AN ANALYSIS OF USING SEMI-PERMEABLE MEMBRANE DEVICES TO ASSESS PERSISTENT ORGANIC POLLUTANTS IN AMBIENT AIR OF ALASKA

A

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Abstract

A region of concern for persistent organic pollutants (POPs) contamination is the Arctic, because of POPs' ability to migrate long distances through the atmosphere toward cold regions, condense out of the atmosphere in those region, deposit in sensitive arctic ecosystems and bioaccumulate in Arctic species. Thus, monitoring of POP concentrations in the Arctic is necessary. However, traditional active air monitoring techniques for POPs may not be feasible in the Arctic, because of logistics and cost. While these issues may be overcome using passive air sampling devices, questions arise about the interpretation of the contaminant concentrations detected using the passive air samplers. In this dissertation semi-permeable membrane devices (SPMDs) containing triolein were characterized and evaluated for use in sampling the ambient air of Alaska for three classes of POPs (organochlorines [OCs], polychlorinated biphenyls [PCBs] and polyaromatic hydrocarbons [PAHs]). In addition, a SPMD-based sampling campaign for POPs was conducted simultaneously at five sites in Alaska during a one-year period. The POP concentrations obtained from the SPMDs were examined to determine the spatial and seasonal variability at the locations.

POP concentrations detected in SPMDs were influenced by exposure to sunlight, concentrations of particulate-bound contaminants and changes in temperature. PAH concentrations in a SPMD mounted in a sunlight-blocking deployment unit were higher than in a SPMD exposed to sunlight ($P = 0.007$). PCB concentrations in SPMD exposed to filtered and non-filtered air were significantly different ($P < 0.0001$). Derived PAH air concentrations measured using SPMD were within a factor of approximately 7 of those obtained from an air sampler in Barrow, Alaska. The field study showed three distinct groups of samples. Barrow was separated from the sub-Arctic samples and a Homer sample (September-December) was distinct from the sub-Arctic samples. The separations suggest different air masses are being sampled by SPMDs. Lower concentrations of total POPs were measured at the coastal sites than the Interior sites.

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List of Abbreviations

AMAP	Arctic Monitoring and Assessment Programme
An	Anthracene
CC	Cis-Chlordane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
Fl	Fluoranthene
FWI	Fresh Water Institute
GC	Gas Chromatography
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexanes
HPLC	High Pressure Liquid Chromatography
Koa	Octanol Air Partitioning Coefficient
Kow	Octanol Water Partitioning Coefficient
MTC	Mass Transfer Coefficient
NAO	North Atlantic Oscillation
NCP	Northern Contaminants Program
OC	Organochlorine
OCP	Organochlorine Pesticide
PAH	Polyaromatic Hydrocarbons
PAS	Passive Air Sampler
PBDE	Polybrominated Diphenyl
PCB	Polychlorinated Biphenyls
Ph	Phenanthrene
PNA	Pacific North American
POP	Persistent Organic Pollutant
Py	Pyrene
R_s	Air Sampling Rate

SPMD	Semi-Permeable Membrane Device
T3	Triiodothyronine
T4	Thyroxine
TC	Trans-Chlordane
UAF	University of Alaska Fairbanks
USGS	United States Geological Survey

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Chapter I
Introduction

1.1. Overview

Scientists have hypothesized that persistent organic pollutants (POPs) migrate long distances through the atmosphere from source regions and condense out in colder regions like the Arctic (Mackay and Wania, 1995; Halsall *et al.*, 1998; Macdonald *et al.*, 2000). For example, dichlorodiphenyltrichloroethane (DDT) residues were discovered in Antarctica in the early 1960s, although they were not known to be used in the region (Sladen *et al.*, 1966). Atmospheric deposition of these organic pollutants onto soil, water and plants can result in the accumulation of these pollutants in geographical locations far from the source regions. The accumulation of pollutants has raised international concerns about potential adverse human and ecological effects from POPs exposure in pristine regions far from contaminate sources (AMAP, 1998).

Persistent organic pollutants are not only persistent in the environment (Doick *et al.*, 2005), but are also lipophilic (Chlou, 1985). The lipophilicity enables them to bioaccumulate in the food chain. When exposure to POPs occurs, the compounds are concentrated within lipid-rich samples. Fat samples from whales, seals and polar bears are routinely sampled to determine exposure to POPs (Kucklick *et al.*, 2000; Hoekstra *et al.*, 2003). In addition, indigenous people of the Arctic are being monitored for POPs exposure (Van Oostdam *et al.*, 2004; Klopov *et al.*, 1998), because their traditional diet includes consumption of large quantities of fat from subsistence foods, such as whale, seal and fish. Human and wildlife exposure to POPs can have toxicological implications; suppressed immune systems, altered reproduction and induced cancers are just some of the health issues.

In an attempt to better protect the Arctic from pollution and other threats, efforts like the Arctic Monitoring and Assessment Programme (AMAP) have been created to counsel the governments of the eight Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on matters relating to threats to the Arctic region (AMAP, 1998). POPs levels have been an important issue in

the AMAP reports. Long-term air monitoring networks in Europe and North America are being established to assess trends in levels of POPs (Hillery *et al.*, 1997; Cortes *et al.*, 1998; Coleman *et al.*, 1997). However, only a small fraction of the total geographical area is being sampled, because of the high cost and difficulties in maintaining traditional air sampling techniques (AMAP, 1998).

Traditional methods of measuring POPs entail the suction of high volumes of air through filters and absorbent traps (Stern *et al.*, 1997). Since a pump is required to draw in large amounts of air, an electrical source must be provided either by a generator or power line. This requirement makes sampling in harsh and remote terrain difficult and expensive. These issues make utilizing passive samplers advantageous, especially in truly remote locations. Continuous improvement in the development of passive sampling devices has led to their potential usefulness in monitoring POPs in air. Recent studies have used semi-permeable membrane devices (SPMDs) developed by the United States Geological Survey (USGS) as passive air samplers (PASs) for monitoring POPs (Söderström *et al.*, 2005; van Drooge *et al.*, 2005). Although promising data on using SPMDs as air monitoring surrogates has been published, certain questions still remain unanswered.

Solutions to the unanswered questions, which focus on the factors influencing POP concentrations within the SPMD, are needed in order to better understand results from SPMDs collected at different times and locations. Because long time intervals are required to collect POPs within the SPMDs, environmental factors like temperature and wind can vary significantly over the sampling period. Therefore, they must be considered in the analysis to make detected POPs levels more quantitative. Wind and temperature are two contributing factors which can influence uptake rates of contaminants into the SPMD (Söderström and Bergqvist, 2004; Shoeib and Harner, 2002a). In addition it is unknown if contaminants bound to particulates are being sampled by the SPMDs (Ockenden *et al.*, 1998a). Photodegradation of contaminants absorbed into SPMDs must also be considered. It has been shown that photolysis of polyaromatic hydrocarbons (PAHs) bound to leaves of plants and spruce needles can occur (Niu *et al.*, 2004; Wild *et al.*,

2005). By taking into account the factors that influence levels of POPs contained in an SPMD, either by minimizing them or adjusting contaminant concentrations, comparisons between POPs levels in SPMDs at different locations and times are possible.

Spatial and temporal comparisons are necessary to investigate geographical and climate variables in relation to POP concentrations. The separation of compounds based on their physical-chemical properties and interactions with environmental surroundings as they are transported has been hypothesized (Gouin *et al.*, 2005b). The hypothesis has been examined on a global scale by relating decreasing ambient temperature and increasing latitude to concentration (Simonich and Hites, 1995). Although concentration varies with temperature and latitude for more volatile compounds on a global scale, many other factors can influence concentrations on regional and local scales. Hydroxyl radical concentrations, snow and ultraviolet light are some variables that can alter concentrations by degrading or removing POPs from the ambient air, while temperature inversions and local point sources can have an opposite effect. For example, air concentrations on two classes of POPs [organochlorines (OCs) and polychlorinated biphenyls (PCBs)] at Alert, Canada, were found to be influenced by two climate distinction patterns: the North Atlantic Oscillation (NAO) and the Pacific North American (PNA) pattern (Hung *et al.*, 2005).

In addition to the environmental surroundings influencing concentrations in the atmosphere, one must also consider the individual physical-chemical properties of the compound. Different individual physical-chemical properties can dictate the environmental fate and behavior of the compound. In an attempt to sort out the impact of multiple variables on analyte levels, statistical software packages are being used to examine input sources and transport pathways (Mai *et al.*, 2003; Howe *et al.*, 2004). By using various data transformation and normalizing techniques, multivariate models can be constructed to obtain the overall picture of the impacts of different variables on the POP concentrations.

Thus, this project was undertaken in an attempt to validate using SPMDs for POP air monitoring in Arctic and sub-Arctic climates by visualizing the spatial differences in

the distribution of POP concentrations at five locations with different sampling intervals. Studies were conducted to characterize SPMDs for POP measurements in the region. The studies included 1) an evaluation of uptake rates at various temperatures; 2) a comparison of POP levels in SPMDs between filtered and non-filtered air to identify the impact of particulates on the SPMD-derived concentrations; and 3) a determination on the effects of photochemistry on the POP concentrations by examining levels between sunlight exposed and non-exposed SPMDs. A one year seasonal measurement of POPs was made at five locations in Alaska: Barrow, Denali National Park and Preserve, Poker Flat Research Range, Trapper Creek and Homer (More details about the locations are presented in chapter 3). A comparison of PAH levels obtained with the SPMDs at the Barrow location was made with PAH levels obtained from an active POP air sampler running at the same time and location. Multivariate analysis models were constructed to examine how POP measurements relate to spatial differences at five locations and different sampling intervals.

The impact of this research is to improve knowledge of POPs in the Arctic by filling in data gaps in Alaska and characterizing an alternative method of POPs measurement. Research on passive air sampling techniques, such as this one, should help improve the geographical coverage of air measurements in the Arctic, while reducing the sampling cost and logistics, and assist in any long-term monitoring efforts. Advances made in characterizing how SPMDs behave in Arctic and sub-Arctic conditions should improve scientists' understanding of what factors to consider when deploying SPMDs and interpreting the data. The results of the multivariate statistical analysis performed in this study should improve knowledge of how POP compounds are distributed in the Arctic and sub-Arctic regions.

1.2. Persistent organic pollutants

1.2.1. Overview

Persistent organic pollutants encompass a wide group of chemicals with similar characteristics that are potentially harmful to the environment and its inhabitants.

Increasing attention over the past decade has focused on POPs because of their ability to migrate long distances, persist in the environment, bioaccumulate in the food chain and potentially cause adverse health effects. Although certain POPs are banned or being phased out in most developed countries, (due to the Stockholm Convention on Persistent Organic Pollutants 1998) some developing and undeveloped countries still rely on them or do not have the necessary resources to regulate them.

When released in the environment, POPs can travel to regions far from their source because of their physical-chemical properties (Appendix Table A-1), which enables them to circulate globally via the atmosphere, oceans, and other pathways. Ultimately, POPs can end up in cold regions as was observed by long-term monitoring programs like the Northern Contaminants Program (NCP) baseline monitoring project. This project was established in 1992 to monitor for persistent organic pollutants (POPs) in Arctic air (Hung *et al*, 2005). Although evidence of long range transport of contaminants have been documented in cases like Arctic haze (e.g. Polissar *et al.*, 2001; Heidam *et al.*, 2004), the detailed process by which organic contaminants transport is still being debated. Some of the routinely discussed hypotheses are "hopping" and "global fractionation (Gouin *et al.*, 2005b)." "Hopping" is the degree to which molecules experience multiple condensation and revolatilization steps as distinct from a single emission, deposition and revolatilization event. While, "global fractionation" is the deposition behavior of the compounds based on their physical-chemical properties as they are transported. Spatial studies have shown compounds to increase, decrease or remain constant with changes in latitude, suggestive of distinctions in the relative importance of deposition versus atmospheric reactions in controlling their atmospheric transport potential (Jaward *et al.*, 2004b). There are also mechanisms that can retard the transport of POPs to the Arctic. Sequestering of POPs by soils (Ockenden *et al.*, 2003) and forests (Su and Wania, 2005) can hinder their migration. However, once these compounds are in the Arctic their persistence is likely to increase, because of decreasing temperature slowing down degradation rates (Eriksson *et al.*, 2003).

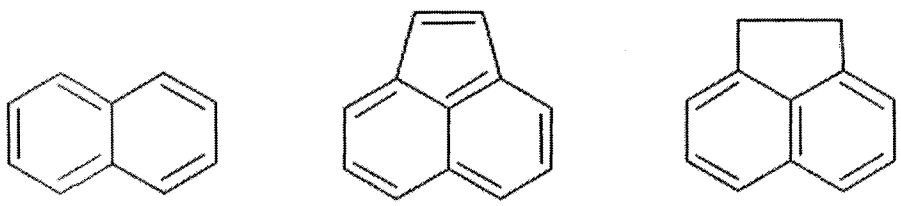
The degradation half-life of POPs in each environmental component (air, soil and water) is necessary to predict the compounds' environmental fate. Rate constants for hydrolysis, photodegradation, and biodegradation are necessary to estimate the POPs' half-lives. Hydrolysis of POPs in water is extremely slow and usually neglected. In the atmosphere, degradation by OH radicals is the most important removal process (Atkinson, 1988). Direct photolysis of POPs can occur in the atmosphere, in surface water, on the surface of soil (Klökffer, 1992) and in snow (Klan, 2001). The biodegradation rate is dependent on the microbial community present and on the quality of the media (snow, soil, plant etc.). Large temperature ranges and changes in ultraviolet inputs in the Arctic can alter the rate constants for degradation.

Once in the Arctic, the chemical must have the potential to deposit into the ecosystem to have notable effect on the area. Unlike the temperate regions where these chemicals are primarily released and where their fate and behavior are well known, the unique Arctic climate and environmental surroundings can have different influences on the fate and behaviors of the POPs. Snowfall has been shown to be a good scavenger of organic contaminants in the vapor or particulate phases (Franz and Eisenreich, 1998). Once on the ground the contaminants within the snow are delivered to soil, vegetation or back to the atmosphere during melting. Concentrations of POPs in freshly fallen snow have been shown to have sharp decreases over time, suggesting the role of physical chemical properties (mainly vapor pressure) in the chemical revolatilization from the snow (Finizio *et al.*, 2005). After deposition has occurred, POPs can also enter the lipid compartment of the lower Arctic food web through consumption of contaminated soil or water (Kelly and Gobas, 2001) and eventually bioaccumulate to top predators (Borga *et al*, 2004; Christensen *et al.*, 2005). Ultimately, these chemicals may have the potential to cause unwanted health issues in the ecosystem.

1.2.2. Polyaromatic hydrocarbons

Polyaromatic hydrocarbons are a group of POPs consisting of benzene rings fused together in a cluster-like arrangement. PAHs consist only of hydrogen and carbon (Figure

1.1). They are found throughout the environment and come from either natural or anthropogenic, human-induced, sources. A natural source of PAHs is forest fire. However, PAHs mainly arise from combustion-related or oil-related anthropogenic sources, such as coal-, oil- and gas-burning facilities, vehicles emissions, waste incinerators and industrial activities, such as oil refining, coke and asphalt production, aluminum production, etc. (Back, *et al.*, 1991; Nikolaou *et al.*, 1984). PAHs cause concern because of their global emission, persistence and carcinogenic, mutagenic and toxic effects (Kim Oanh *et al.*, 2002).



(a) Naphthalene (b) Acenaphthylene (c) Acenaphthene

Figure 1.1. Chemical structures of three simple PAHs found in the environment.

Although PAHs have similar chemical structures, their individual physical-chemical properties vary. For example, naphthalene, a simple PAH consisting of two aromatic rings, has a vapor pressure of 0.085 mm Hg, while perylene, a five member aromatic ring structure, has vapor pressure of 4.59×10^{-6} mm Hg (Bidleman, 1984). These differences in physical-chemical properties determine the fate and distribution of PAHs in the environment. A key physical-chemical property for assessing and categorizing chemicals in terms of their persistence and potential for long-range transport is their octanol-air partition coefficient (Koa) (Mackay and Wania, 1995). Koa is a unitless number used to define the partitioning of a compound between octanol and air. It is obtained from measuring the ratio of the compound's concentration in octanol to its air concentration in the vapor phase of a two-phase system at equilibrium. PAHs containing more aromatic rings typically have higher values of Koa, which means they are more likely to be found in environmental organic phases such as soil, vegetation, and the

organic portion of aerosol particles. Values of Koa for PAHs are typically expressed in logarithmic form, because of their large values and wide ranges. For example, naphthalene, a simple two ring compound has, a log Koa of 5.13 while dibenzo(*ah*)anthracene, a PAH consisting of five benzene rings fused together, has a log Koa value of 13.91 (MacKay *et al.*, 1992).

In addition to the physical-chemical properties of the individual PAHs, the different environmental matrices impacting the PAHs play an important role in dictating how PAHs will behave. One of the major compartments determining the fate and transport of PAHs is the atmosphere (Bidleman, 1998). Seasonal trends in PAHs have been observed at monitoring stations in Arctic Canada, where the average PAH levels during the winter (October–April) were an order of magnitude higher than those observed during the summer (May-September) (Macdonald *et al.*, 2000). Higher levels in the wintertime could be a direct result of increased emissions from domestic heating from lower latitudes and lack of UV radiation for photolysis. However, seasonality in ambient air concentrations can also be influenced by factors such as wet deposition, inversions, reactions with OH radicals, photolysis, scavenging by vegetation, wind speed and direction, and mixed boundary layer height. In addition, changes in temperature can also influence the gas to particle ratio and atmospheric reaction rates of PAHs (Fernandez *et al.*, 2002). These environmental influences highlight the importance of considering trends in seasonality for PAHs based not just on primary emissions, but also on local meteorology and boundary layer height.

1.2.3. Polychlorinated biphenyls

Polychlorinated biphenyls are a group of POPs consisting of 209 congeners with different arrangements of chlorine atoms off the biphenyl ring (Figure 1.2). They are man-made and used in the past as coolants and lubricants in electrical equipment (transformers, capacitors, etc.) because of their non-flammability and electrical-insulating properties. The historical global production of PCBs is estimated at 1.3 million tons based on manufacturers' reports (Breivik *et al.*, 2002). Whereas their stability was a

desired property for industrial use, their persistent nature means they linger in the environment long after their use has been phased out. Although currently banned from production in most countries, PCBs are still routinely detected around the world (AMAP, 1998). PCBs are released in the environment from improper disposal or leakage from transformers and capacitors. Once PCBs are released they can be found in runoff water, bound to soil or volatilizing slowly into the ambient air.

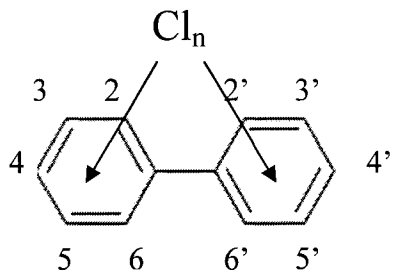


Figure 1.2. Illustration of biphenyl with possible arrangements of (1-10) chlorine atoms to form the 209 congers of PCBs.

The individual chemical make up of each congener will help determine its environmental behavior and fate. The various arrangements and numbers of chlorine atoms on the biphenyl ring is directly associated with the changes in physical-chemical properties between different congers. PCB congeners containing one chlorine atom can move world-wide without being deposited, whereas congeners with 8-9 chlorines tend to be deposited closer to the source because of lower vapor pressure. The concentration of volatile PCB compounds or PCB congers containing one chlorine atom is lower in tropical areas and higher in temperate or Polar Regions (Wania and Mackay, 1996). As with PAHs, PCBs have a wide range of Koas and are easier to represent in the logarithmic form. Log Koa for PCBs increases with the number of chlorine substitutes (Table 1.1). Equations used to estimate values of log Koa for PCB congers have been developed by Zhang *et al.* (1999) and calculated values range from 7.54 to 13.36 at 0°C. These high partition coefficients allow PCBs to favor organic components in soils or plants. Once bound to the organic component degradation is likely to decrease and

persistence increase. Half-life of PCBs in soil has been measured to be 10.9 years for PCB 28 and 11.2 years for PCB 52 (Doick *et al.*, 2005).

Like other classes of POPs, PCBs can bioaccumulate in top predator species and cause potential health problems, because of their persistent nature. The presence of PCBs in biological systems has been linked to health effects such as reproductive disorders (Reijnders, 1988) and effects on vitamin A and thyroid hormone metabolism (Brouwer *et al.*, 1989). Top predators (polar bears, northern fur seals and glaucous gulls) inhabiting the Arctic also have indications of immunosuppression (AMAP, 2004). However, it is unknown as to what is exactly causing the effects. While PCB exposure is expected to be a contributing factor, many other processes must also be considered.

Table 1.1. The values of log Koa are increased and altered with the addition and different positioning of the chlorine atoms off the biphenyl ring. (Developed from measurements by Harner and Bidleman, 1996).

PCB Conger	Number of Chlorine Atoms	Log Koa (measured at 20° C)
3	1	7.01
49	4	8.57
53	4	8.24
66	4	9.22
77	4	9.96
95	5	9.06
96	5	8.77
101	5	9.31
105	5	10.27
118	5	10.8
126	6	10.61
138	6	10.09
153	6	10.04
171	7	10.51
180	7	10.75

1.2.4. Organochlorines

Organochlorines are defined as organic compounds containing chlorine atoms. PCBs are considered a part of the organochlorine group, but are separated into their own class because of their large numbers. The OCs that will be the focus of the thesis are some chlorine-containing pesticides and their metabolites. A routinely studied OC pesticide is p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), which is broken down to either dichlorodiphenyldichloroethylene (DDE) or dichlorodiphenyldichloroethane (DDD) (Figure 1.3). Extensive usage of DDT started in the United States in 1946 and increased until 1959. It then declined steadily until it was officially banned in 1972 (Kutz *et al.*, 1991), because of its persistence and health effects. However, increased usages of other harmful OC pesticides like toxaphene (a complex mixture of chemicals that consist mainly of chlorinated bornanes) replaced DDT. These compounds are currently banned in the United States, but screening is still being conducted because of the extensive usage. Release of OC pesticides primarily occurred during their use as insecticides for agricultural and health purposes (vector control). However other release mechanisms included loss during manufacturing, formulation, packaging, and disposal. Direct release into the ambient air is a result of aerial spraying or volatilization from contaminated soil or water.

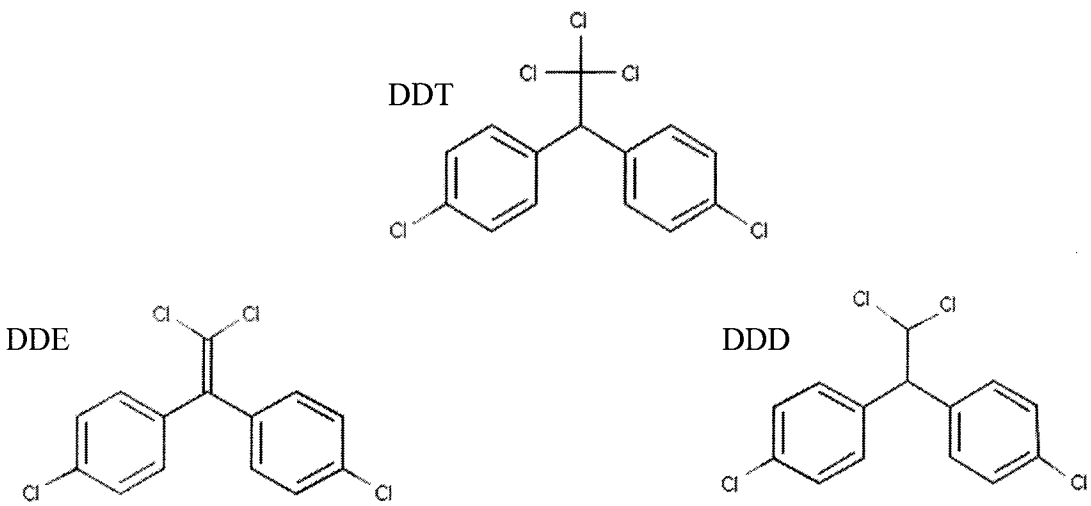


Figure 1.3 Chemical structure of dichlorodiphenyltrichloroethane (DDT) and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD).

The physical-chemical properties of OCs result in their persistence, long-range transport potential and toxicological effects. High octanol to air partitioning coefficients and long half-lives are factors that contribute to their potential for long-range transport and slow degradation. Higher values of Koa should result in OC enrichment of organic phases (e.g. soil or plants), thus making the compounds less susceptible to degradation. Log Koas have been measured by Shoeib and Harner (2002b) for 19 OC pesticides and ranged approximately 3 orders of magnitude at 25°C, from 7.4 for hexachlorobenzene (HCB) to 10.1 for p,p'-DDD. Half-lives for OCs have been calculated for the Arctic and range from 4-17 years based on air concentrations (Hung *et al.*, 2005). The long half-life enables OCs to bioaccumulate in the Arctic food web and cause health effects. Studies of glaucous gulls breeding in the Barents Sea have reported that high blood levels of OC contaminants were negatively correlated with thyroxine (T4) and the T4 to triiodothyronine (T3) ratio (Verreault *et al.*, 2004). Alterations in hormone levels might cause reproductive, behavioral, and developmental stress on the ecosystem.

