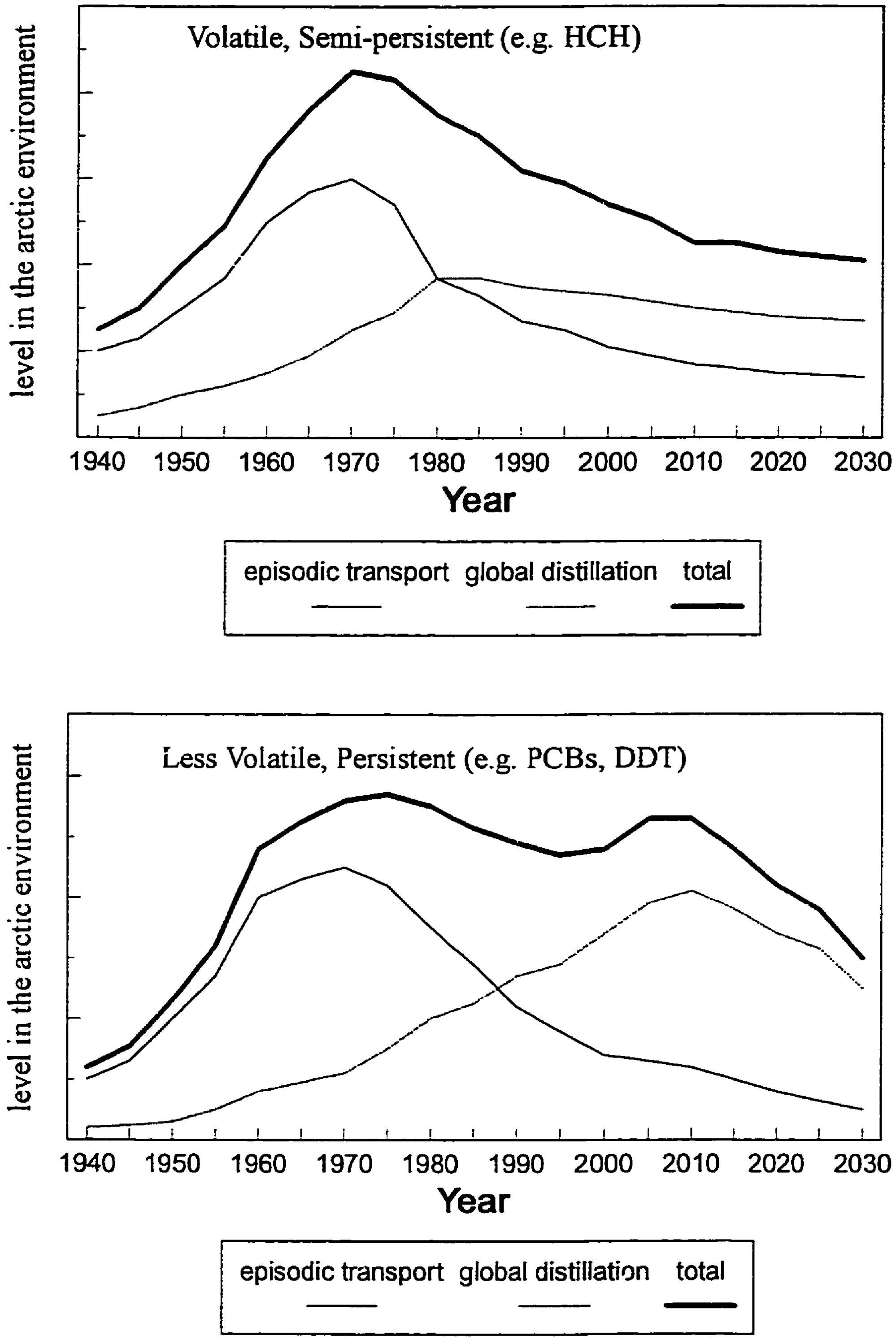
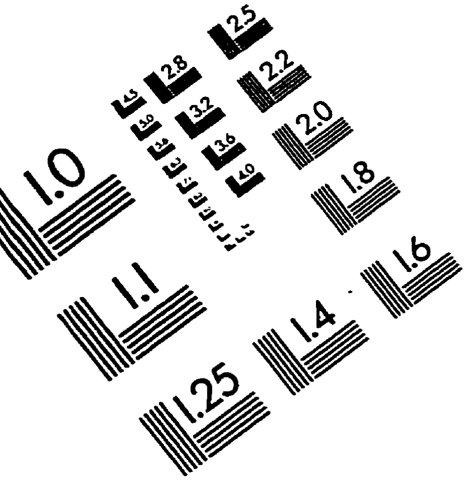
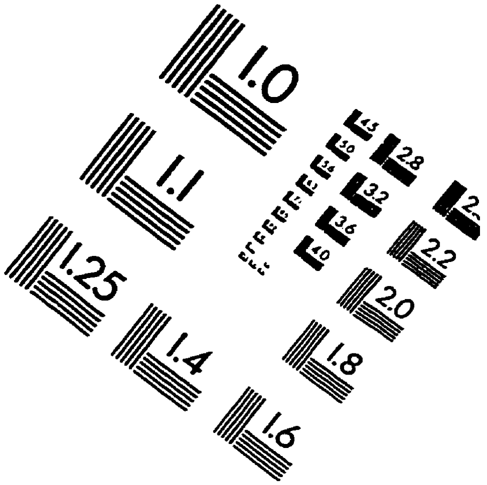
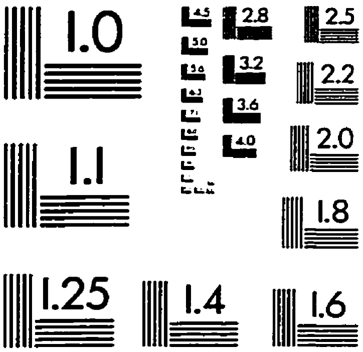