1.3. Passive air sampling

1.3.1. Basic principles

Passive air sampling is based on diffusion of analyte from the surrounding environment to the collecting medium, as a result of the concentration gradient between the environment and the collecting medium. No active movement of air is required, but a static air layer or porous material must be crossed before the analyte can enter the collecting medium. Analyte continues to accumulate in the collecting medium until equilibrium is achieved or sampling is stopped. The collection potential for the analyte is dependent on the passive sampling medium to air partition coefficient, which is a ratio of the analyte concentration in the medium divided by the concentration in air when the two phases are in equilibrium (Shoeib and Harner, 2002a). When the sampling is terminated by the user, three factors determine the concentration: exposure time, medium collection capability for the analyte of interest and atmospheric concentration. Results are based on a time weighted average. If the sampling rate and analyte concentration in medium are

known, determination of average air concentration is possible. However, two conditions must be met for calculating average air concentration. First, the trapped analyte cannot be released even when the surrounding environment has zero levels of the analyte of interest. Second the sampling rate needs to be a linear function of analyte concentration in the air throughout the sampling time.

When these conditions are met, movement of analyte from the environment to the sampled medium can be described by Fick's first law of diffusion (Cross, 2003). When mass transfer is controlled by permeation through a membrane, gas sampling can be described by:

$$M = \frac{SA}{Lm} P_1 t \qquad \text{Equation (1)}$$

where M is the amount of analyte in sampled medium, t is time in seconds, S is the permeability coefficient of a given compound (cm^2/ min), A is the cross section of the diffusion path (cm^2), Lm is the membrane thickness (cm), and P_1 is partial pressure of the analyte near the outside membrane surface. The ideal gas law can be used to convert analyte partial pressure into concentration in air by:

$$P_1 = aC_0 . \qquad \text{Equation (2)}$$

Here a consists of the universal gas constant (R) and temperature (T) (a= RT). When temperature is constant, S, A, a and Lm are constant and can be written in term of k, the calibration constant as:

$$\frac{1}{k} = \frac{SAa}{Lm} \qquad \text{Equation (3)}$$

So, the concentration of the analyte in air can be calculated once M and t are known by substituting equations 2 and 3 into 1 and solving for C_0:

$$M = \frac{SA}{Lm} aC_0 t \qquad \text{Equation (4)}$$

$$M = \frac{1}{k} C_0 t \qquad \text{Equation (5)}$$

$$C_0 = \frac{Mk}{t} \qquad \text{Equation (6)}$$

Active sampling requires a power supply, needs routine maintenance, is not very mobile and costs substantially more than passive air sampling. The advantages to passive sampling include simplicity in deployment, no maintenance and low cost. Thus, in truly remote locations passive air sampling may be the only option. In addition, concurrent measurements at the local, regional, and global scale are not always possible with active samplers, due to logistical difficulties and increased costs. Unlike active samplers, several passive air samplers (PASs) can be deployed simultaneously to obtain spatial distributions of POPs. However, although the PASs are simpler to deploy and maintain, interpretation of the result can be far more complicated than for active air samplers. The amount obtained of a compound from the passive sampler is converted to estimated atmospheric concentration based on developed air sampling rates.

1.3.2 Persistent organic pollutants

Several different types of PASs have been used to sample POPs. These include polymer-coated glass samplers (POG) (Harner *et al.*, 2003), semi-permeable membranes devices (SPMDs) (Bartkow *et al.*, 2004), polyurethane foam (PUF) (Gouin *et al.*, 2005a), XAD-2, a styrene-divinylbenzene copolymer, (Wania *et al.*, 2003), butter (Kalantzi *et al.*, 2001), solid-phase microextraction (SPME) (Zeng *et al.*, 2004), and tristearin-coated fiberglass sheets (Müller *et al.*, 2000). In addition, vegetation has been routinely used as a passive biomonitor for POPs in the ambient air (Howe *et al.*, 2004). Biomonitoring is attractive because samples are abundant and deployment is not necessary. However, the concentration capacity and air sampling rate changes with different species and age of the plants, the sampling location and season (Ockenden *et al.*, 1998b). On the other hand, man-made PASs require deployment, but their uniform design enables better comparisons between sites and control of the sampling time.

Monitoring of POPs at local, regional and continental scales to examine spatial and temporal distributions is frequently being achieved with man-made PASs. Assessments of spatial distributions of polybrominated diphenyls (PBDEs), PCBs and OCs have been made with PASs on an urban-rural transect in Toronto, Canada (Gouin *et*

al., 2005b; Harner *et al.*, 2004). The vertical distribution of PCBs, PAHs and OCs was evaluated with polymer-coated glass (POG) samples in the atmospheric boundary layer of an urban area (Farrar *et al.*, 2005). The spatial and temporal distributions of POPs around the Great Lake Basins were evaluated with PUF as PASs (Gouin *et al.*, 2005a). On a continental scale, the atmospheric distributions for α and γ hexachlorocyclohexanes (HCHs) were evaluated with 40 PASs across North America (Shen *et al.*, 2004). In addition, OCs, PBDEs and PCBs were measured concurrently with PASs in 22 countries across Europe (Jaward *et al.*, 2004a).

The basic principle for uptake of contaminants into these various passive sampling medium is shown in Figure 1.4. There are three possible phases during sampling: linear, curvilinear and near equilibrium. The linear phase is relatively short, in comparison to the other phases, and the rate of uptake in the linear phase can be expressed as amount of volume sequestered per unit time. Following the linear phase is the curvilinear phase which is partly integrative, consisting of both linear and equilibrium processes. The near equilibrium phase is relatively long and the amount of compound in the PAS is expressed as the PAS to air partitioning coefficient.

The generalized uptake model can be express with a first-order one-compartment model (Mayer *et al.*, 2003):

$$C_{pas} = \frac{K_1}{K_2} * (1 - e^{-K_2 * t}) \qquad \text{Equation (7)}$$

Here C_{pas} is the concentration of the contaminant in the PAS, K_1 is the uptake rate constant, K_2 is the elimination rate constant, and t is the time of sampling.

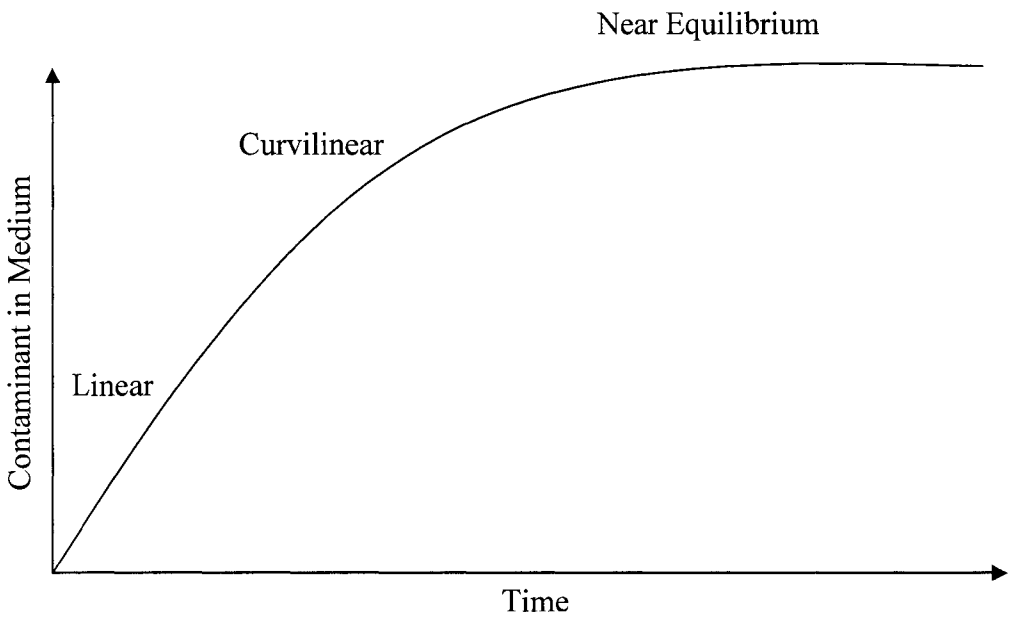


Figure 1.4. Schematic uptake curves of contaminant into passive air samplers showing the three phases.

1.3.3 Semi-permeable membrane devices

1,2,3-Tri[cis-9-octadecenoyl] glycerol (triolein) containing semi-permeable membranes devices were developed by United States Geological Survey (USGS) for monitoring of POPs in water. SPMDs were designed to mimic fish, especially the fat that could bioconcentrate contaminants. A standard SPMD consists of a thin wall (75-95 μm) of low-density polyethylene membrane surrounding approximately 1 mL of triolein. Triolein was selected because it is the major storage fat found in aquatic organisms, and the triolein-water partition coefficient and the octanol-water partition coefficient (Kow) of hydrophobic, organic compounds like fat and triolein are very similar (Chiou, 1985). During water studies, abnormally high concentrations of contaminants in field and laboratory blanks for SPMDs were being detected because of airborne concentrations of the compounds in the lab and field. Eventually, researchers realized the source and the potential use of SPMDs as passive air samplers (Petty *et al.*, 1993). Since then, SPMDs have been deployed in various parts of the world for passive air sampling of POPs (Table 1.2). Initially in air, SPMDs were used to identify new and existing organic pollutants.

Eventually more SPMDs were simultaneously deployed at multiple locations to examine spatial and temporal distributions of organic contaminants and speculate about potential sources of POPs.

Table 1.2. SPMDs used in various parts of the globe for sampling of POPs in ambient air.

Location	Compound	Reference
Austria, the Czech Republic, Poland, Slovakia, Sweden	PAHs, nitrated PAHs	Söderström *et al.*, 2005
High mountains of Central Pyrenees, Catalonia, Spain.	HCB, PCBs	van Drooge *et al.*, 2005
Metropolitan area of Australia	PAHs	Bartkow *et al.*, 2004
Urban-rural Toronto, Canada	PCBs, PAHs	Harner, *et al.*, 2004
South UK to north Norway	PCBs , HCB	Meijer *et al.*, 2004; Jaward *et al.*, 2004a; Ockenden *et al.*, 1998a
Southern Italy	PAHs	Isidori *et al.*, 2003
Thailand	PAHs	Söderström *et al.*, 2003
Western Wadden Sea, Netherlands	PCBs, HCB	Booij and van Drooge., 2001
Northwest England	PAHs	Lohmann *et al.*, 2001
Lancaster University	PCBs	Ockenden *et al.*, 1998c
Costal air north of Santa Cruz, CA	OCs	Prest *et al.*, 1995
National Fisheries Contaminant Research Center	PCBs	Petty *et al.*, 1993

An SPMD functions as a PAS through diffusion of analyte through the membrane resulting in absorption in the triolein. The uptake in the SPMD can be hindered by three possible barriers in the absence of wind: an air boundary at the membrane-air interface, the membrane and the triolein. The diffusive mass transfer in the air boundary layer at the membrane-air interface is governed by the area of the SPMD and the mass transfer coefficient (MTC) (Shoeib and Harner, 2002a). Turbulence around the membrane will likely increase the MTC. The uptake through the membrane is restricted by both diffusion and membrane permeability. Although the membrane is composed of dense polymer chains, formation of transient cavities with diameters up to 10 Å resulting from random thermal motion of the polymer chains enables dissolution of organic compounds into the membrane and transfer of contaminants to the triolein (Huckins *et al.*, 1993). The resistance to diffusive mass transfer in the triolein is small in comparison to the resistance in the membrane and the air boundary layer, and can be ignored.

The uptake of a compound in a SPMD is similar to other PASs and occurs in three different phases: the linear, curvilinear and equilibrium phases (Figure 1.4) as described in section 1.3.2. Calculated contaminant air concentrations (C_a) detected by SPMDs have been described elsewhere (Ockenden *et al.*, 2001; Shoeib and Harner, 2002a) and can be determined from the accumulated amount (M_s) using the following equation:

$$M_s = V_s K_{sa} C_a (1 - \exp(\frac{-R_s t}{V_s K_{sa}})) \qquad \text{Equation (8)}$$

Here K_{sa} is the SPMD-air partition coefficient, V_s is the SPMD triolein volume, R_s is the air sampling rate, and t is time. The amount taken up (M_s) by a SPMD depends on several factors: the physical-chemical properties of the compound; the ambient air concentration; time of exposure; volume of SPMD and the environmental sampling conditions. The air sampling rate and the time a chemical remains in the linear and the curvilinear phases are independent of the ambient concentrations but depend on the volume of sampler, the physical-chemical properties of the compound at the sampling site and the environmental factors. Different temperatures and wind speed can alter air sampling rates.

Sampling rates have been developed for PAHs and PCBs during the linear uptake phase (Table 1.3). These rates were determined by deploying multiple SPMDs next to an active sampler and removing them sequentially at different times to obtain an uptake rate. The mass in the SPMD was plotted against time to obtain a slope (M_s/t), which is divided by the air concentration (C_a) obtained from the active air sampler for the sampled time period. The R_s can then be expressed with the following equation:

$$R_s = \frac{M_s}{C_a t} \qquad \text{Equation (9)}$$

Air sampling rates into SPMDs have also been developed using performance reference compounds (PRCs), compounds similar to the analyte but not detected in the environment (van Drooge *et al.*, 2005; Huckins *et al.*, 2002; Ockenden *et al.*, 2001). Here the air sampling rate is calculated from the first order dissipation rate constant (K_e) of the PCRs that are spiked into SPMDs prior to sampling using:

$$R_s = V_s K_{sa} K_e \qquad \text{Equation (10)}$$

The air sampling rate is a very useful value because it gives a relative amount of air volume sampled by the SPMD. Air sampling rate can be further transformed by dividing it by the area of the SPMD to obtain the MTC or the gaseous deposition velocity. In stagnant air the MTC will likely be the same as the molecular diffusivity in air (Shoeib and Harner, 2002a).

Table 1.3. Air sampling rates developed in the field for contaminants into SPMD.

Compound	R_s (m^3d^{-1})	Temperature (°C)	Reference
PCB 28	3.8	23	Shoeib and Harner, 2002a
PCB 44	3.5		
PCB 52	3.9		
PCB 99	3.3		
PCB 101	3.4		
PCB 128	5.2		
PCB 137/138	5.4		
PCB 153	4.1		
PCB 180	7.9		
PCB 77	3.5		
PCB 81	3.7		
PCB 105	4.0		
PCB 114	4.2		
PCB 118	4.3		
PCB 126	9.9		
PCB 156	4.9		
Fluorene	1.8	22	Bartkow *et al.*, 2004
Phenanthrene	4.4		
Anthracene	4.1		
Fluoranthene	4.5		
Pyrene	2.0		
Benzo(a)anthracene	4.1		
Chrysene	6.1		
Benzo(b,k)fluoranthene	2.1		
Benzo(e)pyrene	1.3		
Benzo(a)pyrene	0.6		
Indeno(1,2,3-c,d)pyrene	1.7		
Benzo(g,h,i)perylene	0.7		

Sampling of compounds using SPMD is performed either in the linear or equilibrium phase because the results are easier to interpret. When SPMDs have reached equilibrium with the ambient air, the average air concentrations can be estimated. This method has the advantage that the site specific effects of the environmental conditions on the sampling are insignificant in some cases. However, the time to approach or reach equilibrium and the SPMD equilibrium partition coefficient also depend on the

environmental conditions. These will change with site conditions, thus the user has to demonstrate that steady state has been accomplished.

Sampling in the linear phase enables the detection of contaminants in a shorter period compared to equilibrium phase, which enhances the ability to detect intermittent pollutant releases. However, this sampling phase is affected by environmental factors at the sampling location. Over an integrated time period and across a spatially separated network of SPMDs, temporal and geographical variations in temperature, precipitation, wind speed and sunlight can be high. When these factors are accounted for or minimized, comparisons of concentrations at different locations and times are more quantitative. One way to minimize the influence of these environmental factors is with a deployment unit that shields the SPMD from these elements. Concentrations of PAHs inside SPMD exposed to wind were two times higher than SPMD protected by a metal umbrella (Söderstrom and Bergqvist, 2004). The deployment unit can also limit possible photolysis, by UV-radiation, of a contaminant absorbed by SPMD and keep particulate matter from depositing onto the SPMD. Both of these processes can alter contaminant concentrations within the SPMD. It is unknown if SPMDs are able to sample contaminants bound to particulates by allowing the particulates to adhere to the membrane and allowing the POPs on the particulates to diffuse through the membrane. In addition, it is likely that large temperature changes will influence the air sampling rate. Although no study has examined uptake in the air at low Arctic temperatures, studies in water have shown approximately a factor of 3 increase in contaminant concentrations for SPMDs exposed at 2 versus 20°C (Booij *et al.*, 2003).

Chapter II
Research objective and hypotheses

2.1. Research objective

Persistent organic pollutants migrate to cold regions (Figure 2.1) and can cause harm to the ecosystem. Monitoring POP concentrations to investigate trends, distribution and types of POPs in the ecosystem is necessary to determine unwanted effects to the cold regions. Several environmental factors are known to influence the atmospheric concentrations of POPs locally, regionally and globally. In addition, the physical-chemical properties of each compound can influence its behavior.

The purpose of this research is to evaluate, qualitatively and quantitatively, POP concentrations in the ambient air of Alaska using triolein containing SPMDs. Evaluation of the SPMDs as sampling devices was performed to better understand factors that can influence concentrations of POPs detected in SPMD. Measurements of POP concentrations in Alaska were conducted based on POP levels detected in the ambient air using SPMDs at five locations (Barrow, Denali National Park and Preserve, Poker Flat Research Range, Trapper Creek and Homer) and deployed for approximately four simultaneous three-month intervals. The POP concentrations at the Barrow location were compared to an active sampler that measured the same POPs. In addition, SPMDs were exposed to sunlight, particulates, and different temperatures, because the temporal and geographical variations of the environmental surroundings can influence air sampling rate. By characterizing or minimizing the factors that influence the air sampling rate of contaminants into SPMD, better interpretation of the POP concentrations determined at different locations and times using the SPMDs can be conducted.

Several possible factors have been shown to influence POP concentrations within SPMDs. Therefore, experiments were conducted to examine the effect of these factors on the POP concentrations and a deployment unit was developed to minimize some effects to allow for better comparisons of POP concentrations at different locations. The

deployment unit for the SPMDs was designed to decrease exposure to sunlight and turbulence around the SPMDs.

Multivariate statistics were used to relate and obtain a spatial distribution of POP concentrations measured in SPMDs at five locations (Barrow, Denali National Park and Preserve, Poker Flat Research Range, Trapper Creek and Homer) in Alaska during different sampling times. Three classes of POPs were evaluated: PCBs, PAHs and OCs.

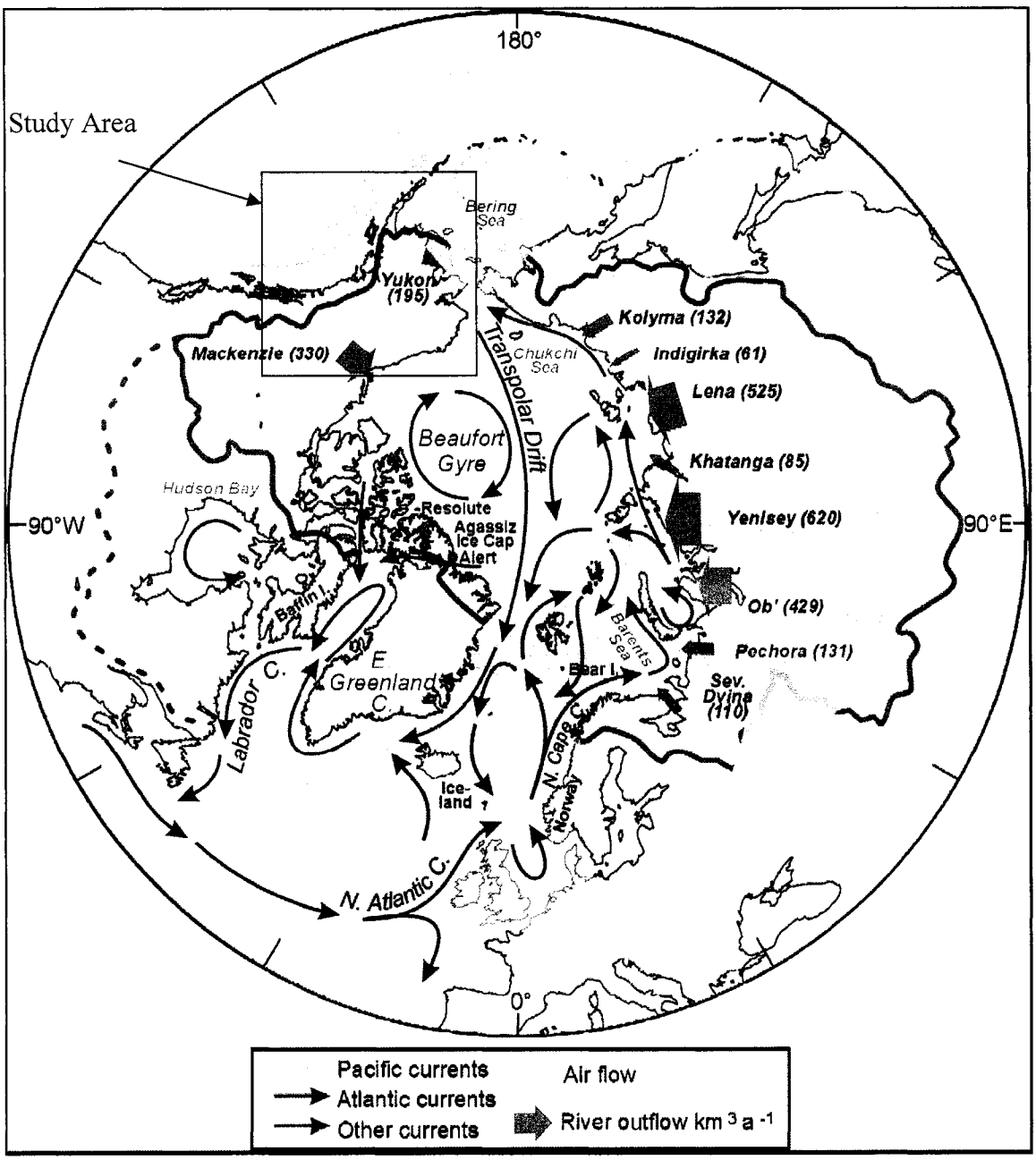


Figure 2.1. Three major pathways for migration of POPs into the Arctic: ocean, river and wind currents (modified form Macdonald *et al.*, 2005).

2.2. Research questions and experimental design

In evaluating, qualitatively and semi-quantitatively, POP concentrations in SPMDs, the following research questions and hypothesis were tested.

Question 1:

Does sunlight exposure decrease the measured POP concentrations in SPMDs?

Null Hypothesis:

H_0: There is no difference in POP concentrations in sun-exposed and non-exposed SPMDs (sun = no sun).

Design:

Two SPMDs were deployed at Poker Flat Research Range during the summer months. One SPMD was exposed to sunlight, while the other had decreased sunlight exposure. Qualitative and quantitative comparisons of POP concentrations between sun exposed and non-exposed SPMD were made.

Question 2:

Do SPMDs sample for particulate POPs?

Null Hypothesis:

H_0: There is no difference in POP concentrations between SPMDs in filtered air and non-filtered air (filtered air = non-filtered).

Design:

SPMDs were connected to the tail end of two active air samplers and exposed to the same air. One of the active samplers contained a quartz-fiber filter to remove particulate in the air prior to the air reaching the SPMD. The other active sampler contained no filter prior to the SPMD. Qualitative and quantitative comparisons of POP concentrations between filtered and non-filtered air exposed to SPMD were made.

Question 3:

Do changes in temperature influence the POP concentrations observed in SPMDs?

Null Hypothesis:

H_0: There is no difference in POP concentrations in SPMDs for different temperatures ($Temperature_1 = Temperature_2 = Temperature_3$).

Design:

SPMDs were sealed in deployment units and exposed to three OCs. The deployment units were kept at different temperatures. Quantitative comparisons of POP concentrations in SPMDs exposed to different temperatures were made.

Question 4:

Do calculated POP concentrations in SPMDs relate to actual air concentrations?

Null Hypothesis:

H_0: There is no difference in POP concentrations between calculated SPMD concentrations and concentrations determined from an active air sampler (SPMD = Active).

Design:

SPMDs were deployed next to an active sampler in Barrow, Alaska. Measurements of POP concentration in SPMDs were converted to average air concentrations with air sampling rates from the literature. Quantitative comparisons of POP concentrations between POPs collected by SPMDs and active air sampler in Barrow, Alaska were made.

Question 5: Are POP concentrations in SPMDs measured at the five locations in Alaska the different?

Null Hypothesis:

H_0: There is difference in POP concentrations at the five locations in Alaska measured by SPMDs. (Barrow = Poker Flat = Denali National Park = Trapper Creek = Homer)

Design:

SPMDs were deployed for three-month time intervals for one year at five locations in Alaska. Qualitative and semi-quantitative comparisons of POP concentrations in SPMDs at five different locations in Alaska were evaluated with principal component analysis.

Chapter III

Materials and methods

3.1. Passive sampler

United States Geological Survey-developed SPMDs containing triolein (US patent 5,395,426) were purchased from Environmental Sampling and Technologies Inc., Saint Joseph, MO. The SPMD is constructed of a lay-flat, low-density polyethylene (LDPE) tube that contains transport corridors approximately 10 Å in diameter (Figure 3.1). Inside the polyethylene walls is one milliliter of triolein. The dimensions of the overall SPMD are 91.4 cm length and 2.5 cm width. The polyethylene membrane thickness is 75-95 μm. This gives an overall surface area of 456 cm^2. In addition, a loop is formed at both ends of the polyethylene to facilitate deployment. The SPMDs were shipped in individually-sealed pint-size steel canisters purged with argon. They were stored at -40°C before deployment from the University of Alaska Fairbanks (UAF).

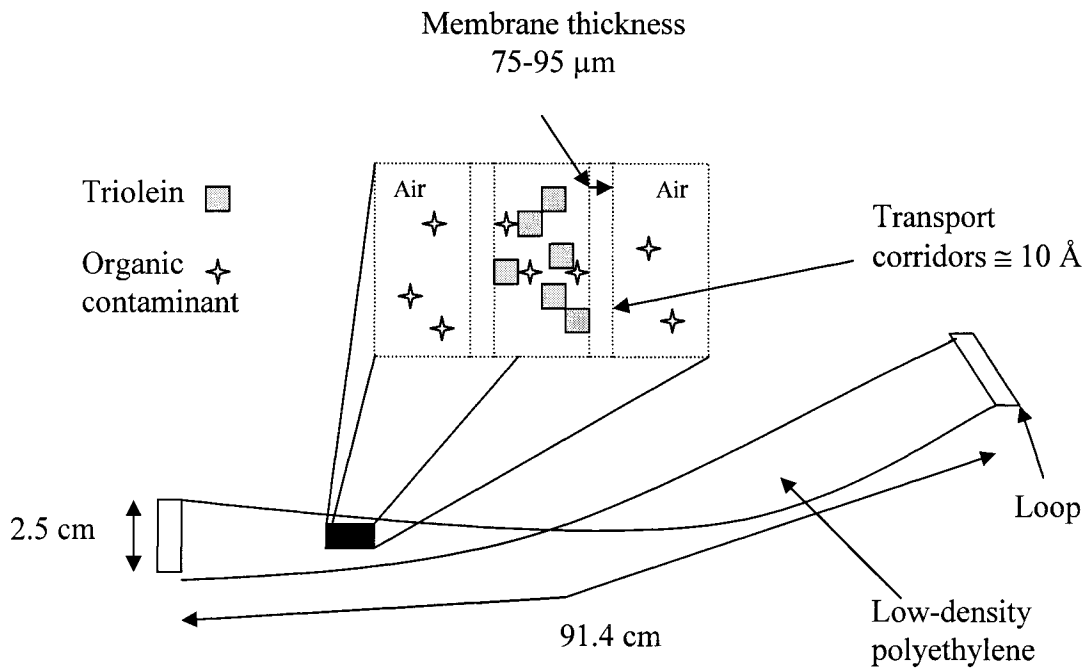


Figure 3.1. Schematic diagram of a standard 1-mL triolein SPMD constructed of a lay-flat, low-density polyethylene strip which contains transport corridors approximately 10 Å in diameter. The ends of the low-density polyethylene strip have loops to facilitate the deployment.

3.2. Deployment units

The deployment unit is constructed of a steel cylindrical-shaped gallon canister containing a steel quart cylindrical-shaped canister with a removable lid for exchanging SPMDs and a hook for hanging the unit (Figure 3.2). The quart-sized canister (14.5 cm height x 13.5 cm diameter) housed the SPMD along the internal wall. The SPMD was wrapped around nine screws (each 4 cm in length). The screens are mounted diagonally from one another along the internal wall. A mesh screen covers the canister to prevent insects from entering the SPMD housing unit. The quart-size canister fits inside the gallon-sized canister (19 cm height x 16.5 cm diameter) and is held in place with three screws (each 4 cm in length) running through both canisters. The bottom of the gallon-sized canister was removed to allow airflow into the unit. An eye screw was mounted on the bottom of the deployment unit for additional stability during deployment. All deployment units were rinsed with acetone and baked at 300°C prior to deployment.

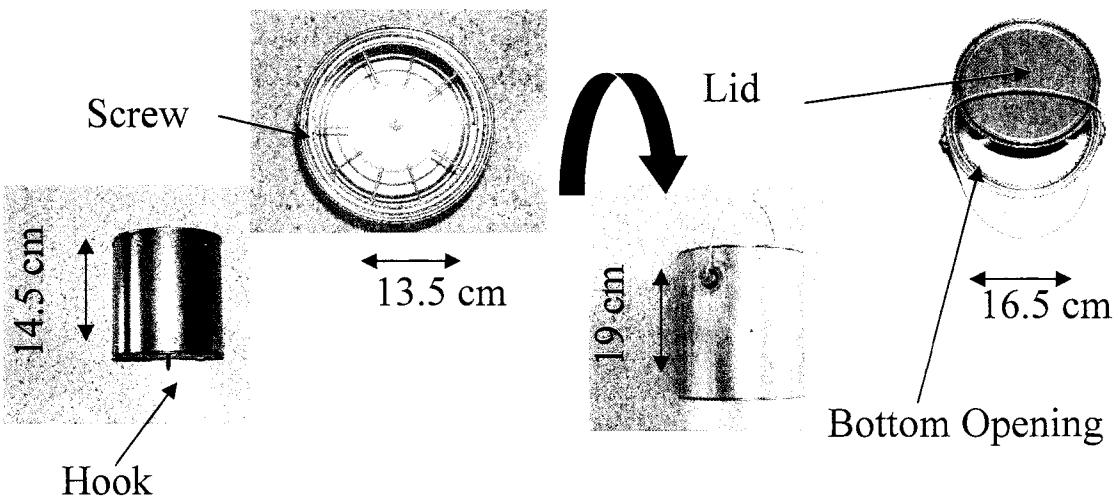


Figure 3.2. Illustration of a deployment unit used to house and protect the SPMD from the environmental elements during deployment.

3.3. Field studies

3.3.1. Sites

Semi-permeable membrane devices were deployed at five sites (Figure 3.3) in Alaska from August 2002 to September 2003. These sites were chosen because of on-going research and their accessibility from UAF. All locations, except Barrow, are located off the main north-south highway of Alaska.

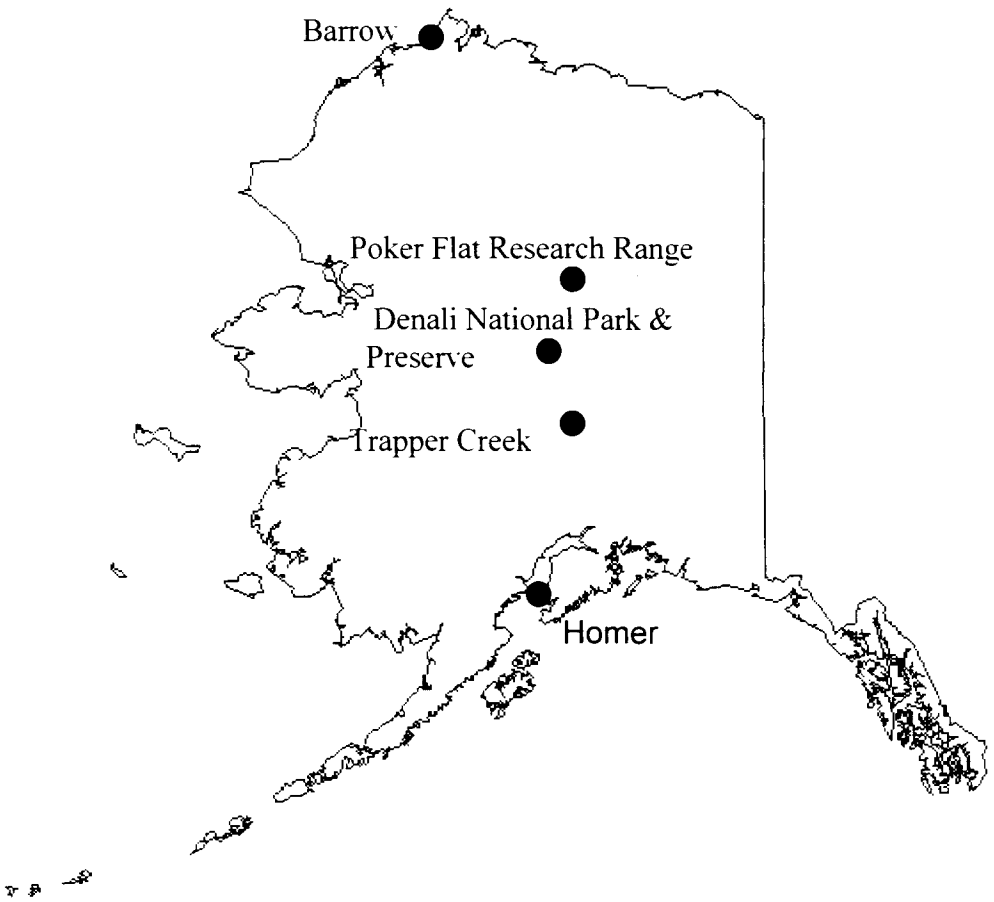


Figure 3.3. A map of Alaska depicting the five locations (Barrow, Poker Flat Research Range, Denali National Park and Preserve, Trapper Creek and Homer) set up for deployment of SPMDs.

Each location is characterized by its own unique geographical features. Barrow (71° 18'1"N, 156° 44'9"W) is the northern-most city in Alaska and is located next to the Arctic Ocean and north of the Brooks Range. It is a treeless lowland plain area. The samplers were hung on a deck at the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory just outside of Barrow in close proximity to an ongoing active POPs air sampler. South of the Brooks Range and north of the Alaska Range lies the Poker Flat Research Range (65° 07'2"N, 147° 26'1"W). The area is marked by low rolling hills and is tree covered. The samplers were hung on a meteorological tower next to an atmospheric sampling station. Lying on the north flank of the Alaska Range is the Denali National Park and Preserve (63° 43'22"N, 148° 58'1"W) site. The samplers were deployed from a metal platform located on a hill top at the end of a dirt road. Just south of the Alaska Range is the Trapper Creek (62° 18'56"N, 150° 18'56"W) site. Samplers were located on an open grass field next to an elementary school. The southern most sampling site is Homer (59° 39'27"N, 151° 39'7"W), a costal area. The sampling site is directly off the Sterling Highway with the Kachemak Bay to the west. The samplers were hung on a tree next to a ranger station.

A minimum of two deployment units were hung on objects ranging from 3 to 10 meters high. The objects used for hanging include: meteorological towers at Poker Flat Research Range and Denali National Park and Preserve, a fence at Trapper Creek, a wooden deck at Barrow and a tree at Homer. One deployment unit housed four consecutive 3-month SPMDs during the year, while an additional unit housed an SPMD for the whole year. The one-year samples were archived for future analysis after extraction and clean-up. The time and ability to drive to each site determined the allotted deployment time, with the exception of Barrow, since personnel were on site to exchange SPMDs. Each individual SPMD was transferred to the site in their original sealed containers and placed back into the original container during retrieval. Due to a miscommunication with the personnel in Barrow the first SPMD was deployed for a longer time interval than planned. Instead of leaving the SPMD exposed for

approximately three months, the first sample was exposed for six months. The sample is reported as a 6-month instead of a 3-month sampling time.

A high-volume air sampling project for POPs in Barrow occurred at the same time as this study. The active sampler made measurements using methods conforming to those made at other Arctic Monitoring and Assessment Programme (AMAP) sites. The active sampler measured weekly average concentrations of POPs in the ambient air from March 2002 to April 2003 at the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory outside of Barrow, Alaska.

3.3.2. Reproducibility of SPMDs for POPs

Four SPMDs were deployed at Poker Flat Research Range from May 29, 2003, to August 16, 2003, to examine the reproducibility of the uptake of POPs into the SPMDs. Deployment units were hung approximately 4 meters above the ground and adjacent to one another on a meteorological tower. The reproducibility of the SPMDs was examined with relative standard deviation (RSD) in percent. Relative standard deviation percent was calculated by dividing the standard deviation of the individual concentration of POPs detected in SPMDs (n= 4) by the average and multiplying by 100. The error bars for the reported POP concentrations in section 4.8 to 4.10 are developed from the RDS% in SPMDs from Poker Flat Research Range.

3.3.3. Evaluation of SPMD exposure to UV

Two SPMDs were deployed at Poker Flat Research Range from June 12, 2003, to August 16, 2003, to examine differences in POP concentrations between a sun-exposed SPMD and a non-sun-exposed SPMD. Instead of using a non-transparent lid on the sun-exposed deployment unit, a rectangular shaped piece of glass (166 mm length x 123 mm width and 3 mm thick) covered one unit during the exposure time. Although glass absorbs UV radiation, it was necessary to cover the deployment unit to protect the SPMD from rain, wind, and falling particles. An Aligent 8453 UV-visible spectrophotometer was used to measure how much of the UV was allowed through the glass. Comparisons

in PAHs were made between the two SPMDs with Wilcoxon Sign-Rank test (with degrees of freedom = 14 and alpha = 0.05). The test was performed using JMP 6 statistical software.

3.3.4. Sequestering of particulate POPs

A study was conducted to quantify the effectiveness of SPMDs at collecting particulate POPs. Two sealed containers housing SPMDs were attached to the outflow of an active sampler at Fairbanks. An electric pump maintained a flow rate of $\cong$ 30 mL/min through the sampler. A Teflon filter was installed between the active sampler and one of the SPMDs to remove particulate POPs prior to the SPMD, while another SPMD was simultaneously run without a filter prior to the SPMD. Comparisons in POP concentrations for the three classes (OCs, PCBs and PAHs) were made between the two SPMDs with a Wilicoxon Sign-Rank test (alpha = 0.05).

3.4. Analytical analysis of SPMD field samples

3.4.1. Dialysis and gel permeation clean-up

After retrieval from the field, the canisters containing SPMDs were stored at -40°C. All samples were shipped on ice to Environmental Sampling and Technologies Inc. for dialysis (US patent 5,098,573) and gel permeation clean-up. Prior to dialysis, samples were surface cleaned with 1 M hydrochloric acid for 30 seconds and spiked with 2,4,5 tetrachlorobenzene, anthracene d10 (Accustandard Inc., New Haven, CT) and octachloronapthalene (Ultra Scientific, North Kingstown, RI). Gel permeation clean-up (GPC) was performed with an autosampler (Alcott 718), high performance liquid chromatography (HPLC) pump (SSI model 300), ultraviolet (UV) HPLC detector (LDC model 1203) and fraction detector (Isco Foxy 200). A 300 mm x 21.20 mm phenogel column (pore size 10 μm) was used to separate interfering compounds from analytes. Method parameters were as follows: flow rate = 3.0 mL/min, mobile phase = 100% methylene chloride, wavelength = 250 nm and runtime = 30 min. The collected fractions

were reconstituted in hexane to approximately 2 mL, sealed in amber glass ampoules and shipped to UAF.

3.4.2. Fraction separation

Once all samples were received from Environmental Sampling and Technologies Inc., they were shipped to the Fresh Water Institute (FWI) Winnipeg, Canada, for further analysis. Chemical analysis, starting with the fraction separation, was performed at the same laboratory and with the same procedures as the air samples that were collected in Barrow, Alaska, with the active sampler. The analysis has been described previously in the literature (Fellin *et al.*, 1996; Halsall *et al.*, 1997a, 1998; Stern *et a*l., 1997). Samples were split into two aliquots: one for OCs screening including PCBs and one for PAHs screening.

The organochlorine aliquots were separated into three fractions based on increasing polarity. Separation was made with a glass column packed with Florisil ® (8 g; 1.2% v/w water deactivated) and anhydrous sodium sulfate (≅ 1 g) on top. Each column was rinsed with hexane prior to the application of the analyte. The first fraction was eluted with 35 mL of hexane and contained PCBs and most of the OCs. The second fraction was eluted with 35 mL of a hexane:dichloromethane mixture (85:15) and contained polar compounds like toxaphene and chlordane. The final fraction was eluted with 50 mL of a hexane:dichloromethane mixture (1:1) and contained the more polar compounds like dieldrin and heptachlor epoxide. The collected fractions were transferred to volumetric flasks and reconstituted with hexane. Nitrogen evaporation was used to bring the samples to 250 μL. Extracts were spiked with aldrin to adjust for any volume errors, vortexed and transferred to 2-mL gas chromatography (GC) vials containing 0.5 mL glass inserts.

The polyaromatic hydrocarbon aliquots were separated into two fractions to separate alkanes from PAH compounds. Separation was performed on a glass column packed with 11 g silica (100-200 mesh), 1 g aluminum oxide (5% deactivated), and approximately 1 g sodium sulfate. The alkane fraction was eluted first with 25 mL of

hexane and discarded. The PAH fraction was eluted with 25 mL 1:1 hexane to dichloromethane. Fractions were concentrated with a rotary evaporator, and toluene was used as a wash to transfer the remaining solvent to a 1 mL volumetric test tubes. Volumetric test tubes were spiked with internal standard containing six deuterated PAHs (naphthalene d8, acenaphthylene d10, phenanthrene d10, fluoranthene d10, pyrene d10, and benzo (g,h,i) perylene d12 [Supelco Chromatography Products, Oakville, Ontario]) and brought up to 1 mL with toluene. Samples were vortexed and transferred to 2-mL GC vials for instrumental analysis.

3.4.3. OCs and PCBs instrumental analysis

Organochlorine and PCB fractions were separated and quantified by capillary GC on a Varian 3600 (Varian Instrument, Palo Alto, CA) with a 60 m x 0.25 mm internal diameter (i.d.) DB-5 (J&W Scientific, Folsom, CA) column (film thickness = 0.25 μm) and ^{63}Ni electron capture detector (ECD). Splitless injection was used with the inlet temperature set at 220°C and detector temperature at 300°C. H_2 was used as the carrier gas (1 mL/min) and N_2 as the makeup gas (40 mL/min). The temperature program was as follows: initial temperature = 100°C with 2 min hold; increase to 150°C at 15°C/min ; increase from 150°C to 265°C at 3°C/min and hold at 265°C for 15.44 min. Individual compounds were quantified with external standard mixtures (Ultra Scientific, North Kingstown, RI).

3.4.4. PAHs instrumental analysis

Polyaromatic hydrocarbon fractions were separated and quantify by gas chromatography coupled to a mass spectrometry (GC/MS) using capillary gas chromatography on a Aligent GC (model HP6890) with a 30 m x 0.25 mm i.d. DB-5MS (J&W Scientific, Folsom, CA) column (film thickness = 0.25 μm) and quantified with a mass selective detector (model HP5970) in selective ion mode. Splitless injection was made with the inlet temperature set at 260°C and detector temperature at 300°C. Helium was used as the carrier gas (1 mL/min) and N_2 as the makeup gas (50 mL/min). The

temperature program was as follows: initial temperature = 90°C with 2 min hold; increase to 120°C at 10°C/min; increase to 250°C at 20°C/min; and increase from 250°C to 300°C at 3°C/min with no hold. Samples were quantified with PAH standards (Supelco Chromatography Products, Oakville, Ontario) prepared from stock solutions and the 6 internal standards spiked prior to instrumental analysis.

3.5. Quality control and assurance

Blank SPMDs in originally-sealed containers traveled to all field locations during deployment and retrieval. Field blanks were processed with the same procedures as field samples. Minimum detection limits (MDLs) were calculated as the mean amount in field blank. When a compound was below the blank levels, the MDL was set at the instrument detection limit (IDL). Overall accuracy at FWI was assessed by analyzing NIST certified reference materials and making comparisons with other laboratories.

3.6. Laboratory studies

3.6.1. Uptake study of POPs into SPMDs

The uptake kinetics of contaminants into SPMD were examined by conducting studies on contaminant concentrations over a three month period and at various temperatures. The studies should assist in determination of how temperature affects uptake rates into the SPMDs.

A Vici Dynacalibrator Model ® 230 generated low concentration of contaminants for the uptake study. Three OCs in neat form (lindane, DDT and DDE [Sigma-Aldrich, Milwaukee, WI]) were placed separately into high rate permeation tubes (HRTs) (Kin-Tek, La Marque, TX). The permeation tubes were placed inside an oven set at 121°C. Compressed air was used as the carrier gas. Two trap filters (hydrocarbon trap [Restek, Bellefonte, PA] and all pure trap [Alltech, Deerfield, IL]) were placed after the compressed air tank but prior to the Dynacalibrator to remove contaminants from the compressed air. A canister housing one SPMD was placed after the filters and prior to the

oven where the OCs were being released in gas phase for the initial study as a background level check for the OCs of interest in the compressed air tank.

The initial study consisted of five SPMDs housed in individually-sealed units placed in sequence and kept at room temperature. The housing units are the same quart-sized canisters used in the deployment units that housed the SPMDs in the field, but sealed with the lid. A 5 mm diameter hole was inserted on top and bottom of the canister for insertion of a Swagelok ® tube fitting to allow air flow through the canister. The last two housing units containing SPMDs in the sequence were removed after one month. After two, three and four months a housing unit was removed from the tail end of the sequence. The second study was a replicate of the first except the housing units were kept at approximately -20°C and one housing unit was used instead of two for the first month. The final study consisted of three housing units in sequence, but each kept at a different temperature (≅ 7, 2 and -8°C). All housing units were removed after approximately 1.5 months. During the entire study, flow rates and temperatures were measured and recorded daily.

3.6.2. Analytical analysis of SPMDs in the laboratory

Samples were sent to Environmental Sampling and Technologies Inc. for dialysis and gel permeation clean-up, using the same methods used for the field samples, and shipped back to UAF in sealed amber ampoules. The three OCs were separated and quantify by GC/MS using a capillary gas chromatography (Finnigan GCQ Plus) with a 30 m x 0.25 mm i.d. Restek-5MS column (film thickness = 0.25 μm) and a mass selective detector (Finnigan GCQ Plus) in selective ion mode. Injection was made by splitless injection with the inlet temperature set at 225°C and detector temperature at 300°C. Helium was used as the carrier gas and a constant velocity was set 40 cm/sec. The temperature program was as follows: initial temperature = 100°C with 2 min hold; increase to 160°C at 15°C/min with a 4 min hold at 160°C and increase to 270°C at 5°C/min with no hold. Quantification was obtained from a calibration curve made using the same three OCs.

3.7. Multivariate analyses

3.7.1. Principal component analysis

In order to visualize the spatial differences in POP concentrations obtained in SPMDs between the five locations and different sampling periods, a principal component analysis (PCA) model with 2 principal components was created. PCA calculations were performed on the data set, which consisted of 66 columns (variables = POPs) and 16 rows (samples = location and sampling time) with the units ng/SPMD.

Preprocessing of the data prior to analysis is important in performing PCA. It ensures the data is appropriate for PCA. Transformation can remove background effects, normally distribute the data set or standardized the data that is measured in different units. All POP concentrations in the X-matrix were transformed by multiplying with the term 1 divided by standard deviation. By scaling each column in X- matrix (POP concentration) with the inverse of the standard deviation of the corresponding variable, it ensures that each scaled variable is assigned the same variance (Esbensen, 2002). Outliers were also evaluated before interpretation of the data. The evaluation was based on the relative magnitude of an outlier's residual to the model. No outliers were detected in the models.

The PCA was performed using the Unscrambler® version 8.0.5. The Barrow September to March sample was kept out of the analysis because of its longer deployment time. In addition, variables (POPs) with more than 50% of the values below the minimum detection limits were kept out of the analysis. A value that was below minimum detection limit and used in the model was assigned the number zero to maintain the integrity of the model. The values used in the model are listed in Appendix A, Table 1. To ensure the data were not being over-fitted, an evaluation of the total explained variance was constructed as a function of increasing PCs (Figure 3.4). When the data are being over-fitted, a decrease in the X variance explained is seen after a maximum percentage is reached. This was not the case in any of the models. The settings for the PCA can be viewed in Appendix C1.

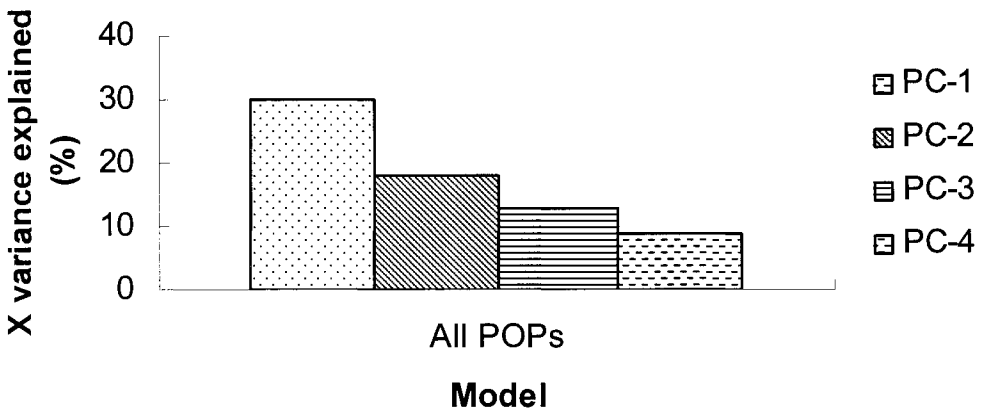


Figure 3.4. Each additional PC adds less explained variance to the total and the majority of the explained variance is described in PC-1 and PC-2.

Chapter IV

Results

Chapter 4 of the thesis only presents the results. The POP concentrations measured within the SPMDs for the different studies are the majority of the results. Other results include principal component analyses and statistical tests. There are no interpretations of the POP concentrations or comparisons to other studies discussed in chapter four. They will be presented in the chapter 5.

4.1. Quality assurance

Several steps were taken to ensure the quality of the data as mentioned in the materials and methods section (chapter 3). Recovery standards ranged from 68-129% for field and blank samples (Table 4.1). No adjustments were made to sample concentrations based on recovery standards. Two separate minimum detection limits (MDLs) were developed from blank SPMDs, one for Barrow and one for the other sites (Tables 4.2 and 4.3) because the Barrow location is more remote and isolated from POPs point sources. Compounds that were not detected in blank samples were set at the instrument detection limits (IDLs) (Table 4.4). Trifluralin, a chlorinated herbicide compound was detected in field blanks at an average concentration of 23 ng/SPMD and was kept out of any further analysis. Field samples with levels below MDL were flagged and reported as below detection limit (BDL).

Table 4.1. Recovery (%) of compounds spiked onto SPMD prior to dialysis.