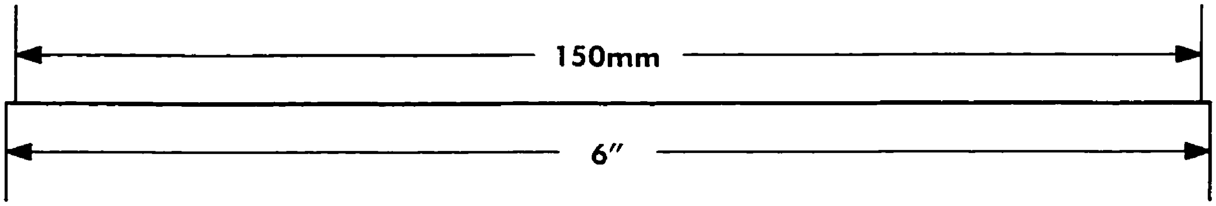
Figure 8. Hypothetical contribution of episodic long-range transport and global distillation to the overall level of contaminants in the arctic environment. a.) volatile compounds such as HCH and lower chlorinated PCBs b.) less volatile compounds such as DDT and higher chlorinated PCBs.

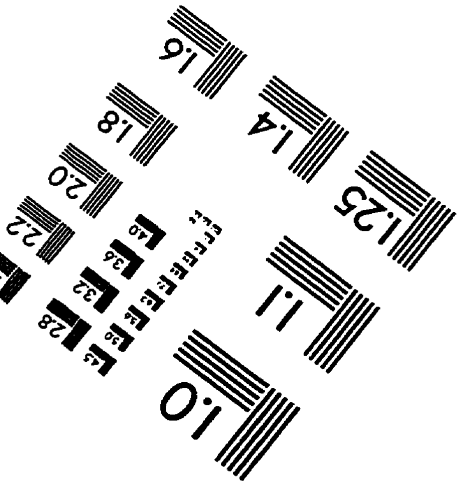
IMAGE EVALUATION TEST TARGET (QA-3)

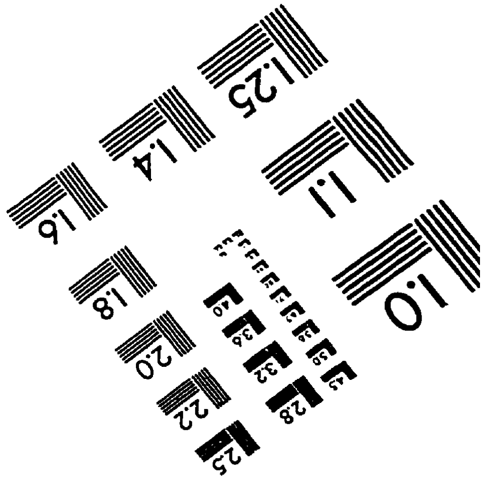












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