Sample	Recovery (%)	
	Octachloronaphthalene	Anthracene d10
Blank	86	98
Barrow Blank	118	83
Barrow 8-13 to 2-28	109	97
Barrow 2-28 to 6-15	74	68
Barrow 6-15 to 9-15	80	88
PFRR[1] 9-6 to 12-4	106	122
PFRR[1] 12-4 to 3-5	115	103
PFRR[1] 3-5 to 6-2	103	124
PFRR[1] 6-2 to 9-2	108	113
DNP[2] 9-3 to 11-29	121	87
DNP[2] 11-29 to 3-1	129	102
DNP[2] 3-1 to 5-30	113	85
DNP[2] 5-30 to 8-29	127	92
TC[3] 11-29 to 3-1	96	85
TC[3] 3-1 to 5-30	102	100
TC[3] 5-30 to 8-29	94	89
Homer 9-1 to 11-30	112	98
Homer 11-30 to 3-2	115	98
Homer 6-1 to 8-31	104	101

[1]PFRR= Poker Flat Research Range, [2]DNP= Denali National Park and Preserve and [3]TC= Trapper Creek.

Table 4.2. MDLs developed from blank SPMDs for speciated POPs at Barrow, Alaska (ND= Not Detected).

Compound	MDL (ng/SPMD)	Compound	MDL (ng/SPMD)
1,2,4,5 Tetrachlorobenzene	ND	PCB3	ND
1,2,3,4 Tetrachlorobenzene	ND	PCB4/10[6]	ND
Pentachlorobenzene	0.14	PCB7	ND
Hexachlorobenzene	0.20	PCB6	0.50
Alpha-Hexachlorocyclohexane	ND	PCB8/5	ND
Beta-Hexachlorocyclohexane	ND	PCB19	ND
Gamma-Hexachlorocyclohexane	1.16	PCB18	ND
Delta-Hexachlorocyclohexane	ND	PCB17	ND
C[1]	0.25	PCB24/27[6]	ND
Heptachlor	0.35	PCB16/32[6]	ND
Octachlorostyrene	ND	PCB26	ND
C1A[1]	ND	PCB25	0.40
C1B/U6[1]	0.08	PCB31	ND
C2/U5[2]	0.07	PCB28	ND
C3[2]	0.07	PCB33	ND
C5[3]	0.21	PCB22	ND
U3[4]	ND	PCB45	ND
U1[5]	ND	PCB46	ND
Oxychlordane	ND	PCB52	0.25
Trans-Chlordane	0.51	PCB49	0.17
Cis-Chlordane	0.34	PCB47	ND
Trans-Nonachlor	0.16	PCB48	ND
Cis-Nonachlor	ND	PCB44	0.18
Heptachlor Epoxide	ND	PCB42	ND
Dieldrin	ND	PCB41/71[6]	ND
2,4'-Dichlorodiphenyldichloroethylene (op-DDE)	0.46	PCB64	ND
4,4'-Dichlorodiphenyldichloroethylene (pp-DDE)	0.53	PCB40	ND
2,4'-Dichlorodiphenyldichloroethane (op-DDD)	ND	PCB74	ND
4,4'-Dichlorodiphenyldichloroethane (pp-DDD)	0.14	PCB70/76[6]	ND
2,4'-Dichlorodiphenyltrichloroethane (op-DDT)	0.19	PCB66	0.22
4,4'-Dichlorodiphenyltrichloroethane (pp-DDT)	0.78	PCB95	ND
Mirex	ND	PCB56/60	ND
Photo Mirex	0.92	PCB91	ND
Pentachloroanisole	0.31	PCB84/89[6]	1.16
Apha-Endosulfan	ND	PCB101	0.20
Methoxychlor	ND	PCB 99	ND
Endrin	ND	PCB83	1.23
Trifluralin	23.09	PCB97	0.44
3Chloro-Veratrol	ND	PCB87	ND
4Chloro-Veratrol	ND	PCB85	ND
Endrin ketone	ND	PCB136	ND
Toxaphene 2	0.10	PCB110	ND
Toxaphene 3	0.10	PCB82	ND
Sum Toxaphene (2+3 and others)	3.56	PCB151	ND
PCB1	ND	PCB135/144[6]	ND

Table 4.2. (continued)

Compound	MDL (ng/SPMD)	Compound	MDL (ng/SPMD)
PCB149	0.13	PCB200	ND
PCB118	ND	PCB170	ND
PCB134	ND	PCB190	ND
PCB114	ND	PCB198	ND
PCB131	ND	PCB199	ND
PCB146	ND	PCB196/203[6]	ND
PCB153	0.22	PCB189	ND
PCB132	ND	PCB208	ND
PCB105	ND	PCB195	ND
PCB141	ND	PCB207	ND
PCB179	ND	PCB194	ND
PCB137	ND	PCB205	ND
PCB130/176[6]	ND	PCB206	ND
PCB138	0.14	PCB209	ND
PCB158	ND	Naphthalene	3.56
PCB129/178[6]	ND	2-Methylnaphthalene	2.56
PCB175	ND	1-Methylnaphthalene	2.46
PCB187	ND	Biphenyl	2.80
PCB183	ND	Acenaphthylene	0.40
PCB128	ND	Acenaphthene	0.72
PCB185	ND	Fluorene	1.42
PCB174	ND	Phenanthrene	1.56
PCB177	ND	Anthracene	ND
PCB171	ND	4,5-Methylenephenanthrene	ND
PCB156	ND	9,10-Dimethylanthracene	ND
PCB157/201[6]	ND	Fluoranthene	2.02
PCB172/197[6]	ND	Pyrene	1.50
PCB180	ND	Retene	0.24
PCB193	ND	Benzo(a)anthracene	0.78
PCB191	ND	Chrysene	ND

[1]C, C1A, C1B/U6= minor component of technical chlordane; [2]C2/U5, C3= heptachloro compound of technical chlordane; [3]C5= component of technical chlordane; [4]U3= intermediate metabolite of chlordane; [5]U1= photoheptachlor; [6]PCBs with two numbers and a '/' could not be separated on the chromatogram.

Table 4.3. MDLs developed from blank SPMDs for speciated POPs at all locations except Barrow, Alaska (ND= Not Detected).

Compound	MDL (ng/SPMD)	Compound	MDL (ng/SPMD)
1,2,4,5 Tetrachlorobenzene	0.56	PCB3	ND
1,2,3,4 Tetrachlorobenzene	0.23	PCB4/10[6]	0.10
Pentachlorobenzene	0.40	PCB7	0.11
Hexachlorobenzene	0.10	PCB6	0.37
Alpha-Hexachlorocyclohexane	0.20	PCB8/5	0.40
Beta-Hexachlorocyclohexane	ND	PCB19	ND
Gamma-Hexachlorocyclohexane	2.03	PCB18	0.28
Delta-Hexachlorocyclohexane	ND	PCB17	0.23
C[1]	0.21	PCB24/27[6]	ND
Heptachlor	0.41	PCB16/32[6]	0.19
Octachlorostyrene	ND	PCB26	0.24
C1A[1]	0.10	PCB25	0.28
C1B/U6[1]	0.27	PCB31	ND
C2/U5[2]	0.23	PCB28	ND
C3[2]	0.13	PCB33	0.52
C5[3]	0.23	PCB22	0.09
U3[4]	0.02	PCB45	0.28
U1[5]	0.16	PCB46	0.07
Oxychlordane	ND	PCB52	0.10
Trans-Chlordane	0.17	PCB49	0.45
Cis-Chlordane	0.23	PCB47	0.50
Trans-Nonachlor	0.21	PCB48	ND
Cis-Nonachlor	ND	PCB44	0.64
Heptachlor Epoxide	ND	PCB42	0.13
Dieldrin	0.03	PCB41/71[6]	ND
2,4'-Dichlorodiphenyldichloroethylene (op-DDE)	0.60	PCB64	0.36
4,4'-Dichlorodiphenyldichloroethylene (pp-DDE)	0.51	PCB40	0.44
2,4'-Dichlorodiphenyldichloroethane (op-DDD)	ND	PCB74	ND
4,4'-Dichlorodiphenyldichloroethane (pp-DDD)	0.20	PCB70/76[6]	0.19
2,4'-Dichlorodiphenyltrichloroethane (op-DDT)	0.14	PCB66	0.24
4,4'-Dichlorodiphenyltrichloroethane (pp-DDT)	1.33	PCB95	ND
Mirex	ND	PCB56/60[6]	0.05
Photo Mirex	0.03	PCB91	0.15
Pentachloroanisole	0.32	PCB84/89[6]	0.20
Apha-Endosulfan	ND	PCB101	0.05
Methoxychlor	ND	PCB 99	0.14
Endrin	0.03	PCB83	ND
Trifluralin	22.60	PCB97	0.11
3-Chloro-Veratrol	ND	PCB87	0.14
4-Chloro-Veratrol	ND	PCB85	1.75
Endrin ketone	ND	PCB136	0.17
Toxaphene 2	0.45	PCB110	0.42
Toxaphene 3	0.62	PCB82	ND
Sum Toxaphene (2+3 and others)	4.56	PCB151	0.09
PCB1	ND	PCB135/144[6]	0.05

Table 4.3. (continued)

Compound	MDL (ng/SPMD)	Compound	MDL (ng/SPMD)
PCB149	ND	PCB200	ND
PCB118	ND	PCB170	ND
PCB134	ND	PCB190	ND
PCB114	ND	PCB198	ND
PCB131	ND	PCB199	ND
PCB146	0.10	PCB196/203[6]	ND
PCB153	0.20	PCB189	ND
PCB132	0.08	PCB208	ND
PCB105	ND	PCB195	ND
PCB141	0.04	PCB207	ND
PCB179	0.08	PCB194	ND
PCB137	ND	PCB205	ND
PCB130/176[6]	ND	PCB206	ND
PCB138	0.23	PCB209	ND
PCB158	ND	Naphthalene	4.02
PCB129/178[6]	ND	2-Methylnaphthalene	3.54
PCB175	ND	1-Methylnaphthalene	2.64
PCB187	0.06	Biphenyl	3.50
PCB183	0.04	Acenaphthylene	ND
PCB128	ND	Acenaphthene	1.62
PCB185	ND	Fluorene	3.54
PCB174	0.05	C1 Fluorenes	ND
PCB177	ND	Phenanthrene	2.62
PCB171	ND	Anthracene	0.30
PCB156	ND	4,5-Methylenephenanthrene	0.36
PCB157/201[6]	ND	9,10-Dimethylanthracene	ND
PCB172/197[6]	ND	Fluoranthracene	2.30
PCB180	0.07	Pyrene	2.20
PCB193	ND	Retene	ND
PCB191	ND	Benzo(a)anthracene	ND
		Chrysene	ND

[1]C, C1A, C1B/U6= minor component of technical chlordane; [2]C2/U5, C3= heptachloro compound of technical chlordane; [3]C5= component of technical chlordane; [4]U3= intermediate metabolite of chlordane; [5]U1= photoheptachlor; [6]PCBs with two numbers and a '/' could not be separated on the chromatogram.

Table 4.4. IDLs developed for POPs measured by FWI.

Compound	IDL (pg)	Compound	IDL (pg)
1,2,4,5 Tetrachlorobenzene	0.335	PCB3	0.354
1,2,3,4 Tetrachlorobenzene	0.142	PCB4/10[6]	0.305
Pentachlorobenzene	0.040	PCB7	0.135
Hexachlorobenzene	0.027	PCB6	0.290
Alpha-Hexachlorocyclohexane	0.029	PCB5/8[6]	0.234
Beta-Hexachlorocyclohexane	0.097	PCB19	0.336
Gamma-Hexachlorocyclohexane	0.029	PCB18	0.318
Delta-Hexachlorocyclohexane	0.033	PCB17	0.318
C[1]	0.033	PCB24/27[6]	0.187
Heptachlor	0.033	PCB16/32[6]	0.191
Octachlorostyrene	0.022	PCB26	0.170
C1A[1]	0.037	PCB25	0.116
C1B/U6[1]	0.037	PCB31	0.178
C2/U5[2]	0.037	PCB28	0.119
C3[2]	0.037	PCB33	0.151
C5[3]	0.037	PCB22	0.099
U3[4]	0.037	PCB45	0.168
U1[5]	0.037	PCB46	0.203
Oxychlordane	0.035	PCB52	0.223
Trans-Chlordane	0.037	PCB49	0.173
Cis-Chlordane	0.037	PCB47	0.145
Trans-Nonachlor	0.035	PCB48	0.198
Cis-Nonachlor	0.032	PCB44	0.141
Heptachlor Epoxide	0.035	PCB42	0.120
Dieldrin	0.034	PCB41/71[6]	0.120
2,4'-Dichlorodiphenyldichloroethylene (op-DDE)	0.051	PCB64	0.095
4,4'-Dichlorodiphenyldichloroethylene (pp-DDE)	0.039	PCB40	0.116
2,4'-Dichlorodiphenyldichloroethane (op-DDD)	0.063	PCB74	0.123
4,4'-Dichlorodiphenyldichloroethane (pp-DDD)	0.058	PCB70/76[6]	0.137
2,4'-Dichlorodiphenyltrichloroethane (op-DDT)	0.054	PCB66	0.179
4,4'-Dichlorodiphenyltrichloroethane (pp-DDT)	0.059	PCB95	0.102
Mirex	0.067	PCB56/60[6]	0.125
Photo Mirex	0.054	PCB91	0.062
Pentachloroanisole	0.026	PCB84/89[6]	0.121
Apha-Endosulfan	0.037	PCB101	0.144
Methoxychlor	0.147	PCB 99	0.120
Endrin	0.520	PCB83	0.120
Trifluralin	0.340	PCB97	0.118
3-Chloro-Veratrol	0.062	PCB87	0.093
4-Chloro-Veratrol	0.019	PCB85	0.093
endrin ketone	0.047	PCB136	0.187
Toxaphene 2	5.000	PCB110	0.110
Toxaphene 3	5.000	PCB82	0.084
PCB1	1.541	PCB151	0.106

Table 4.4. (continued)

Compound	IDL (pg)	Compound	IDL (pg)
PCB135/144[6]	0.083	PCB200	0.050
PCB149	0.132	PCB170	0.054
PCB118	0.084	PCB190	0.052
PCB134	0.109	PCB198	0.053
PCB114	0.069	PCB199	0.050
PCB131	0.087	PCB196/203[6]	0.053
PCB146	0.085	PCB189	0.051
PCB153	0.085	PCB208	0.057
PCB132	0.116	PCB195	0.063
PCB105	0.066	PCB207	0.058
PCB141	0.064	PCB194	0.053
PCB179	0.064	PCB205	0.064
PCB137	0.059	PCB206	0.058
PCB130/176[6]	0.075	PCB209	0.065
PCB138	0.087	Naphthalene	0.72
PCB158	0.050	2-Methylnaphthalene	0.72
PCB178/129[6]	0.070	1-Methylnaphthalene	0.72
PCB175	0.070	Biphenyl	0.79
PCB187	0.064	Acenaphthylene	0.79
PCB183	0.065	Acenaphthene	0.79
PCB128	0.072	Fluorene	0.67
PCB185	0.043	C1 Fluorenes	0.67
PCB174	0.074	Phenanthrene	0.67
PCB177	0.074	Anthracene	0.67
PCB171	0.065	4,5-Methylenephenanthrene	0.67
PCB156	0.051	9,10-Dimethylanthracene	0.67
PCB157/201[6]	0.067	Fluoranthene	0.79
PCB172/197[6]	0.038	Pyrene	0.79
PCB180	0.048	Retene	0.79
PCB193	0.051	Benzo(a)anthracene	1.14
PCB191	0.049	Chrysene	1.14

[1]C, C1A, C1B/U6= minor component of technical chlordane; [2]C2/U5, C3= heptachloro compound of technical chlordane; [3]C5= component of technical chlordane; [4]U3= intermediate metabolite of chlordane; [5]U1= photoheptachlor; [6]PCBs with two numbers and a '/' could not be separated on the chromatogram.

4.2 Evaluation of SPMDs

4.2.1 Reproducibility

Four SPMDs deployed at Poker Flat Research Range from May 29, 2003, to August 16, 2003, were screened for an assortment of POPs to examine reproducibility. The recovery standards ranged from 101 to 118%. No adjustments to concentrations were made due to the recovery standards. The reproducibility of SPMDs was determined using relative standard deviation (RSD). Calculations of RSDs ranged from 2 to 22% with median at 11% for PAHs (Table 4.5), 4 to 76% for PCBs with median at 27% (Table 4.6), and 3 to 94% for OCs with median at 27% (Table 4.7). Less variation was seen within the PAH group. This could be due to the analytical procedure used for screening PAHs as opposed to the chlorinated compounds. The PAHs were analyzed with GC/MS, which is based on retention time and mass to charge ratio of selective ions, so there is more certainty in identifying the compound. PCBs and OCs had larger variations with hepatchlor epoxide having the largest RSD at 94%.

Table 4.5. Mean levels and RSD (n= 4) for PAHs detected in SPMDs deployed at Poker Flat Research Range for approximately three months.

PAH	Average (ng/SPMD)	RSD%
Naphthalene	11.8	22
2-Methylnaphthalene	11.7	17
1-Methylnaphthalene	10.2	16
Biphenyl	3.6	6
Acenaphthylene	0.9	6
Acenaphthene	4.8	12
Fluorene	13.3	7
Phenanthrene	105	11
Anthracene	2.6	10
Benzo(a)anthracene	1.3	6
4,5-Methylenephenanthrene	5.7	15
Fluoranthene	21.1	12
Pyrene	9.2	5
9,10-Dimethylanthracene	8.4	2
Retene	2.4	17

Table 4.6. Mean levels and RSD (n= 4) for PCBs detected in SPMDs deployed at Poker Flat Research Range for approximately three months.

PCB	Average (ng/SPMD)	RSD (%)
PCB4/10[1]	BDL[2]	15
PCB7	0.4	30
PCB5/8[1]	0.8	7
PCB18	0.6	15
PCB17	0.4	7
PCB16/32[1]	0.2	27
PCB26	0.4	12
PCB25	3.3	4
PCB33	0.5	60
PCB45	0.8	10
PCB52	0.8	17
PCB49	0.6	9
PCB47	0.8	14
PCB44	0.4	11
PCB64	0.3	47
PCB70/76[1]	0.6	35
PCB95	0.3	77
PCB84	0.3	43
PCB101	0.4	36
PCB99	0.2	46
PCB87	BDL[2]	30
PCB85	17.6	47
PCB110	0.4	34
PCB151	0.1	24
PCB149	0.3	24
PCB118	0.4	27
PCB153	0.3	53
PCB138	0.3	54

[1]PCBs with two numbers and a '/' could not be separated on the chromatogram. [2]BDL= Below Detection Limit and the reported RSD% for the compounds is obtained from actual values not reported.

Table 4.7. Mean levels and RSD (n= 4) for OCs detected in SPMDs deployed at Poker Flat Research Range for approximately three months.

Organochlorine Compound	Average (ng/SPMD)	RSD (%)
1,2,4,5 Tetrachlorobenzene	3.5	23
1,2,3,4 Tetrachlorobenzene	BDL[1]	9
Pentachlorobenzene	0.8	18
Hexachlorobenzene	5.3	19
Alpha-Hexachlorocyclohexane	1.6	16
Gamma-Hexachlorocyclohexane	3.9	15
C[2]	2.5	3
Heptachlor	0.6	17
Octachlorostyrene	0.1	41
C1A[2]	0.8	19
C1B/U6[2]	BDL[1]	57
C2/U5[3]	BDL[1]	31
C3[3]	0.2	29
C5[4]	0.6	27
U3[5]	0.2	38
U1[6]	0.4	20
Oxychlordane	0.2	3
Trans-Chlordane	3.6	23
Cis-Chlordane	3.0	22
Trans-Nonachlor	1.1	21
Cis-Nonachlor	0.2	19
Heptachlor Epoxide	0.2	94
Dieldrin	1.2	48
2,4'-Dichlorodiphenyldichloroethylene (op-DDE)	0.9	27
4,4'-Dichlorodiphenyldichloroethylene (pp-DDE)	12.9	30
2,4'-Dichlorodiphenyldichloroethane (op-DDD)	BDL[1]	29
4,4'-Dichlorodiphenyldichloroethane (pp-DDD)	1.2	45
2,4'-Dichlorodiphenyltrichloroethane (op-DDT)	1.0	43
4,4'-Dichlorodiphenyltrichloroethane (pp-DDT)	12.4	38
Photo Mirex	3.0	37
Pentachloroanisole	3.2	12
Apha-Endosulfan	0.8	78
Endrin	0.5	72
Trifluralin	135.2	80
3-Chloro-Veratrol	1.0	59
Toxaphene 3	2.5	32
Sum Toxaphene (3 and others)	227.7	19

[1]BDL= Below Detection Limit and the reported RSD% for the compounds is obtained from actual values not reported; [2]C, C1A, C1B/U6= minor component of technical chlordane; [3]C2/U5, C3= heptachloro compound of technical chlordane; [4]C5= component of technical chlordane; [5]U3= intermediate metabolite of chlordane and [6]U1= photoheptachlor.

4.2.2. Comparison of exposed and non-exposed SPMD to sunlight

Polyaromatic hydrocarbon levels in SPMDs exposed to sunlight were examined at the Poker Flat Research Range. One of the deployment units was covered with a glass lid as described in section 3.3.3. The light transmitted through the glass cover was observed to begin at approximately 305 nm and increased with increasing wavelength (Figure 4.1).

The recoveries standard (anthracene d10) spiked prior to dialysis of SPMDs were 97% (SPMD-sun) and 85% (SPMD-no sun) no adjustments were made to concentrations. Individual PAH concentrations were typically higher in the non-exposed SPMD than the exposed SPMD and total PAH concentrations in the non-exposed SPMD were approximately a factor of two greater than in the exposed SPMD. The calculated percent difference [%different = ((sun-no sun)/ average)*100] had a median value of -69% between the concentrations in the SPMD for sun and decreased sun exposure (Table 4.8).

A Wilcoxon Sign-Rank test was performed on the data because of non-normality in the PAH concentrations measured in the SPMDs to examine if there were differences between PAH concentrations measured between the two SPMDs. The Wilcoxon Sign-Rank test is a nonparametric alternative to the paired t-test. The results from a two tail Wilcoxon Sign-Rank test showed the no-sun PAH concentrations measured in the SPMD were significantly different (P =0.007) than PAH concentrations measured in the sun-exposed SPMD. The alpha level was set at 0.05, meaning the null hypothesis (there is no difference in PAHs concentrations between exposed and non-exposed SPMD) was rejected.

No chromatogram was collected for the second fraction (no sun) during the initial sequence run on the GC/ECD, because of an error with the computer program. The sample was rerun several weeks later at FWI; however, the recovery standards and the volume correction standard were poor and no comparison was made for the PCBs or OCs, which are eluted in the second fraction. It was believed a majority of the solvent had evaporated from the initial puncture hole in the septum on the GC vial.

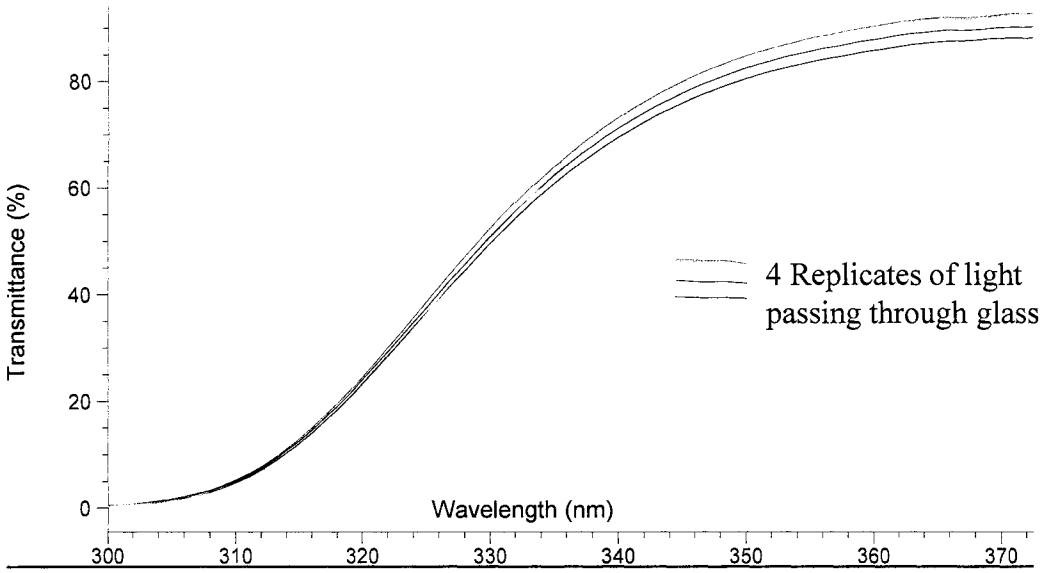


Figure 4.1. Graph showing the percentage of light transmittance vs. wavelength through the piece of glass used to expose the SPMD to sunlight (n= 4).

Table 4.8. A comparison between glass covered SPMD and steel covered SPMD in the PAH levels from SPMDs deployed at Poker Flat Research Range (ND= Not Detected).

PAH	Sun (ng/SPMD)	No Sun (ng/SPMD)	Percent Difference (%)
Naphthalene	7.2	9.6	-28.2
2-Methylnaphthalene	9.3	8.8	5.1
1-Methylnaphthalene	7.9	7.8	0.5
Biphenyl	2.8	3.0	-6.2
Acenaphthylene	0.4	0.7	-69.1
Acenaphthene	2.6	8.0	-102.1
Fluorene	5.0	14.6	-98.1
Phenanthrene	24.1	72.8	-100.4
Anthracene	1.9	1.2	43.1
Benzo(a)anthracene	1.2	1.1	14.0
4,5-Methylenephenanthrene	0.9	3.3	-112.4
Fluoranthene	6.5	14.7	-77.9
Pyrene	4.6	6.0	-25.6
9,10-Dimethylanthracene	ND	7.9	-200.0
Retene	ND	1.4	-200.0
Sum	76.7	163.3	

4.2.3. Comparison of filtered and non-filtered SPMD

Differences in POP concentrations between filtered and non-filtered air-exposed SPMDs are presented in Tables 4.9- 4.12. The recovery standards were good in both cases for octachloronaphthalene and anthracene d10 (98 and 108% in the filtered air case and 97 and 128% in the non-filtered air case). PAH levels were frequently higher in the filtered air SPMDs. 2-Methylnaphthalene showed the largest percent difference [%difference = ((filtered- no filtered)/ average)*100] at 88% more in the SPMD exposed to filtered air than the SPMD exposed to non-filtered air. A two-tail Wilcoxon Sign-Rank test performed on the PAH levels from the non-filtered and filtered air SPMDs resulted in a P value of 0.064. However, PCB levels were frequently higher in the SPMD exposed to non-filtered when compared to the SPMD exposed to filtered air. The differences between the PCB levels in the SPMDs were typically higher as the degree of chlorination increased. A Wilcoxon Sign-Rank test performed on filtered and non-filtered PCB levels obtained from the SPMD showed a P value of <0.001. The OC levels in filtered and non-filtered air SPMDs were typically the same except for a few cases. The Wilcoxon Sign-Rank test performed on the OC levels had a P value of 0.667 for a two-tailed test. Overall, higher levels of POPs were seen in these samples than the other samples collected in this study. Higher concentrations were expected due to longer exposure time and vacuum pump induced airflow around the SPMDs.

Table 4.9. Organochlorine compound levels detected in SPMDs exposed to filtered and non-filtered air.

OC	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
1,2,4,5 Tetrachlorobenzene	3.4	1.2	94
1,2,3,4 Tetrachlorobenzene	0.9	0.7	20
Pentachlorobenzene	0.9	0.5	67
Hexachlorobenzene	3.5	3.3	7
Alpha-Hexachlorocyclohexane	1.5	1.8	-21
Beta-Hexachlorocyclohexane	0.0	0.1	-200
Gamma-Hexachlorocyclohexane	95.4	114.7	-18
Delta-Hexachlorocyclohexane	0.2	0.2	-19
C[1]	5.1	3.5	39
Heptachlor	2.3	1.4	46
Octachlorostyrene	0.2	0.3	-22
C1A[1]	2.2	1.3	49
C1B/U6[1]	3.5	3.9	-11
C2/U5[2]	0.8	0.9	-13
C3[2]	3.6	6.1	-50
C5[3]	7.0	5.2	28
U3[4]	1.0	1.4	-33
U1[5]	6.4	4.8	30
Oxychlordane	4.4	4.3	3
Trans-Chlordane	11.4	3.0	117
Cis-Chlordane	12.1	6.3	63
Trans-Nonachlor	3.9	1.4	94
Cis-Nonachlor	2.6	2.0	24
Heptachlor Epoxide	0.4	0.2	55
Dieldrin	2.6	3.5	-29
2,4'-Dichlorodiphenyldichloroethylene	9.7	7.1	31
4,4'-Dichlorodiphenyldichloroethylene	195.0	161.3	19
2,4'-Dichlorodiphenyldichloroethane	8.8	11.5	-27
4,4'-Dichlorodiphenyldichloroethane	3.0	3.9	-27
2,4'-Dichlorodiphenyltrichloroethane	8.1	6.3	25
4,4'-Dichlorodiphenyltrichloroethane	45.4	59.2	-27
Mirex	0.1	0.3	-108

Table 4.9. (Continued)

	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
Photo Mirex	2.1	2.7	-24
Pentachloroanisole	3.4	1.6	72
Apha-Endosulfan	1.0	1.0	0
Methoxychlor	0.5	2.3	-130
Endrin	5.3	6.9	-26
3-Chloro-Veratrol	0.4	0.4	10
4-Chloro-Veratrol	0.6	0.8	-16
Endrin	5.3	6.9	-26
Toxaphene 2	7.3	9.2	-24
Toxaphene 3	32.3	69.0	-72
Sum Toxaphene (2+3 and others)	136.4	91.3	40
Sum	690.53	662.35	

[1]C, C1A, C1B/U6= minor component of technical chlordane; [2] C2/U5, C3= heptachloro compound of technical chlordane; [3]C5= component of technical chlordane; [4]U3= Intermediate metabolite of chlordane and [5]U1= Photoheptachlor.

Table 4.10. PCB levels detected in SPMDs exposed to filtered and non-filtered air.

PCB	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
PCB4/10[1]	1.8	1.7	10
PCB7	1.3	1.2	7
PCB6	1.7	1.9	-11
PCB8/5[1]	6.4	7.4	-16
PCB19	1.7	1.5	16
PCB18	9.3	10.5	-12
PCB17	7.5	8.4	-12
PCB24/27[1]	0.7	0.8	-19
PCB16/32[1]	4.6	4.9	-5
PCB26	7.4	7.2	3
PCB25	8.2	6.1	29
PCB33	17.4	19.0	-9
PCB22	4.2	4.3	-4
PCB45	2.0	1.8	6

Table 4.10. (Continued)

OC	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
PCB46	2.0	2.1	-8
PCB52	20.8	21.8	-5
PCB49	17.8	18.4	-3
PCB47	27.2	27.4	-1
PCB44	10.6	11.5	-8
PCB42	6.1	6.1	1
PCB41/71[1]	1.7	4.6	-90
PCB64	4.6	3.6	25
PCB40	4.1	2.5	46
PCB70/76[1]	19.3	18.1	6
PCB66	13.3	13.1	2
PCB95	3.2	4.7	-37
PCB56/60[1]	2.2	2.9	-30
PCB91	2.5	3.6	-35
PCB84/89[1]	4.2	5.0	-18
PCB101	8.2	13.6	-49
PCB 99	3.6	6.6	-60
PCB83	16.2	22.7	-33
PCB97	2.1	3.7	-55
PCB87	3.3	6.0	-58
PCB110	6.1	10.3	-51
PCB82	0.2	0.3	-58
PCB151	1.0	1.9	-60
PCB135/144[1]	1.1	2.2	-62
PCB149	3.9	8.8	-77
PCB118	4.4	13.0	-99
PCB134	0.2	0.4	-86
PCB114	1.4	2.1	-39
PCB131	0.1	0.1	-67
PCB146	1.0	2.3	-79
PCB153	3.0	10.0	-107
PCB132	0.9	2.5	-89
PCB105	1.0	4.6	-126
PCB141	0.7	2.4	-114
PCB179	0.6	1.0	-43
PCB137	0.2	0.8	-122
PCB130/176[1]	0.4	0.9	-74
PCB138	3.2	12.1	-116
PCB158	0.4	1.5	-117
PCB129/178[1]	0.2	0.7	-108
PCB175	ND	0.2	-200

Table 4.10. (Continued)

PCB	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
PCB187	0.8	2.8	-115
PCB183	0.4	1.6	-126
PCB128	0.1	0.8	-145
PCB185	0.1	0.3	-102
PCB174	0.4	1.8	-132
PCB177	0.3	1.4	-136
PCB171	0.1	1.2	-172
PCB157/201[1]	ND	0.4	-200
PCB172/197[1]	ND	0.3	-200
PCB180	0.4	3.3	-154
PCB193	2.1	16.0	-153
PCB200	ND	0.5	-200
PCB170	0.2	1.8	-160
PCB198	ND	0.1	-200
PCB199	0.1	0.8	-157
PCB196/203[1]	0.1	1.2	-160
PCB195	ND	0.3	-200
PCB207	ND	0.1	-200
PCB194	ND	0.8	-200
PCB206	ND	0.1	-200
Sum	282.16	388.00	

[1]PCB with two numbers and a '/' could not be separated on the chromatogram.

Table 4.11. PAH levels detected in SPMDs exposed to filtered and non-filtered air.

PAH	Filter (ng/SPMD)	No Filter (ng/SPMD)	Percent Difference (%)
Naphthalene	53.8	23.9	77
2-Methylnaphthalene	61.8	23.9	88
1-Methylnaphthalene	44.8	19.9	77
Biphenyl	5.3	3.8	32
Acenaphthylene	1.9	1.5	23
Acenaphthene	3.5	2.0	55
Fluorene	11.2	14.2	-24
Phenanthrene	202.1	172.4	16
Anthracene	5.2	5.7	-11
Benzo(a)anthracene	13.6	13.9	-2
4,5-Methylenephenanthrene	27.2	23.0	17
Fluoranthene	214.8	196.9	9
Pyrene	509.1	243.1	71
9,10-Dimethylanthracene	10.5	18.2	-54
Retene	9.3	20.2	-74
Sum	1173.92	782.46	

4.3. Laboratory uptake studies

4.3.1. Calculated air mixing ratios

Ambient air mixing ratios (C) within the sealed canisters were calculated based on gravimetric loss of compound from permeation tubes using the following equations:

$$C = \frac{\frac{(P_1 - P_2)}{t} K_m}{F_t} \qquad \text{Equation (11)}$$

P_1 is the initial permeation tube weight in ng, P_2 is the final permeation tube weight in ng, t is the time in minutes, K_m is the molar constant in cc/ng and F_t is the total airflow in cc/min. The units used present the results in parts per million and values obtained were converted to parts per billion.

The K_m is calculated with the equation:

$$K_m = \frac{\frac{(T)R^*}{P_l}}{MW} \qquad \text{Equation (12)}$$

T is temperature in Kelvin, R^* is the universal gas constant in J/(mol*K), P_l is pressure in Pascal (J/m^3) and MW is molecular weight. The final units are in m^3/g and converted to cc/ng for equation 11. The mixing ratios calculated for the study are illustrated in Figure 4.2. The error bars in Figure 4.2 are based on standard deviation of the flow rate.

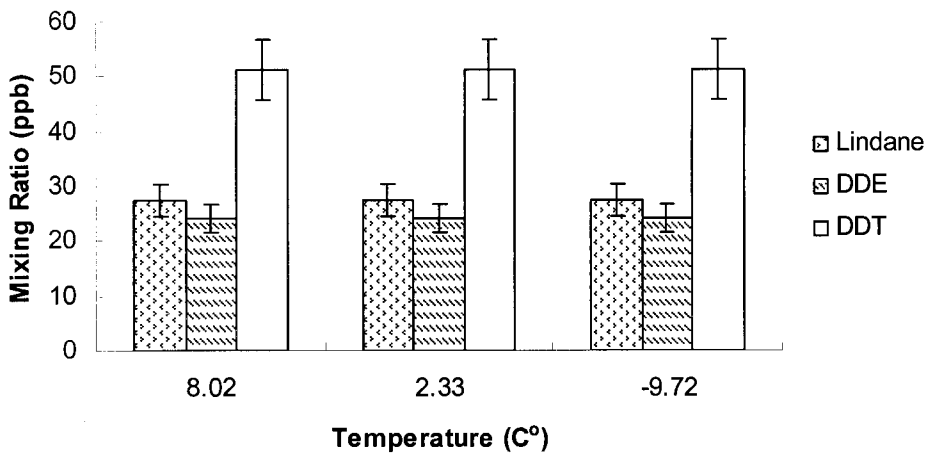


Figure 4.2. The air mixing ratios and standard deviations were calculated for ambient air contaminants generated by the Vici Dynacalibrator.

4.3.2. Up-take rate into SPMDs at 20°C and -20°C

SPMDs were exposed to lindane, DDE and DDT for approximately one, two, three or four months. A blank SPMD was exposed for four months to the compressed air used in the uptake study. Lindane, DDE and DDT were detected in the blank at the following concentrations: 1.1 µg/SPMD, 12.1 µg/SPMD and 0.53 µg/SPMD. Concentrations in the blank were well below what was detected in the exposed SPMDs, so no adjustments were made to any concentrations. Air concentrations for sequentially sealed canisters were altered because of the sequestering of contaminants by the SPMDs in prior canisters. The different retrieval times in addition to the altered air concentrations made contaminant levels in the SPMDs skewed toward longer deployment times, since

canisters were removed from the tail-end of the line of canisters after the allocated times. Two one-month SPMDs were exposed and RSD% (lindane 0.2%, DDE 6.0% and DDT 4.2%) were developed from the detected concentrations. Air concentrations between these two canisters were not substantially different because they were at the tail-end of the line of samplers and the air concentrations reaching them were already depleted to a point where sequestering of contaminants by the first one month SPMD did not significantly change the air concentration reaching the next canister. Average flow rate for the setup was 552±27 cc/min and the average temperature was 19.5±0.6°C.

Similar results and problems were associated with the -20°C study. Air concentrations for sequentially sealed canisters were altered following the method used in the 20°C uptake study. The different retrieval times in addition to the altered air concentrations made contaminant levels in the SPMDs skewed toward longer deployment times. The average flow rate was 531±69 cc/min and average temperature was -19.7±1.5°C for the entire study. The altered air concentrations and different removal times made comparison between different deployment times for the uptake rate impossible because of the unknown air concentrations the SPMDs were being exposed to inside the canisters. Thus, no results for the uptake rates at 20°C and -20°C are being reported.

4.3.3. Exposure of SPMD at different temperatures

Semi-permeable membrane devices were exposed simultaneously to three different temperatures (≅ 8, 2, and -10°C). The air concentrations were altered like they were in the prior uptake studies because of the sequestering of contaminants by upstream SPMDs. However, since SPMDs were removed simultaneously, calculation of altered contaminant air concentrations entering the next canister was possible. Altered air mixing ratios were calculated based on initially generated air mixing ratios for each compound and the levels of each contaminant sequestered by the SPMDs prior to the next canister (Figure 4.3). The error bars in Figure 4.3 are based on standard deviation of the flow rate.

During the experiment the average air flow was 517±61.5 cc/min and the average air temperatures were 2.3±0.7, 8.0±0.6 and -9.7±0.9.

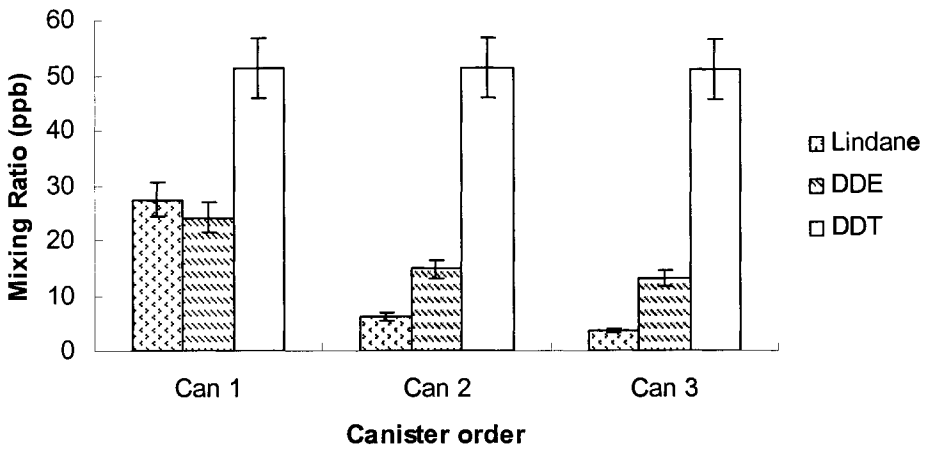


Figure 4.3. The recalculated air mixing ratios entering the next canister based on the uptake of contaminants into the SPMDs in prior canisters after 43 day of sampling.

Comparison of the air sampling rates at different temperatures were generated with equation 6 ($R_s = M_s/C_a t$) (Figures 4.4-4.6) because air concentrations were altered within the different canisters by prior SPMDs. The error bars reported in Figures 4.4-4.6 are based on standard deviation of the flow rates and temperatures in the system. Here M_s is the contaminant measured in the SPMD in μg, C_a is the air concentration in $\mu g/m^3$ (calculated from the air mixing ratio and temperature) and t is the sampling time in days. Since air sampling rate relates concentration in the air and the SPMD, it is more appropriate to compare air sampling rates than concentrations measured in SPMDs at different temperatures because of the change in ambient air concentrations within the previous canister by the SPMDs. The air sampling rate increases with increasing temperature in an exponential fashion. It should be noted that only three data points were used to draw the exponential increase. However, functions of temperatures are typically exponential in the environment, so the exponential increase with temperature is reasonable. Here uptake into the SPMD is decreasing because of temperature drops and not a change in the air concentration of each contaminant during sequestering of

contaminants by upstream SPMDs. A 74%, 88% and 98% drop in the air sampling rate values were seen for lindane, DDE and DDT, respectively, for a temperature drop of 8.0 to -9.7°C.

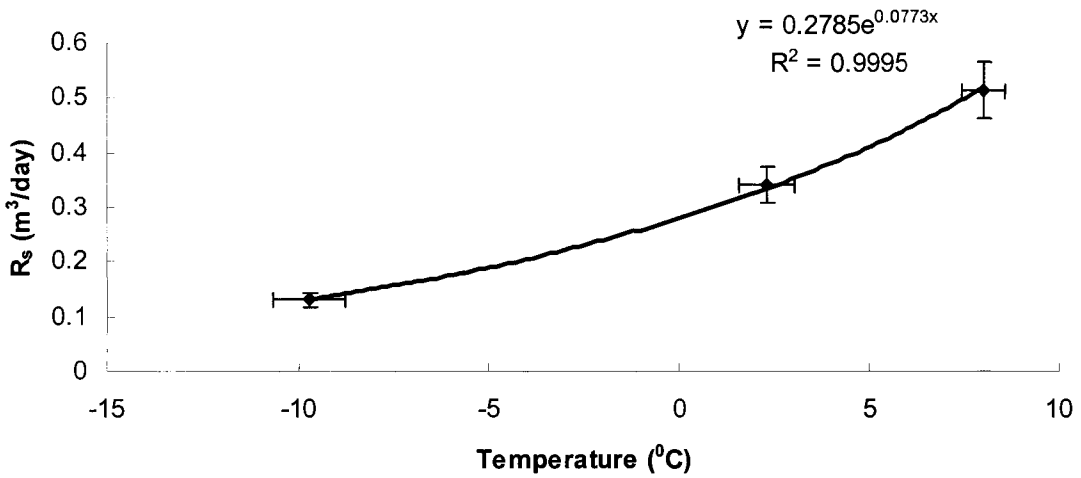


Figure 4.4. The lindane air sampling rates and standard deviations at three different temperatures developed using equation 9.

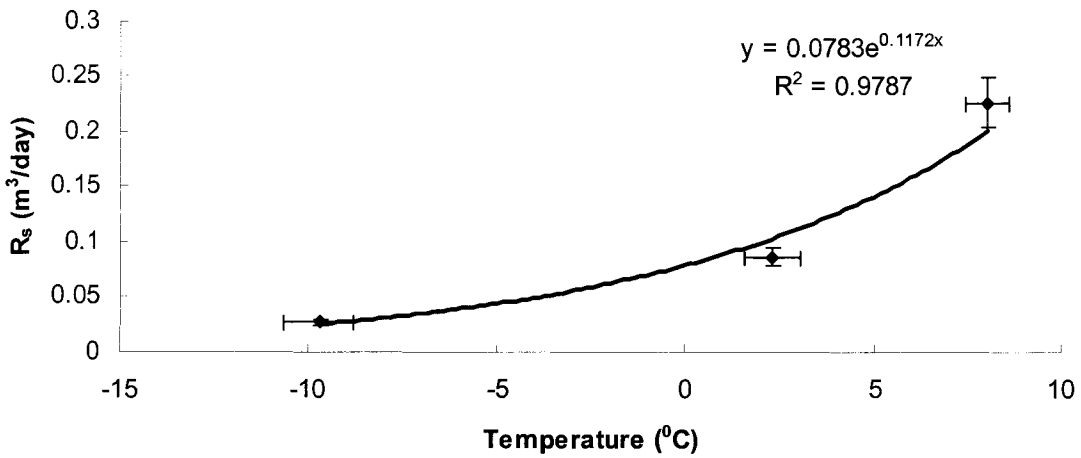


Figure 4.5. The DDE air sampling rates and standard deviations at three different temperatures developed using equation 9.

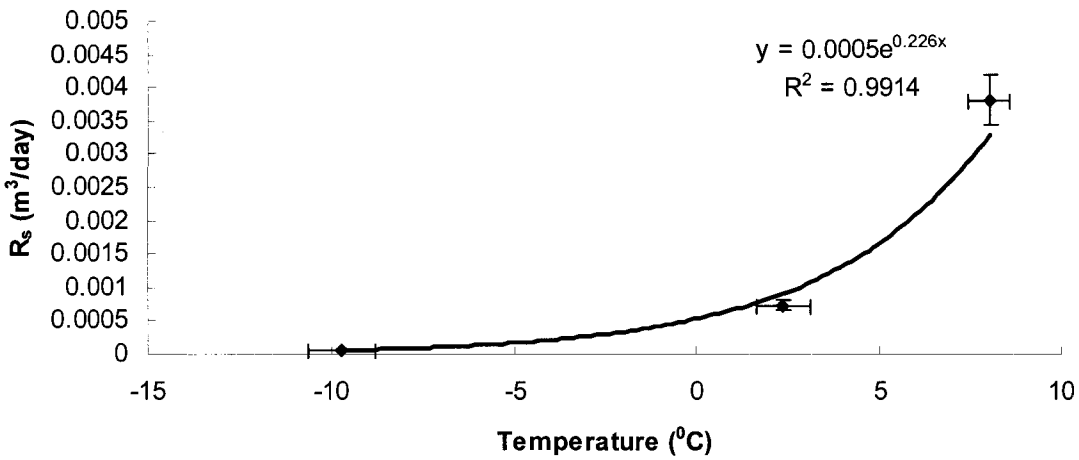


Figure 4.6. The DDT air sampling rates and standard deviations at three different temperatures developed using equation 9.

4.4. Comparison of SPMD to active sampler

A comparison of PAH levels detected in SPMDs and converted to atmospheric concentrations was made to PAH levels determined from an overlapping active sampler in Barrow, Alaska. Five PAHs (fluorene, phenanthrene, anthracene, fluoranthene and pyrene) were compared because of their lower RSD% in the SPMDs and reported uptake values in the literature (Table 1.2). Measured concentrations from the periods sampled by the active sampler that were closest to the SPMD exposure periods were used for comparison (Appendix C1). The concentrations from the active air sampler were reported as gas and particulate phase PAHs. It is assumed that the uptake in the SPMD was in the linear phase, so PAH concentrations in SPMDs deployed from August 13, 2002, to February 28, 2003, were converted to atmospheric concentrations using equation 6. The average temperature was -14°C for the exposure period. The uptake rate obtained from the literature was generated at an average temperature of 22°C. Thus, one would expect the derived air concentrations from SPMDs deployed at the cooler Barrow temperature to be lower. This was the case with the phenanthrene, anthracene, fluoranthene and pyrene calculated air concentrations; however, the fluorene calculated air concentration was slightly higher than the average concentration obtained from the active sampler (Table 4.12). Active sampler concentrations of phenanthrene, anthracene, fluoranthene and pyrene were approximately 3 to 7 times higher than SPMD derived air concentrations.

Further examination compared the ratios of PAH concentrations determined from SPMDs to those determined using the active air sampler (Table 4.13). Since the fluorene level was over estimated in the SPMD, other PAH ratios to fluorene were not in good agreement between the passive and active air sampling. However, the anthracene/ fluoranthene and anthracene /pyrene ratios were in good agreement between the passive and active air samplers.

Table 4.12. A comparison of calculated atmospheric PAH concentrations from an SPMD deployed from August 13, 2002, to February 28, 2003, to average concentrations from an active air sampler taking samples from August 16, 2002, to February 24, 2003.

PAHs	Passive (pg/m^3)	Active (pg/m^3)
Fluorene	216.7	202.4
Phenanthrene	48.4	131.2
Anthracene	0.8	5.2
Fluoranthene	9.3	48.6
Pyrene	13.5	38.8

Table 4.13. A comparison of PAH ratios between calculated atmospheric concentrations from an SPMD deployed from August 13, 2002, to February 28, 2003, to average concentrations from an active air sampler taking samples from August 16, 2002 to February 24, 2003.

PAH Ratio	Passive	Active
Fluorene / Phenanthrene	4.5	1.5
Fluorene / Anthracene	277.6	38.5
Fluorene / Fluoranthene	23.4	4.2
Fluorene /Pyrene	16.1	5.2
Phenanthrene / Anthracene	62.0	25.0
Phenanthrene /Fluoranthene	5.2	2.7
Phenanthrene /Pyrene	16.1	5.2
Anthracene / Fluoranthene	0.1	0.1
Anthracene /Pyrene	0.1	0.1
Fluoranthene /Pyrene	0.7	1.3

4.5. POP concentrations measured in SPMDs at five locations

4.5.1 Barrow

Due to a miscommunication with the personnel in Barrow the first SPMD was deployed for a longer time interval than planned. Instead of leaving the SPMD exposed for approximately three months, the first sample was exposed for six months. POP concentrations were typically higher in the first deployed sample, which was expected due to the longer deployment time (Tables 4.14-4.16). γ-Hexachlorocyclohexane (γ-

HCH) had the highest concentrations in the SPMDs ranging from 28.3 to 63.2 ng/SPMD for the three time-integrated samples (Table 4.14). Concentrations of PCBs were frequently low with most around the MDL (Table 4.15). PAH levels ranged from not detected in C2 Fluorene to 42.6 ng/SPMD for phenanthrene (Table 4.16).

Table 4.14. OC levels detected in SPMDs deployed at Barrow, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)		
Start	8/13/2002	2/28/2003	6/15/3003
Stop	2/28/2003	6/15/2003	9/15/2003
1,2,4,5 Tetrachlorobenzene	17.5	10.5	2.0
1,2,3,4 Tetrachlorobenzene	2.4	0.4	0.3
Pentachlorobenzene	6.9	1.1	2.2
Alpha-hexachlorocyclohexane	9.6	2.5	3.5
Hexachlorobenzene	32.9	13.1	11.7
Pentachloroanisole	3.2	1.9	1.2
Gamma-Hexachlorocyclohexane	63.2	28.3	42.1
Delta-Hexachlorocyclohexane	0.0	ND	ND
Octachlorostyrene	0.3	0.2	0.2
Oxychlordane	0.2	0.2	0.2
2,4'-Dichlorodiphenyldichloroethylene	4.1	1.4	2.3
4,4'-Dichlorodiphenyldichloroethylene	26.2	7.9	11.5
2,4'-Dichlorodiphenyldichloroethane	0.0	0.0	0.0
4,4'-Dichlorodiphenyldichloroethane	0.2	ND	BDL[1]
2,4'-Dichlorodiphenyltrichloroethane	0.8	0.5	0.6
4,4'-Dichlorodiphenyltrichloroethane	2.9	1.4	1.6
Photomirex	1.6	0.0	1.7
C[2]	1.3	1.3	1.5
Heptachlor	0.5	0.4	0.5
C1A[2]	0.5	0.3	0.5
C2/U5[3]	0.2	0.1	0.2
C3[3]	0.1	0.2	0.1
C5[4]	3.0	1.0	2.2
U3[5]	0.1	0.0	ND
U1[6]	0.2	0.2	0.2
Trans-Chlordane	2.0	1.0	2.1
Cis-Chlordane	1.9	1.3	1.9
Trans-Nonachlor	0.8	0.6	0.8
Cis-Nonachlor	0.3	0.2	0.3
Toxaphene 2	1.1	1.1	1.0
Toxaphene 3	2.0	0.5	ND
Sum Toxaphene = (2+3 and others)	20.6	6.2	14.4

[1]BDL=Below Detection Limit; [2]C, C1A= minor component of technical chlordane; [3]C2/U5, C3= heptachloro compound of technical chlordane; [4]C5= component of technical chlordane; [5]U3= intermediate metabolite of chlordane and [6]U1= photoheptachlor.

Table 4.15. PCB levels detected in SPMDs deployed at Barrow, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)		
Start	8/13/2002	2/28/2003	6/15/3003
Stop	2/28/2003	6/15/2003	9/15/2003
PCB4/10[1]	0.4	0.2	0.3
PCB7	0.3	0.1	ND
PCB6	1.1	BDL[2]	BDL[2]
PCB5/8[1]	ND	0.3	ND
PCB19	ND	0.1	ND
PCB18	1.0	0.4	0.7
PCB17	0.4	0.3	0.3
PCB24	ND	0.1	ND
PCB16/32[1]	ND	0.1	ND
PCB26	0.7	0.8	0.6
PCB25	2.1	2.0	1.9
PCB22	ND	0.2	ND
PCB45	ND	0.5	ND
PCB46	ND	0.0	ND
PCB52	1.2	0.7	1.0
PCB49	0.5	0.4	0.4
PCB47	0.5	0.4	0.4
PCB44	0.7	0.7	0.8
PCB42	ND	0.0	ND
PCB41/71[1]	0.1	ND	ND
PCB64	ND	0.2	0.1
PCB40	0.1	0.1	ND
PCB70/76[1]	0.3	0.4	0.3
PCB66	0.4	0.4	0.3
PCB91	ND	0.1	ND
PCB60/56[1]	ND	0.6	ND
PCB84/89[1]	2.2	1.2	1.6
PCB101	0.5	0.8	0.4
PCB99	0.2	0.2	0.1
PCB83	2.8	BDL[2]	1.6
PCB87	0.1	0.1	0.1
PCB110	0.4	0.3	0.2
PCB151	0.1	0.1	0.1
PCB149	0.2	0.3	0.2
PCB118	ND	0.2	ND
PCB146	ND	0.1	ND
PCB132	ND	0.1	ND
PCB141	ND	0.0	ND
PCB179	0.1	0.1	0.1
PCB187	0.1	0.1	0.1
PCB183	ND	0.04	ND
PCB174	ND	0.04	0.1
PCB180	0.04	0.04	0.1

[1]PCB with two numbers and a '/' could not be separated on the chromatogram. [2]BDL= Below Detection Limit.

Table 4.16. PAH levels detected in SPMDs deployed at Barrow, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
	Start	8/13/2002	2/28/2003	6/15/3003
	Stop	2/28/2003	6/15/2003	9/15/2003
Naphthalene		37.7	9.8	1.9
2-Methylnaphthalene		21.2	9.0	2.6
1-Methylnaphthalene		27.9	7.5	3.2
Biphenyl		40.4	2.0	5.9
Acenaphthylene		1.5	0.5	0.4
Acenaphthene		1.8	1.7	1.1
Fluorene		78.0	5.1	27.3
Phenanthrene		42.6	30.3	24.3
Anthracene		0.6	0.9	2.3
C2 Fluorene		2.4	ND	ND
Benzo(a)anthracene		1.4	0.8	1.1
4,5-Methylenephenanthrene		1.5	1.4	1.4
Fluoranthene		8.3	6.0	5.4
Pyrene		5.4	4.3	3.7
Retene		0.5	0.5	0.4

4.5.2. Poker Flat Research Range

The POP concentrations measured in the SPMDs for the different sampling periods are listed in Tables 4.17-4.19. Within the OCs, the DDT and DDT metabolites were frequently detected. p,p'-DDE, a metabolite of DDT, was detected in the highest concentration within the DDT group with an average concentration of 4.3 ng/SPMD. The sum of the toxaphene levels increased later in the year with concentrations peaking at 65.7 ng/SPMD for the June through September sample. PCB concentrations were generally low like in the Barrow samples. Within the PCB group 2,3,4'-Trichlorobiphenyl (PCB25) had the highest levels with an average concentration of 3.4 ng/SPMD. Concentrations of PAH compounds ranged from 0.6 ng/SPMD for retene to 84.6 ng/SPMD for phenanthrene. The largest difference in concentration throughout the sampling periods was seen in the PAHs with phenanthrene varying between 38.3 and 84.6 ng/SPMD.

Table 4.17. OC levels detected in SPMDs deployed at Poker Flat Research Range, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
Start	9/6/2002	12/4/2002	3/5/2003	6/2/2003
Stop	12/4/2002	3/5/2003	6/2/2003	9/2/2003
1,2,4,5 Tetrachlorobenzene	2.3	3.0	1.8	2.4
1,2,3,4 Tetrachlorobenzene	0.2	0.4	BDL[1]	BDL[1]
Pentachlorobenzene	1.6	1.8	BDL[1]	0.5
Alpha-Hexachlorocyclohexane	1.8	1.3	0.8	1.1
Hexachlorobenzene	2.5	5.0	1.8	2.1
4Chloro-Veratrol	0.2	ND	ND	0.5
Pentachloroanisole	1.7	1.4	1.9	2.7
Gamma-Hexachlorocyclohexane	5.2	5.5	3.1	4.0
Octachlorostyrene	0.2	0.1	0.0	0.1
Oxychlordane	0.7	0.4	0.1	0.2
2,4'-Dichlorodiohenyldichloroethylene	0.6	0.9	0.7	0.9
4,4'-Dichlorodiohenyldichloroethylene	6.7	2.8	5.0	2.8
2,4'-Dichlorodiphenyldichloroethane	0.9	0.0	0.1	0.0
4,4'-Dichlorodiphenyldichloroethane	0.3	0.3	ND	0.8
2,4'-Dichlorodiphenyltrichloroethane	0.8	0.8	0.9	1.6
4,4'-Dichlorodiphenyltrichloroethane	2.4	2.4	6.8	7.9
Photomirex	2.8	4.6	0.0	2.7
Methoxychlor	ND	ND	ND	1.3
C[2]	0.3	2.3	2.1	2.3
C1A[2]	0.8	1.0	0.8	0.9
C3[3]	ND	0.1	0.2	0.3
C5[4]	0.5	0.7	0.6	0.7
U3[5]	0.0	0.1	0.1	0.1
U1[6]	0.2	0.3	0.3	0.4
Heptachlor	0.3	0.7	0.5	0.8
Trans-Chlordane	3.2	4.3	3.2	3.8
Cis-Chlordane	2.7	3.4	2.7	3.2
Trans-Nonachlor	0.7	1.1	0.9	0.9
Cis-Nonachlor	0.3	0.3	0.2	0.4
Toxaphene 2	ND	0.5	2.0	5.3
Toxaphene 3	2.5	2.0	3.9	3.8
Sum Toxaphene (2+3 and others)	12.0	17.4	27.4	65.7

[1]BDL= Below Detection Limit; [2]C, C1A= minor component of technical chlordane; [3]C3= heptachloro compound of technical chlordane; [4]C5= component of technical chlordane; [5]U3= intermediate metabolite of chlordane; [6]U1= heptachlor.

Table 4.18. PCB levels detected in SPMDs deployed at Poker Flat Research Range, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
Start	9/6/2002	12/4/2002	3/5/2003	6/2/2003
Stop	12/4/2002	3/5/2003	6/2/2003	9/2/2003
PCB4/10[2]	0.3	0.3	0.3	0.3
PCB5/8	0.5	0.5	0.5	0.5
PCB18	0.4	0.3	0.4	0.4
PCB17	BDL[1]	0.3	0.3	0.3
PCB26	0.2	0.3	0.3	0.3
PCB25	3.3	3.5	3.3	3.5
PCB28	0.2	0.2	0.5	0.6
PCB22	0.3	0.3	0.2	0.3
PCB46	0.8	0.6	0.8	0.7
PCB52	0.5	0.5	0.5	0.6
PCB49	0.5	0.5	0.7	0.7
PCB47	1.7	1.6	0.6	BDL[1]
PCB41/71[2]	0.1	0.1	0.1	ND
PCB74	0.6	0.5	0.8	0.6
PCB70/76[2]	0.2	0.3	0.4	0.5
PCB66	0.2	0.2	0.2	ND
PCB56/60[2]	0.1	0.1	0.1	0.1
PCB84/89[2]	ND	0.3	0.4	0.4
PCB101	0.2	0.2	0.2	0.2
PCB83	ND	ND	0.1	0.1
PCB97	BDL[1]	BDL[1]	0.1	0.1
PCB136	ND	0.2	0.3	0.4
PCB82	ND	0.1	0.1	0.1
PCB135/144[2]	0.3	0.3	0.3	0.3
PCB149	0.3	BDL[1]	0.3	BDL[1]
PCB131	ND	0.1	ND	ND
PCB146	0.2	0.2	0.3	0.3
PCB105	ND	ND	0.1	0.1
PCB141	0.1	0.2	0.1	0.1
PCB130/176[2]	0.2	0.2	0.4	0.2
PCB175	0.1	0.1	0.1	0.1
PCB187	ND	ND	0.1	0.1
PCB185	ND	ND	0.1	0.1
PCB172/197[2]	0.1	0.1	0.1	0.1
PCB180	0.1	0.1	0.3	0.6
PCB190	ND	0.7	ND	ND

[1]BDL=Below Detection Limit. [2]PCB with two numbers and a '/' could not be separated on the chromatogram.

Table 4.19. PAH levels detected in SPMDs deployed at Poker Flat Research Range, Alaska.

Compounds	Concentrations (ng/SPMD)				
	Start	9/6/2002	12/4/2002	3/5/2003	6/2/2003
	Stop	12/4/2002	3/5/2003	6/2/2003	9/2/2003
Naphthalene		15.1	40.2	16.7	9.2
2-Methylnaphthalene		18.5	21.8	16.2	9.5
1-Methylnaphthalene		17.0	22.4	13.5	7.9
Biphenyl		5.9	8.2	3.6	2.3
Acenaphthylene		1.2	2.6	1.0	0.7
Acenaphthene		3.0	2.3	4.2	5.8
Fluorene		8.0	18.2	12.0	13.4
Phenanthrene		54.2	38.3	65.1	84.6
Anthracene		3.4	2.2	5.4	1.4
C2 Fluorene		4.7	6.9	3.1	11.1
Benzo(a)anthracene		2.2	1.8	1.1	1.0
4,5-Methylenephenanthrene		3.1	1.9	3.7	4.2
Fluoranthene		11.5	8.2	13.5	18.7
Pyrene		7.2	5.9	9.3	8.2
Retene		0.7	0.6	4.0	1.0

4.5.3. Denali National Park and Preserve

Within the organochlorines DDT and DDT metabolites were detected in the highest concentrations (Table 4.20), excluding the sum of toxaphene compounds. p,p'-DDT concentrations ranged from 2.6 to 20.7 ng/SPMD with an average concentration of 9.5 ng/SPMD while p,p'-DDE, a metabolite of p,p'-DDT, concentrations ranged from 2.0 to 11.4 ng/SPMD with an average concentration of 6.6 ng/SPMD. These compounds also showed the highest variation for the POPs with about a ten-fold difference ranging from 2.0 to 20.7 ng/SPMD. The sum of toxaphene levels increased later in the year with concentrations peaking at 89.3 ng/SPMD for the June through September sample. PCB concentrations were generally low and around the MDL (Table 4.21), like the other locations, with a few exceptions. Within the PCB group, PCB25 was more frequently detected at higher levels with an averaged concentration of 3.7 ng/SPMD. The 2,2',3,4,4'-Pentachlorobiphenyl (PCB 85) concentration was elevated in November through March

at 5.2 ng/SPMD but not detected in the March through June or June through August samples. Concentrations of PAH compounds ranged from 0.4 ng/SPMD for retene to 84.2 ng/SPMD for phenanthrene (Table 4.22).

Table 4.20. OC levels detected in SPMDs deployed at Denali National Park & Preserve, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
Start	9/3/2002	11/29/2002	3/1/2003	5/30/2003
Stop	11/29/2002	3/1/2003	5/30/2003	8/29/2003
1,2,4,5 Tetrachlorobenzene	2.4	1.8	1.7	1.2
1,2,3,4 Tetrachlorobenzene	0.4	0.4	0.4	BDL[1]
Pentachlorobenzene	0.9	1.4	1.0	0.5
Alpha-Hexachlorocyclohexane	1.1	0.9	0.9	0.9
Hexachlorobenzene	3.4	3.2	4.0	2.5
Pentachloroanisole	1.9	1.4	1.8	4.7
Gamma-Hexachlorocyclohexane	5.2	5.6	4.3	5.3
Octachlorostyrene	0.0	0.0	0.0	0.0
Oxychlordane	0.2	0.1	0.2	0.1
2,4'-Dichlorodiohenyldichloroethylene	0.6	0.9	0.7	0.8
4,4'-Dichlorodiohenyldichloroethylene	2.0	5.2	11.4	7.8
2,4'-Dichlorodiphenyldichloroethane	0.0	0.2	0.0	ND
4,4'-Dichlorodiphenyldichloroethane	0.4	0.8	0.2	1.5
2,4'-Dichlorodiphenyltrichloroethane	0.7	0.8	0.7	0.6
4,4'-Dichlorodiphenyltrichloroethane	4.5	10.4	2.6	20.7
Photomirex	4.8	4.5	3.0	4.1
C[2]	2.5	2.9	2.1	2.6
C1A[2]	0.8	1.3	0.8	1.0
C3[3]	0.1	0.2	0.1	0.1
C5[4]	0.5	0.7	0.6	0.6
U3[5]	0.1	0.0	0.1	0.1
U1[6]	0.3	0.3	0.3	0.3
Heptachlor	0.5	0.5	0.6	0.6
Trans-Chlordane	3.3	5.1	3.2	4.1
Cis-Chlordane	2.6	4.1	2.7	3.3
Trans-Nonachlor	0.9	1.3	1.0	1.0
Cis-Nonachlor	0.2	0.1	0.2	0.1
Toxaphene 2	BDL[1]	0.5	0.9	0.5
Toxaphene 3	2.1	0.7	1.6	ND
Sum Toxaphene (2+3 and others)	30.3	39.6	26.6	89.3

[1]BDL= Below Detection Limit; [2]C, C1A= minor component of technical chlordane; [3]C3= heptachloro compound of technical chlordane; [4]C5= component of technical chlordane; [5]U3= Intermediate metabolite of chlordane; [6]U1= photoheptachlor.

Table 4.21. PCB levels detected in SPMDs deployed at Denali National Park & Preserve, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
Start	9/3/2002	11/29/2002	3/1/2003	5/30/2003
Stop	11/29/2002	3/1/2003	5/30/2003	8/29/2003
PCB4/10[2]	0.5	0.4	0.4	0.3
PCB7	0.4	BDL[1]	0.4	ND
PCB6	0.3	0.4	0.2	ND
PCB5/8	0.6	0.5	0.5	ND
PCB18	1.3	0.7	0.7	0.3
PCB17	0.4	0.3	0.3	0.3
PCB16/32[2]	ND	ND	0.3	ND
PCB25	3.4	4.5	2.8	3.9
PCB22	0.1	ND	0.1	ND
PCB45	0.3	0.3	0.3	0.3
PCB46	ND	ND	0.3	ND
PCB52	BDL[1]	1.0	0.8	0.8
PCB47	0.6	BDL[1]	BDL[1]	0.6
PCB70/76[2]	0.6	0.6	0.5	0.4
PCB66	ND	0.5	0.4	0.3
PCB91	0.2	0.1	ND	ND
PCB84/89[2]	0.1	0.1	0.1	0.2
PCB101	0.3	0.4	0.3	0.3
PCB99	0.1	0.2	0.1	0.1
PCB97	ND	0.1	0.1	ND
PCB87	0.1	0.1	0.1	0.1
PCB85	1.8	5.2	ND	ND
PCB110	0.2	0.2	0.3	0.3
PCB149	0.3	0.3	0.2	0.3
PCB118	0.2	0.3	0.2	ND
PCB146	ND	0.1	0.1	ND
PCB141	ND	0.1	0.04	ND
PCB130/176[2]	ND	0.1	ND	0.3
PCB179	BDL[1]	0.1	0.1	ND
PCB187	0.1	0.1	0.1	0.1
PCB174	0.1	0.1	0.04	ND
PCB180	0.1	0.1	0.1	0.1
PCB193	ND	0.1	0.1	0.4

[1]BDL=Below Detection Limit. [2]PCB with two numbers and a '/'could not be separated on the chromatogram.

Table 4.22. PAH levels detected in SPMDs deployed at Denali National Park & Preserve, Alaska.

Compounds	Concentrations (ng/SPMD)			
Start	9/3/2002	11/29/2002	3/1/2003	5/30/2003
Stop	11/29/2002	3/1/2003	5/30/2003	8/29/2003
Naphthalene	5.6	13.9	14.4	13.9
2-Methylnaphthalene	9.2	13.8	14.6	14.7
1-Methylnaphthalene	9.7	13.0	13.1	13.4
Biphenyl	7.8	4.6	4.6	4.8
Acenaphthylene	5.0	1.1	1.1	1.4
Acenaphthene	2.2	2.7	3.2	3.5
Fluorene	13.8	9.0	15.3	17.1
Phenanthrene	52.8	40.0	57.9	84.2
Anthracene	5.8	2.6	5.0	8.1
C2 Fluorene	9.3	4.7	7.7	11.5
Benzo(a)anthracene	0.9	1.0	1.7	0.9
4,5-Methylenephenanthrene	2.6	1.8	9.1	3.3
Fluoranthene	8.9	8.6	6.6	7.9
Pyrene	6.4	6.4	4.0	5.0
Retene	0.5	0.5	0.4	0.5

4.5.4. Trapper Creek

During shipment of ampules to FWI, the Trapper Creek sample for September through November was broken, thus no data is presented for that time interval. Some of the highest OC levels were detected in the Trapper Creek samples. The p,p'-DDT concentration was at 142.3 ng/SPMD for the March through May sample, while p,p'-DDE concentration was at 173.9 ng/SPMD for the May through August sample (Table 4.23). The sum of toxaphene concentrations for the May through August sample was at 485.4 ng/SPMD. PCB concentrations were generally low and around the MDL (Table 4.24) like the other locations. PCB25, like at the other locations, was detected at higher levels compared to the other PCBs and had an average concentration of 3.6 ng/SPMD. Concentrations of PAH compounds ranged from 0.4 ng/SPMD for retene to 78.5 ng/SPMD for phenanthrene (Table 4.25).

Table 4.23. OC levels detected in SPMDs Deployed at Trapper Creek, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)		
Start	11/29/2002	3/1/2003	5/30/2003
Stop	3/1/2003	5/30/2003	8/29/2003
1,2,4,5 Tetrachlorobenzene	4.1	3.1	4.7
1,2,3,4 Tetrachlorobenzene	0.9	1.0	0.7
Pentachlorobenzene	1.1	1.2	0.6
Alpha-Hexachlorocyclohexane	0.7	0.9	0.9
Hexachlorobenzene	2.4	3.6	2.6
Pentachloroanisole	1.4	1.7	3.1
Gamma-Hexachlorocyclohexane	4.7	4.8	4.3
Octachlorostyrene	ND	0.03	0.03
Oxychlordane	0.1	0.2	0.1
2,4'-Dichlorodiohenyldichloroethylene	0.9	1.3	1.1
4,4'-Dichlorodiohenyldichloroethylene	9.1	184.0	173.9
2,4'-Dichlorodiphenyldichloroethane	0.03	0.02	0.02
4,4'-Dichlorodiphenyldichloroethane	1.5	8.6	3.9
2,4'-Dichlorodiphenyltrichloroethane	1.5	2.4	1.5
4,4'-Dichlorodiphenyltrichloroethane	12.0	142.3	45.0
Photomirex	1.1	1.4	2.5
Methoxychlor	ND	1.0	ND
C[2]	2.1	2.8	2.5
C1A[2]	0.9	1.1	1.1
C3[3]	0.2	0.2	0.2
C5[4]	0.7	1.0	0.8
U3[5]	0.1	0.1	0.04
U1[6]	0.3	0.4	0.4
Heptachlor	0.8	0.7	0.7
Trans-Chlordane	4.1	4.6	4.5
Cis-Chlordane	3.4	3.9	3.9
Trans-Nonachlor	1.3	1.4	1.4
Cis-Nonachlor	0.1	0.1	0.1
Toxaphene 2	0.5	0.6	0.6
Toxaphene 3	BDL[1]	1.2	1.7
Sum Toxaphene (2+3 and others)	45.0	485.4	162.4

[1]BDL=Below Detection Limit; [2]C, C1A= minor component of technical chlordane; [3]C3= heptachloro compound of technical chlordane; [4]C5 component of technical chlordane; [5]U3= intermediate metabolite of chlordane; [6]U1= photoheptachlor.

Table 4.24. PCB levels detected in SPMDs deployed at Trapper Creek, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
	Start	11/29/2002	3/1/2003	5/30/2003
	Stop	3/1/2003	5/30/2003	8/29/2003
PCB4/10[2]		1.1	1.2	1.0
PCB7		0.3	0.3	BDL[1]
PCB6		0.4	1.6	BDL[1]
PCB8/5[2]		ND	ND	0.5
PCB18		0.4	0.6	0.4
PCB17		0.3	0.4	0.3
PCB16/32[2]		0.2	0.2	0.2
PCB26		1.6	2.1	2.1
PCB25		2.9	4.1	3.6
PCB28		0.5	0.7	0.5
PCB22		ND	ND	0.5
PCB45		ND	0.4	BDL[1]
PCB46		0.8	1.4	0.9
PCB52		0.5	0.6	0.5
PCB49		0.5	BDL[1]	0.5
PCB48		0.5	0.4	0.5
PCB41/71[2]		0.1	0.2	0.3
PCB64		ND	ND	1.6
PCB40		ND	0.5	ND
PCB74		0.7	0.9	0.6
PCB70/76[2]		0.4	0.6	0.4
PCB91		ND	0.4	0.3
PCB56/60[2]		0.1	0.6	0.4
PCB84/89[2]		0.4	0.6	0.5
PCB101		0.2	0.2	0.2
PCB99		ND	1.7	1.4
PCB83		ND	ND	0.1
PCB97		BDL[1]	0.1	0.1
PCB136		0.3	1.9	2.3
PCB82		0.1	0.1	0.1
PCB135/144[2]		0.3	0.4	0.4
PCB149		ND	ND	0.3
PCB134		0.2	0.3	ND
PCB131		0.1	ND	0.2
PCB146		0.2	0.3	0.3
PCB105		0.1	0.1	0.1
PCB141		0.1	0.2	0.1
PCB130/176[2]		0.2	0.5	0.6
PCB175		0.1	0.1	0.1
PCB137		ND	0.6	0.6
PCB187		ND	ND	0.1
PCB185		0.03	0.1	0.1
PCB172/197[2]		0.1	0.1	0.1
PCB180		ND	ND	0.1

BDL=Below Detection Limit. [2]PCB with two numbers and a '/' could not be separated on the chromatogram.

Table 4.25. PAH levels detected in SPMDs Deployed at Trapper Creek, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
	Start	11/29/2002	3/1/2003	5/30/2003
	Stop	3/1/2003	5/30/2003	8/29/2003
Naphthalene		34.6	28.2	26.0
2-Methylnaphthalene		36.5	33.6	26.4
1-Methylnaphthalene		28.2	24.3	18.8
Biphenyl		3.2	3.0	2.6
Acenaphthylene		0.9	0.9	0.9
Acenaphthene		2.0	2.1	2.1
Fluorene		6.3	6.2	8.3
Phenanthrene		39.1	57.6	78.5
Anthracene		2.9	3.4	1.2
C2 Fluorene		6.3	ND	12.5
Benzo(a)anthracene		1.5	1.7	1.0
4,5-Methylenephenanthrene		1.9	2.2	3.9
Fluoranthene		11.7	14.6	14.6
Pyrene		8.9	9.7	9.8
Retene		0.5	0.4	0.6

4.5.5. Homer

During shipment of ampules to FWI, the Homer sample for August through November was broken, thus no data was presented for that time interval. γ-HCH concentrations were detected at higher amounts within the OCs ranging from 6.5 to 42.3 ng/SPMD with an average concentration of 22 ng/SPMD (Table 4.26). DDT and its metabolites were lower at Homer compared to the other four locations. Also, PCBs were not as frequently detected at the Homer site (Table 4.27); concentrations for detected PCBs remained lower and closer to the MDL. PCB25 was again detected at higher concentrations than the other PCB compounds throughout the various time intervals. Concentrations of PAH compounds ranged from 0.7 ng/SPMD for benzo(a)anthracene to 150.2 ng/SPMD for phenanthrene (Table 4.28).

Table 4.26. OC levels detected in SPMDs deployed at Homer, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)		
Start	9/1/2002	11/30/2002	6/1/2003
Stop	11/30/2002	3/2/2003	8/31/2003
1,2,4,5 Tetrachlorobenzene	4.4	9.2	2.4
1,2,3,4 Tetrachlorobenzene	0.3	0.5	BDL[1]
Pentachlorobenzene	0.6	1.5	0.6
Alpha-Hexachlorocyclohexane	1.9	2.1	1.6
Hexachlorobenzene	2.7	7.5	3.5
Pentachloroanisole	1.5	1.9	1.8
Gamma-hexachlorocyclohexane	42.3	6.5	17.5
Octachlorostyrene	0.0	0.1	0.0
Oxychlordane	0.1	0.3	0.1
2,4'-Dichlorodiohenyldichloroethylene	1.3	0.6	0.9
4,4'-Dichlorodiohenyldichloroethylene	6.0	2.3	6.2
2,4'-Dichlorodiphenyldichloroethane	ND	0.1	ND
4,4'-Dichlorodiphenyldichloroethane	BDL[1]	BDL[1]	ND
2,4'-Dichlorodiphenyltrichloroethane	0.5	0.6	0.3
4,4'-Dichlorodiphenyltrichloroethane	1.5	1.4	1.3
Photomirex	2.4	2.4	ND
Methoxychlor	0.7	ND	ND
C[2]	0.9	1.5	0.9
C1A[2]	0.4	0.5	0.4
C5[3]	1.0	0.5	0.7
U3[4]	0.0	0.0	ND
U1[5]	BDL[1]	0.3	BDL[1]
Heptachlor	0.5	0.5	BDL[1]
Trans-Chlordane	1.6	2.2	1.5
Cis-Chlordane	1.3	2.0	1.4
Trans-Nonachlor	0.4	0.7	0.4
Cis-Nonachlor	0.1	0.2	0.1
Toxaphene 2	BDL[1]	2.2	BDL[1]
Toxaphene 3	1.1	5.2	ND
Sum Toxaphene (2+3 and others)	8.5	20.3	5.7

[1]BDL= Below Detection Limit; [2]C, C1A= minor component of technical chlordane; [3]C5 component of technical chlordane; [4]U3= intermediate metabolite of chlordane and [5]U1= photoheptachlor.

Table 4.27. PCB levels detected in SPMDs deployed at Homer, Alaska (ND= Not Detected).

Compounds	Concentrations (ng/SPMD)			
	Start	9/1/2002	11/30/2002	6/1/2003
	Stop	11/30/2002	3/2/2003	8/31/2003
PCB4/10[2]		0.2	0.3	0.2
PCB6		0.4	BDL[1]	ND
PCB18		BDL[1]	0.3	ND
PCB17		BDL[1]	0.2	ND
PCB26		0.5	0.6	0.6
PCB25		1.7	2.3	1.7
PCB52		0.5	0.4	0.8
PCB44		1.2	0.9	0.9
PCB48		0.2	ND	ND
PCB70/76[2]		0.3	0.2	ND
PCB66		BDL[1]	BDL[1]	0.2
PCB84/89[2]		0.7	0.2	0.5
PCB101		0.3	0.2	0.2
PCB83		0.7	ND	0.6
PCB85		ND	2.1	ND
PCB151		0.07	0.07	0.07
PCB114		0.10	0.12	ND
PCB131		0.01	ND	ND
PCB105		0.04	ND	ND
PCB141		0.04	ND	ND
PCB179		0.05	ND	ND
PCB187		0.06	ND	0.07
PCB193		0.20	ND	ND

[1]BDL= Below Detection Limit. [2]PCB with two numbers and a '/' could not be separated on the chromatogram.

Table 4.28. PAH levels detected in SPMDs deployed at Homer, Alaska.

Compounds	Concentrations (ng/SPMD)			
	Start	9/1/2002	11/30/2002	6/1/2003
	Stop	11/30/2002	3/2/2003	8/31/2003
Naphthalene		13.9	6.9	4.0
2-Methylnaphthalene		21.5	10.7	7.3
1-Methylnaphthalene		23.7	11.8	7.5
Biphenyl		7.0	3.5	3.3
Acenaphthylene		8.5	4.2	3.0
Acenaphthene		5.5	2.8	4.0
Fluorene		34.3	17.2	20.1
Phenanthrene		150.2	75.1	68.1
Anthracene		9.1	4.6	4.4
C2 Fluorene		9.3	4.6	4.5
Benzo(a)anthracene		1.4	0.7	0.9
4,5-Methylenephenanthrene		11.7	5.9	4.6
Fluoranthene		24.5	12.3	10.9
Pyrene		21.6	10.8	9.1
Retene		13.5	6.7	1.6

4.6 Principal component analysis

Principal component analysis is a method used to show the variations in a multivariate data matrix X with objects (rows) and variables (column) through a few uncorrelated (orthogonal) principal components (PCs) (Jackson, 1991). The first PC is oriented to explain the most variation in the data set and shows the best linear summary of data matrix X. The second PC is orthogonal to the first and explains the second largest variation in the data set. The PCs can be plotted in two-dimensional space to produce two graphical plots (score and loading plots). The score plot visually represents the relationship between the objects, while the loading plot visually represents how the variables are related to each other. When the two plots are compared the relationship between the objects and variables are revealed based on similarities in location on the two plots.

A principal component analysis was performed on the matrix of the 16 objects (SPMD locations and sampling periods) and 54 variables (compounds). The graphical output of the PCA consisted of two plots, the scores and loadings. Compounds and samples in close proximity to each other in the graphs are considered to be similar. The score plot indicates differences and similarities among sample locations and sampling times (Figure 4.7), while the loading plot indicates relationships among the concentrations of analytes (Figure 4.8). In addition, simultaneous use of the score and loading plots indicates the potential location of the samples with extreme values of a particular POP. For example, fluorene in the score plot is located in the similar location on the graph as the Homer March to June sample in the loading plot.

The first two PCs explained 48% of the total variance. The third PC explained 12%. The first PC, which explains 31% of the total variation in the POP concentrations had a loading ranging from -0.2 to 0.25. The samples or variables that are farther away from the origin of the graph explain most of the variance in the PC models. In the score plot along PC 1 the Trapper Creek March to June and Homer September to December samples are furthest away from the origin and explain the most variance in the model. Evaluation of the data suggests the separation in the samples along the first PC is mainly explained by total POP concentrations measured in SPMDs at the locations. Thus, higher concentrations of total contaminants measured in SPMDs are at the Trapper Creek site during March to June in comparison to the other samples and lower concentrations are measured at Homer March to June samples in comparison to the other samples. Evaluation of the concentrations measured in the SPMDs suggests the second and third PCs were influenced mainly by the POPs' patterns at each sampling site. Three distinct groups are depicted in PC 2 with the Barrow samples and the Homer September-December sample separated from the other samples, which suggest different patterns of variation in the POP concentrations between the three groups.

The clustering or spacing of the samples in relationship to one another suggests relative similarities or differences between the concentrations measured in the SPMDs at the different sampling locations and times. Homer, Trapper Creek and Barrow

concentrations are pretty different from each other because of their separation in the score plot. Denali National Park and Preserve and Poker Flat Research Range SPMD samples are more similar and show less systemic seasonal variation because of their close proximately to each other. Larger seasonal differences are seen in the Homer, Barrow and Trapper Creek samples because of their wide separation between samples from the same location in the score plot.

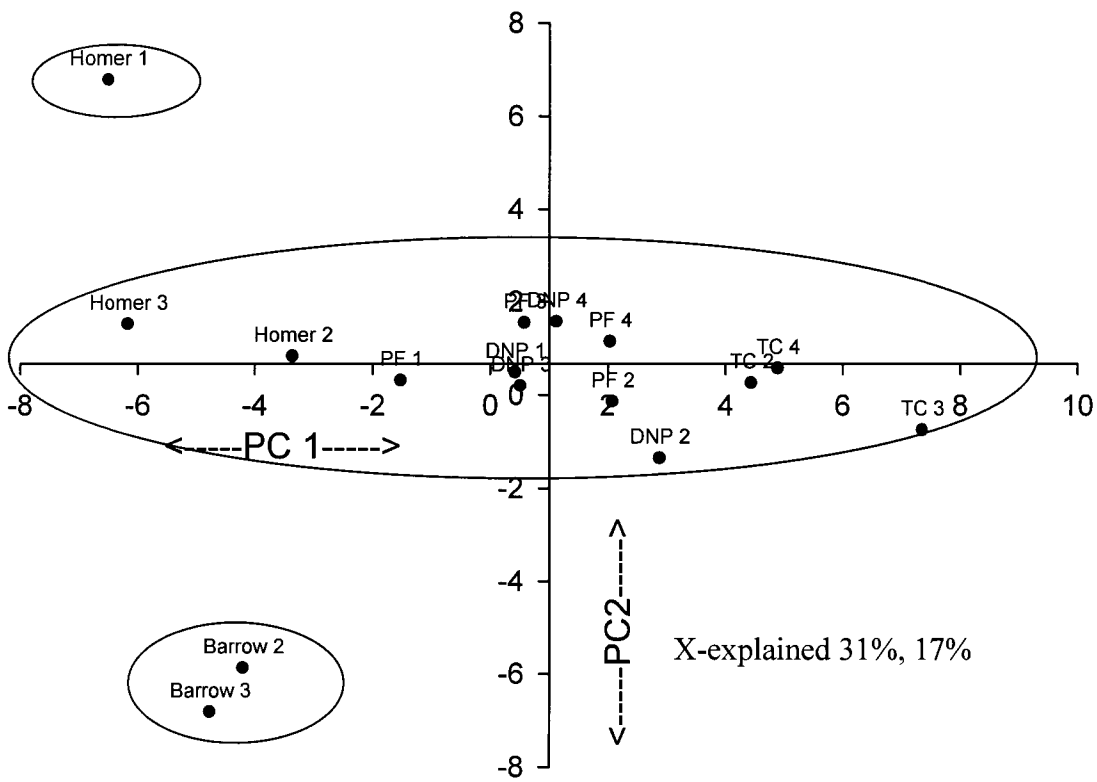


Figure 4.7. The score plot of POP concentrations at five locations and four time intervals gives the position of the samples in the coordinates of the principal components (DNP = Denali National Park and Preserve, TC = Trapper Creek, PF = Poker Flat Research Range, 1 = September-December, 2= December-March, 3= March-June and 4= June-September). Oval outlines represent similar samples.

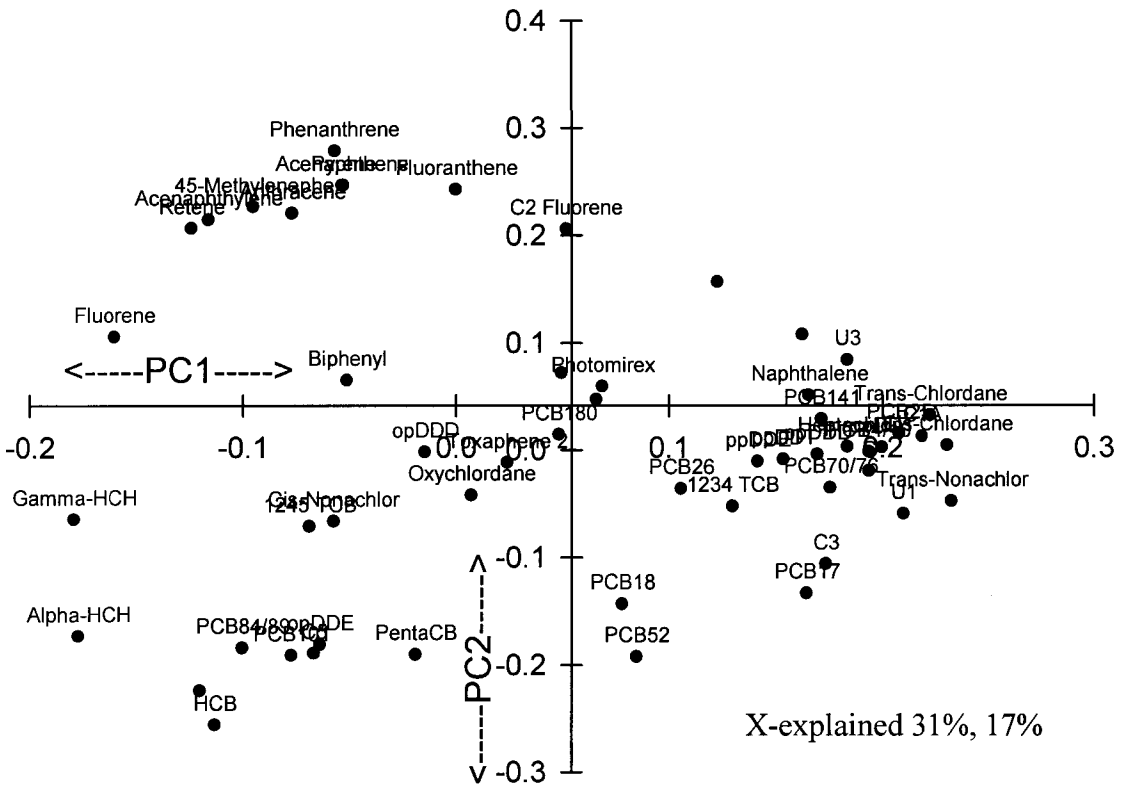


Figure 4.8. The loading plot of POP concentrations at five locations and four time intervals indicates the relationships among compounds and the expected locations of samples in the score plot. Compounds are listed in Appendix B-1.

The compounds that lie near the origin are of little importance to the model in the loading plot (Figure 4.8). Compounds that lie far away from the origin are more important to the model because these variables, with a high degree of systemic variation, usually contained large absolute variances (Esbensen, 2002). The compounds that lie along the same side of the origin along the represented PC are considered to be positively correlated and on opposite sides along a straight line are considered to be negatively correlated. In addition compounds which are 90 degrees to each other through the origin are considered to be independent. Interpretation is necessary to make causal relationships in the correlation. Along PC 1, where 31% of the variance is explained, the majority of the variance is explained by γ and α-HCH and fluorene to the left of the origin and a cluster of compounds located to the right of the origin in Figure 4.8. Evaluation of these compounds' physical-chemical properties suggests differences in volatility could be

causing the separation. The compounds far to the left are considered more volatile than the compounds far to the right along the PC 1 axis. Along PC 2 compounds far from the origin on the positive axis are PAH compounds and compounds far form the origin on the negative axis are organochlorine compounds like hexachlorobenzene (HCB) and PCBs 52 (Figure 4.8). Evaluation of these compounds suggests that the separation could be due to the types of compounds measured. All PAHs were located on the positive side of the origin along PC 2, while organochlorines were more frequently on the negative side. The one distinct difference between the two groups is that the organochlorines contain chlorine atoms and PAHs do not.

4.7. Organochlorines measured in SPMDs

The OCs detected in the SPMDs at the five locations show the following trend for average daily concentrations (the summation of all OCs detected in the SPMD divided by the days of deployment) for all samples: Trapper Creek > Denali National Park and Preserve > Poker Flat Research Range > Homer and Barrow in order of decreasing concentration (Figure 4.9). The summation of toxaphene accounted for the majority of the OC concentration in the SPMDs followed by the DDT group, chlorobenzene group, and HCH group in decreasing order. Typically the more volatile OCs (α-HCH, γ-HCH, HCB, and TCB) were detected at higher levels in the coastal locations (Barrow and Homer). The less volatile compounds (toxaphene, DDT group and chlordane) were detected at higher levels in the interior samples (Poker Flat Research Range, Denali National Park and Preserve and Trapper Creek).

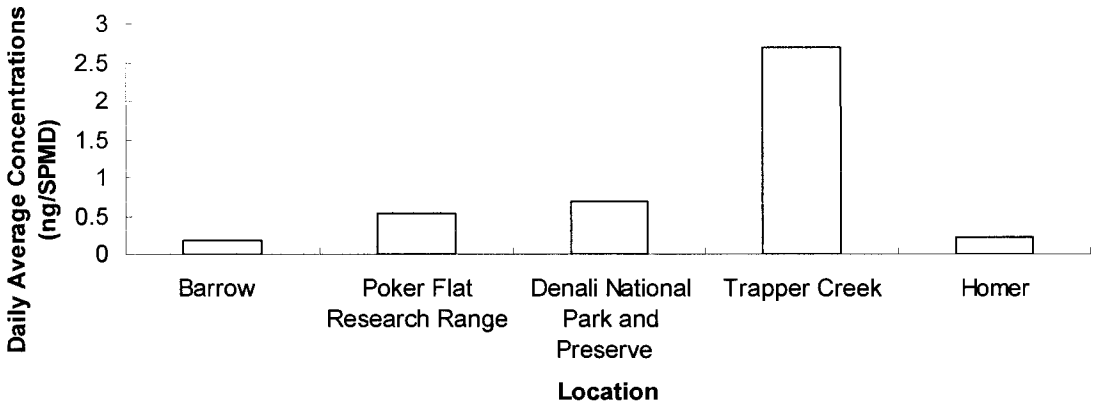


Figure 4.9. The total OCs (sum of all sampling periods) detected in SPMDs divided by the number of days of deployment at five locations in Alaska showed the highest levels to be detected at Trapper Creek.

4.7.1. Chlorobenzenes

Chlorobenzenes are a group of cyclic aromatic compounds consisting of a benzene ring with different arrangements of attached chlorine atoms. They are used mainly as intermediate products in the chemical and pharmaceutical industries. When released in the atmosphere they will exist mainly in the vapor phase at 25°C. The levels of chlorobenzene group compounds are shown in Figure 4.10. HCB was typically detected in the highest amount followed by 1,2,4,5 TCB, PCBz, and 1,2,3,4 TCB in order of decreasing concentration. The exceptions came for four cases (Trapper Creek December-March and June-Sept and Homer September-December and December-March) where 1,2,4,5 TCB had higher levels in the SPMDs. The sum of HCB concentrations at all locations and times totaled 105 ng/SPMD. 1,2,4,5 TCB was close behind at 74.5 ng/SPMD. PCBz and 1,2,3,4 TCB had lower concentrations with summations of 23.8 ng/SPMD and 9.2 ng/SPMD, respectively. Tetrachlorobenzenes and pentachlorobenzene are the most volatile of the OCs measured in the study; however, overall concentrations of these compounds were higher in the colder months than in the warmer months. The average daily temperatures measured at each sampling location are shown in Figure 4.11. An inverse relationship between temperature and concentration of HCB is seen in the Poker Flat, Denali National Park and Preserve and Homer locations.

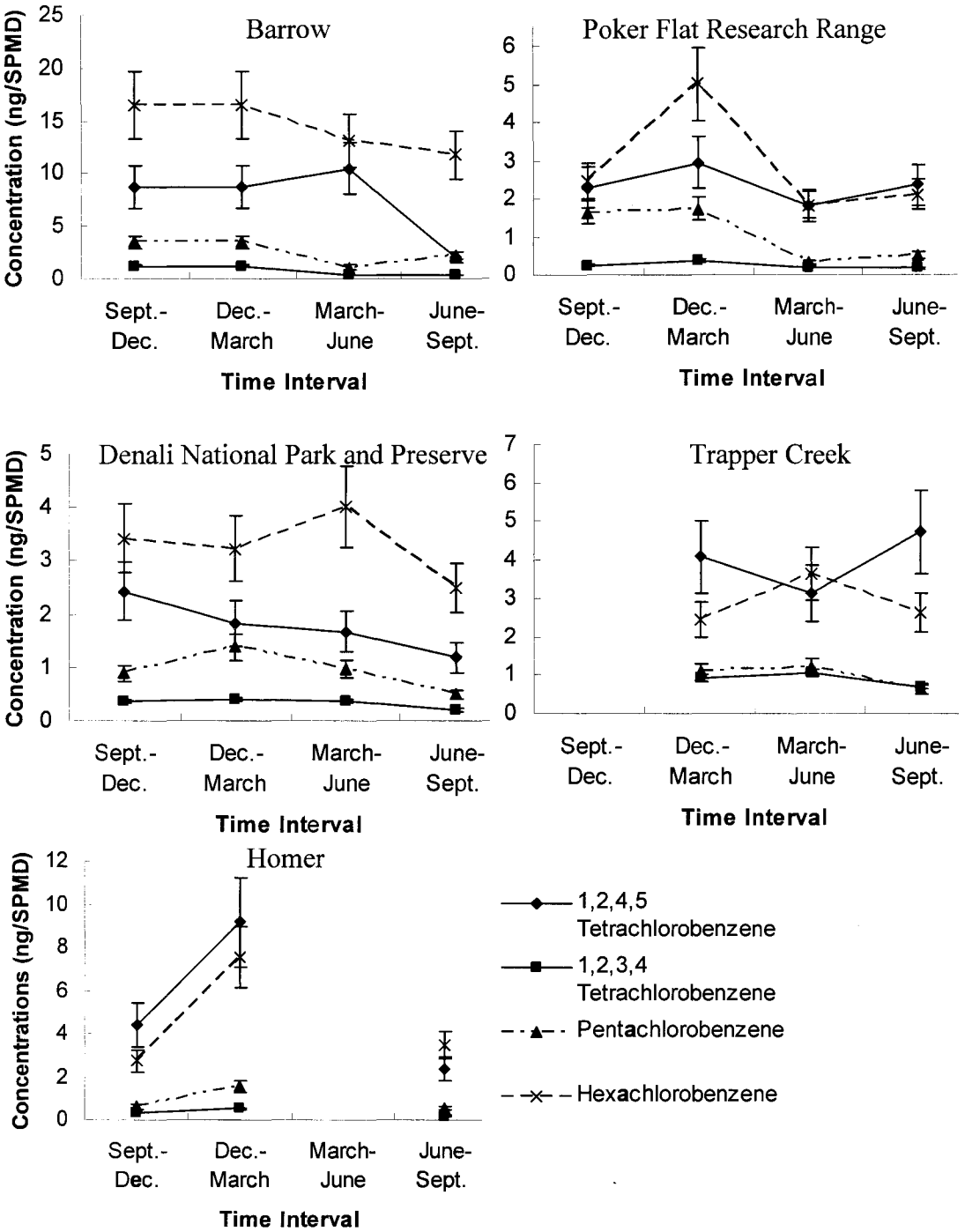


Figure 4.10. Tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

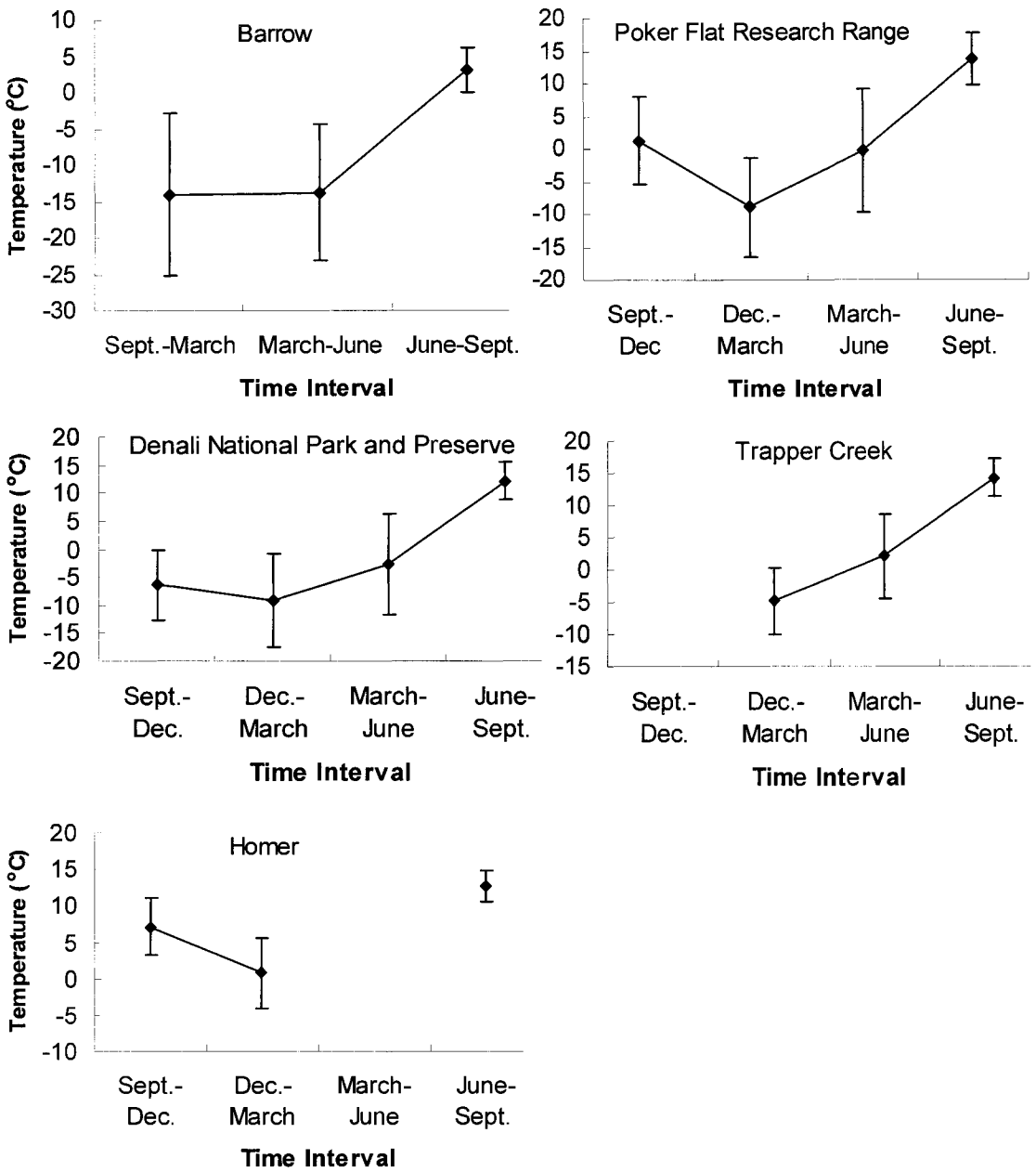


Figure 4.11. The average daily temperatures recorded at the sampling sites during the time intervals corresponding to deployed SPMDs. The first two time intervals (September-December and December-March) in the Barrow plot are the average temperature for September to March. The Trapper Creek September-December and Homer March- June average temperatures are not reported because they correspond to destroyed samples.

4.8.2. Hexachlorocyclohexanes

Hexachlorocyclohexane (HCH) is a chlorinated cyclic saturated hydrocarbon. In the past, technical HCH (a mixture of HCH isomers) and γ -HCH (lindane) have been used extensively as pesticides. Currently, γ -HCH is still used in most countries including the United States because of the lower toxicity in comparison to the other isomers (Willett *et al.*, 1998). Ratios of the isomers are potential useful in determining sources. The levels of HCH isomers are shown in Figure 4.13. γ -HCH had the highest concentrations, followed by α-HCH. β-HCH and δ-HCH were not detected in high enough concentrations to report at all locations and time intervals. A greater seasonality in γ-HCH concentration was noted in the Denali National Park and Preserve and Homer samples. Higher levels of HCH were detected in the costal samples (Barrow and Homer) than in the inland samples. The Interior samples had similar HCH vales ranging from approximately 0.6 ng/SPMD to 5.6 ng/SPMD. The ratio of α-HCH to γ-HCH averaged 0.18 and ranged from approximately 0.05 to 0.35 at the five locations in Alaska (Figure 4.12). These ratios suggest a higher source of γ-HCH in the ambient air of Alaska.

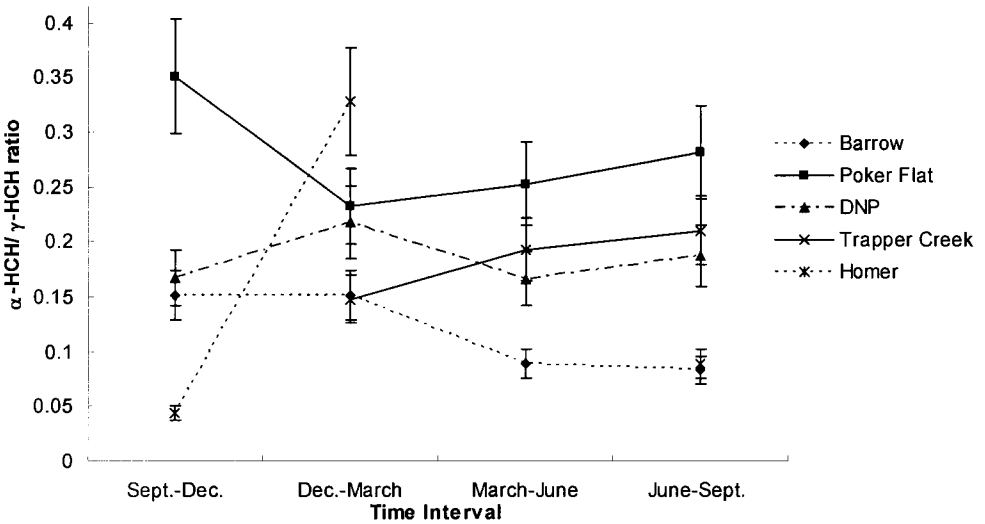


Figure 4.12. α-HCH to γ -HCH ratios detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment. Error bars are based on RSD% of the chemical from the four replicates measured at Poker Flat Research Range.

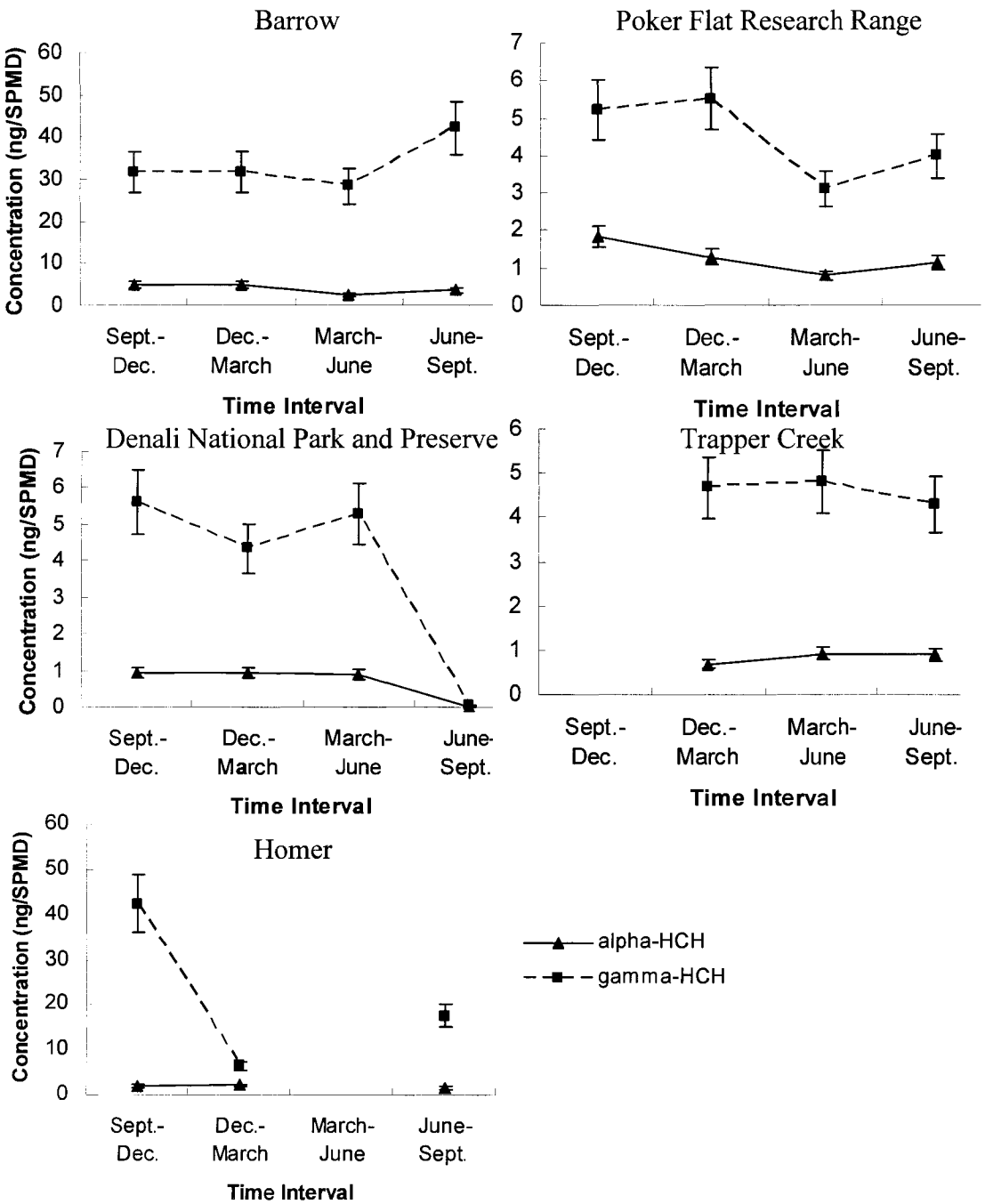


Figure 4.13. α-HCH, and γ-HCH levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and Dec.-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

4.7.3. Chlordanes and nonachlors

Chlordane is a pesticide widely used in the 1980s. A chlordane mixture consists of trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor and heptachlor. The major metabolite of the chlordanes and nonachlors is oxychlordane. Concentrations of chlordanes and nonachlors detected in SPMDs at the five Alaska locations were relatively low and are reported in Figure 4.15. Trans-chlordane typically had the highest concentration followed by cis-chlordane and trans-nonachlor in order of decreasing concentration. Oxychlordane and cis-nonachlor had similar levels and had concentrations lower than trans-nonachlor. Levels in the Interior samples were typically two fold higher compared to the costal samples (Barrow and Homer). The ratio of trans to cis-chlordane detected in SPMDs at all locations average 1.2 and ranged from approximately 0.7 to 1.3 (Figure 4.14). Changes in the ratios can result from differences in degradation rates after release into the atmosphere.

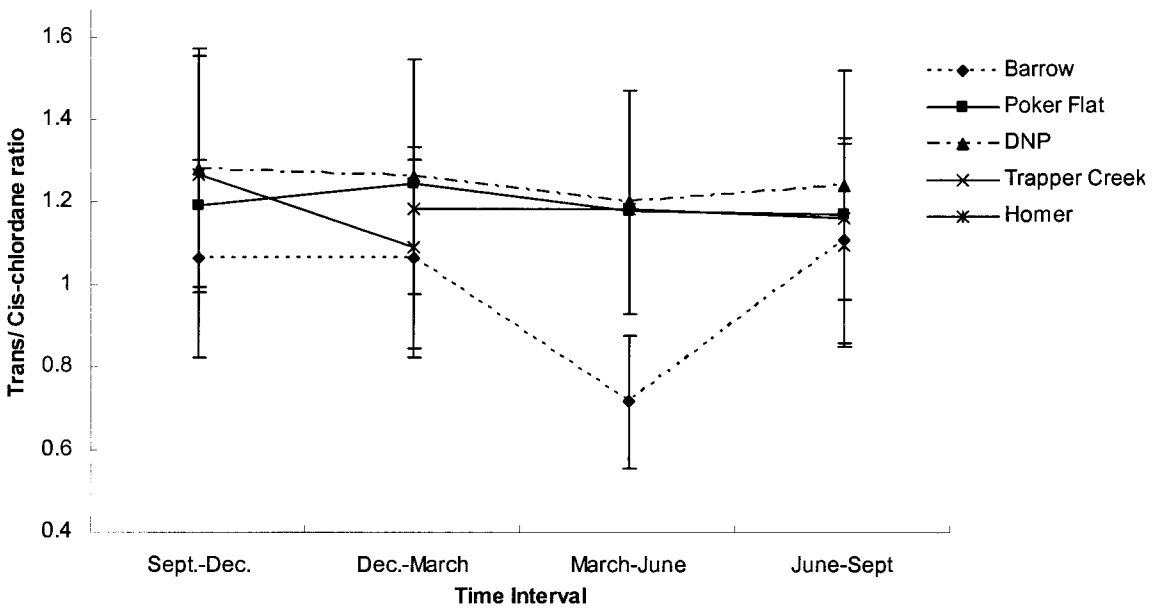


Figure 4.14. Trans to cis-chlordane ratios detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

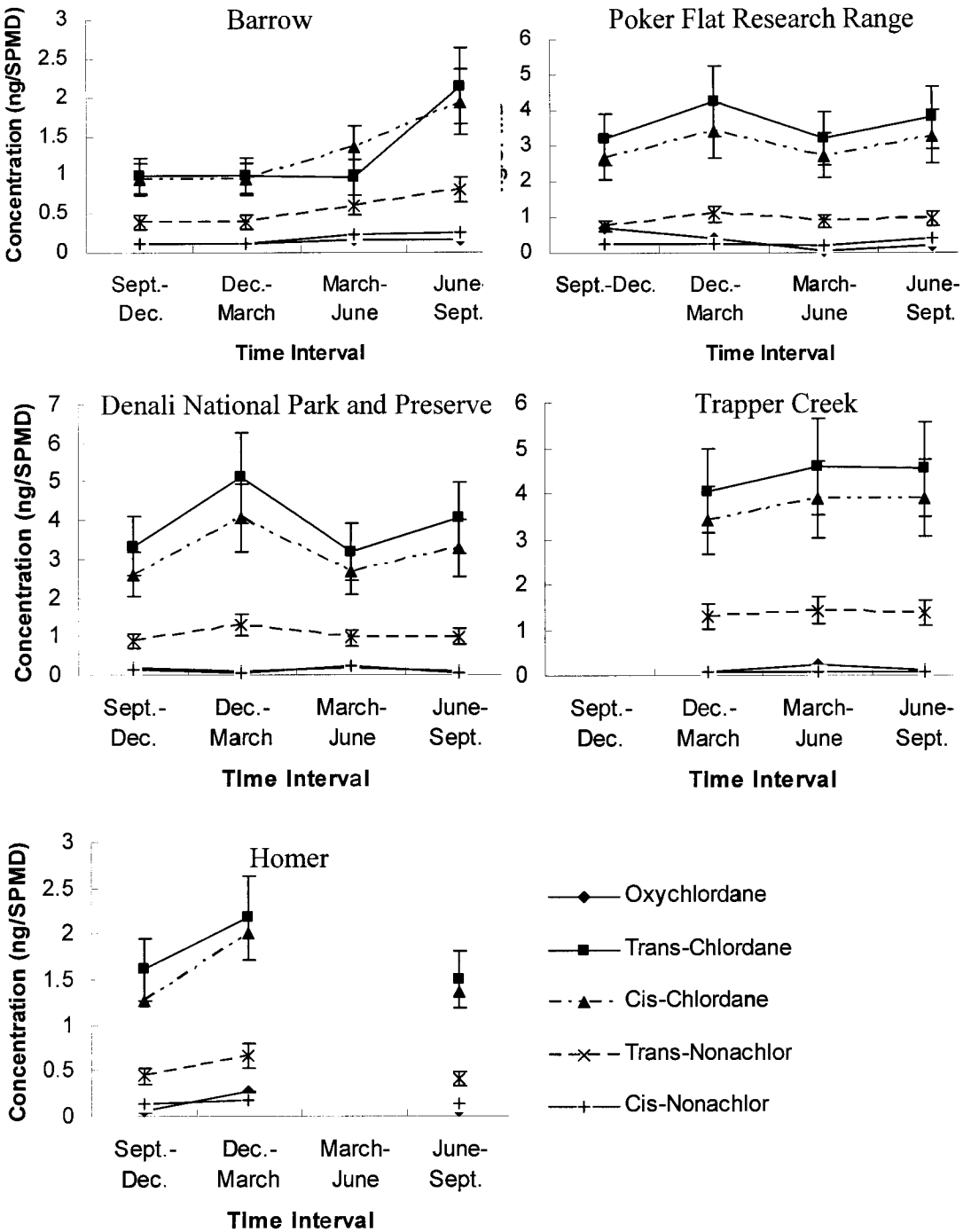


Figure 4.15. Chlordane and nonachlor compounds levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

4.7.4. DDT group compounds

DDT is a pesticide used to control vectors and is currently banned in most countries. DDT can be broken down to DDE and DDD. The percentage of DDT to total DDT (DDT and its metabolites) detected in SPMDs at the five locations in Alaska ranged from 10 to 70% (Figure 4.16). The Interior locations had higher percentages compared to the costal sites (Barrow and Homer). A higher level may suggest fresh input of DDT from source regions or aged DDT (DDT present in the environment that has resisted degradation over time). Concentrations of DDT and its metabolites are reported in Figure 4.17. p,p'-DDE was typically the dominant compound with the exception at two locations (Poker Flat and Denali National Park and Preserve) where p,p'-DDT had higher levels detected in SPMDs for the September to March and the June to September samples in Denali National Park and Preserve, and March to September samples in Homer. The highest levels of p,p'DDT and p,p'DDE were detected in the March to June samples at Trapper Creek with levels at approximately 150 ng/SPMD and 185 ng/SPMD, respectively. The concentrations were around a 100 fold larger than measured at some locations. DDD metabolites were detected in the least amounts at all five sites.

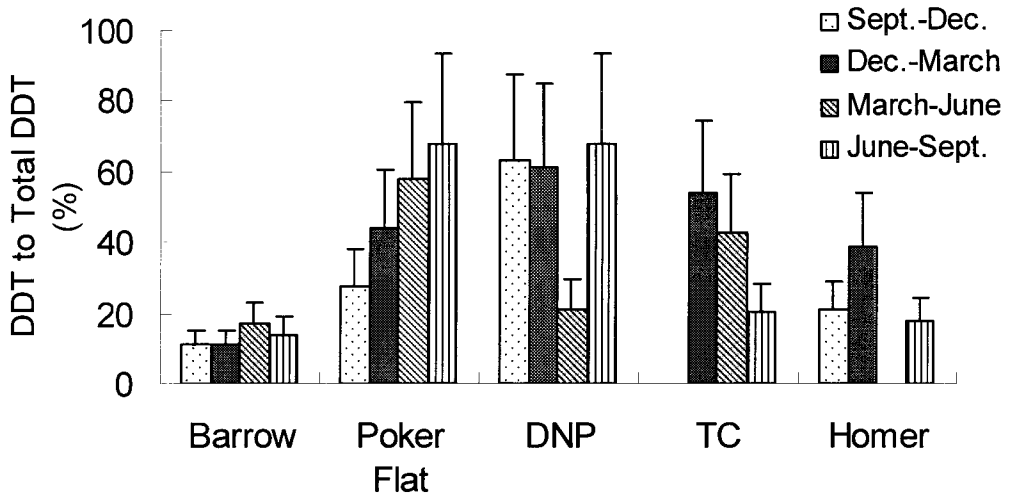


Figure 4.16. The sum of DDT (p,p'-DDT and o,p'-DDT) to total DDT (DDT, DDE, and DDD) expressed as a percentage with a standard deviation. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidental doubled sampling duration. The Trapper Creek September-December and Homer March-June levels are missing because of damage to vials during shipment.

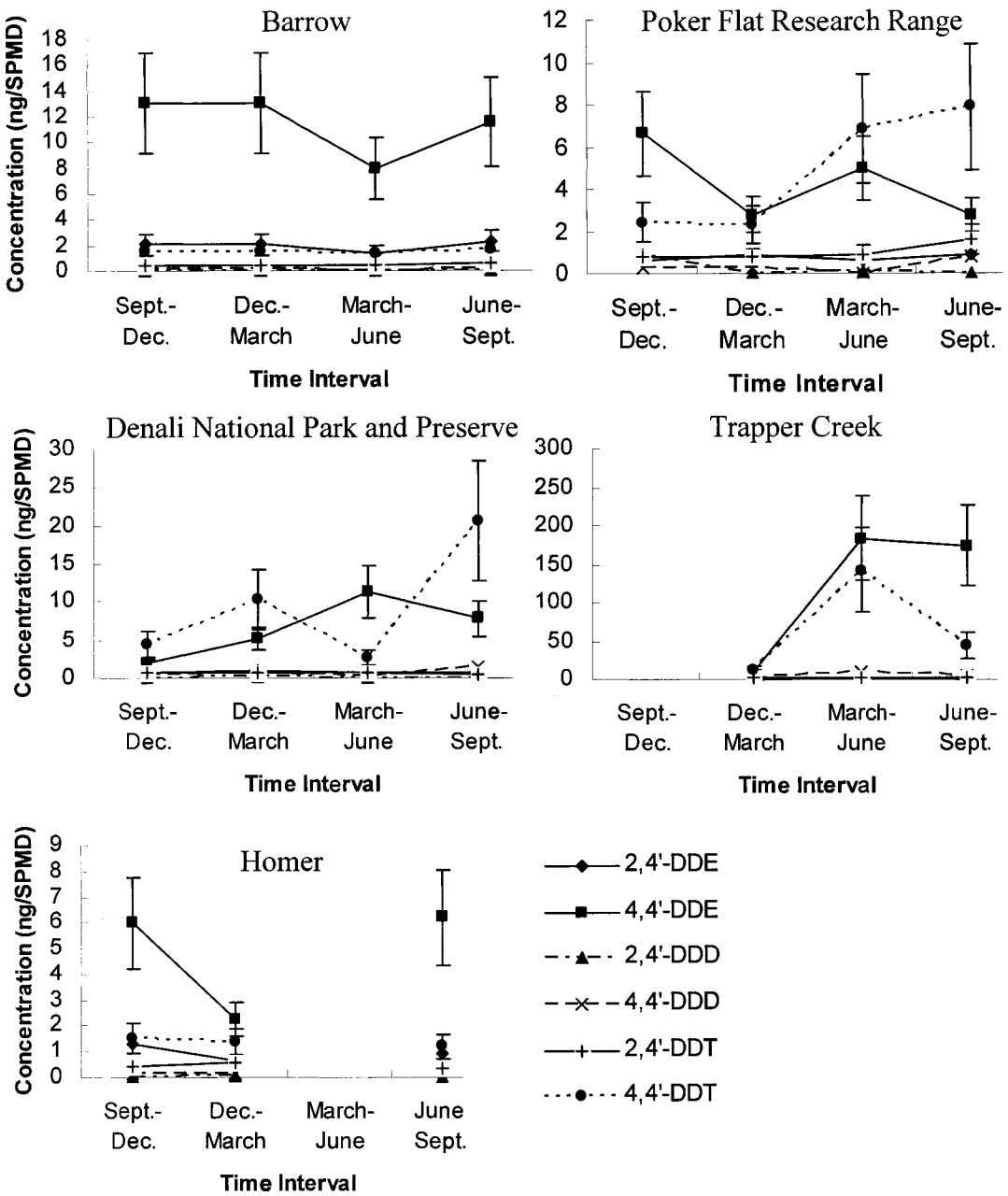


Figure 4.17. DDT and DDT metabolites levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

4.7.5 Toxaphene

Toxaphene is complex mixture of chemicals that consists mainly of chlorinated bornanes. It was used widely as a pesticide in the USA prior to it being banned in the early 1980's because of its environmental persistence and toxicity (Saleh, 1991). The estimated past global production of toxaphene is 1.33 million tons, with the USA accounting for more than 40% of the usage (Li *et al.*, 2001). Although currently banned in the USA, toxaphene is still being applied in Mexico and the former Soviet Union (Voldner and Li, 1993).

The summation of toxaphene detected in SPMDs at all locations for the different time intervals is presented in Figure 4.18. The highest level, approximately 500 ng/SPMD, was detected at Trapper Creek, during the December to March deployment. The Interior sites have relatively higher levels when compared to the coastal sites (Barrow and Homer). No distinct patterns of concentration in relation to the seasons were seen. Summations of toxaphene at each location showed Trapper Creek to have the highest levels followed by Denali National Park and Preserve, Poker Flat Research Range, Barrow and Homer in order of decreasing concentrations.

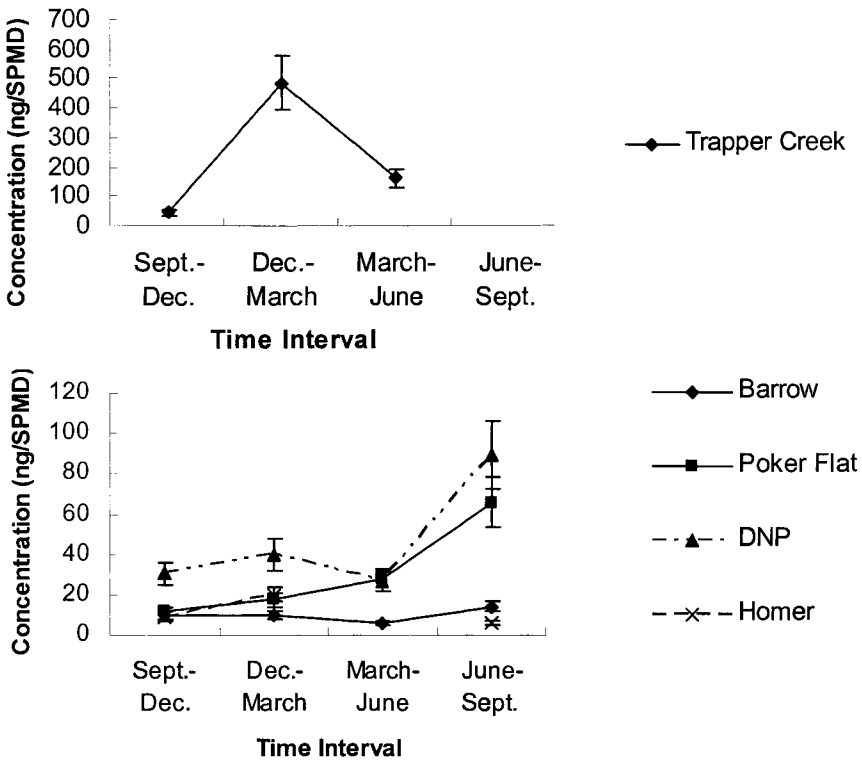


Figure 4.18. The summation of toxaphene represented at five locations in Alaska. Trapper Creek levels were placed on a separate graph because of the scale difference. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

4.8. Polychlorinated biphenyls measured in SPMDs

Overall PCB levels were relatively low in comparison to the other contaminants. Summation of PCB concentrations ranged from approximately 7 ng/SPMD to 25 ng/SPMD (Figure 4.19). The highest summation of PCB levels was detected at the Trapper Creek site. Concentrations were further separated into six groups based on the degree of chlorination (Figure 4.20). The tri-chlorinated PCBs were typically dominant in concentration at all the sites with the exception of Barrow, where penta-chlorinated PCBs dominated. The highly chlorinated hepta group was detected in the lowest concentration at all the sites. No strong seasonal trends were observed when the concentrations were

compared to the recorded average temperatures at each site. The individual groups were fairly similar in concentrations at all the sites.

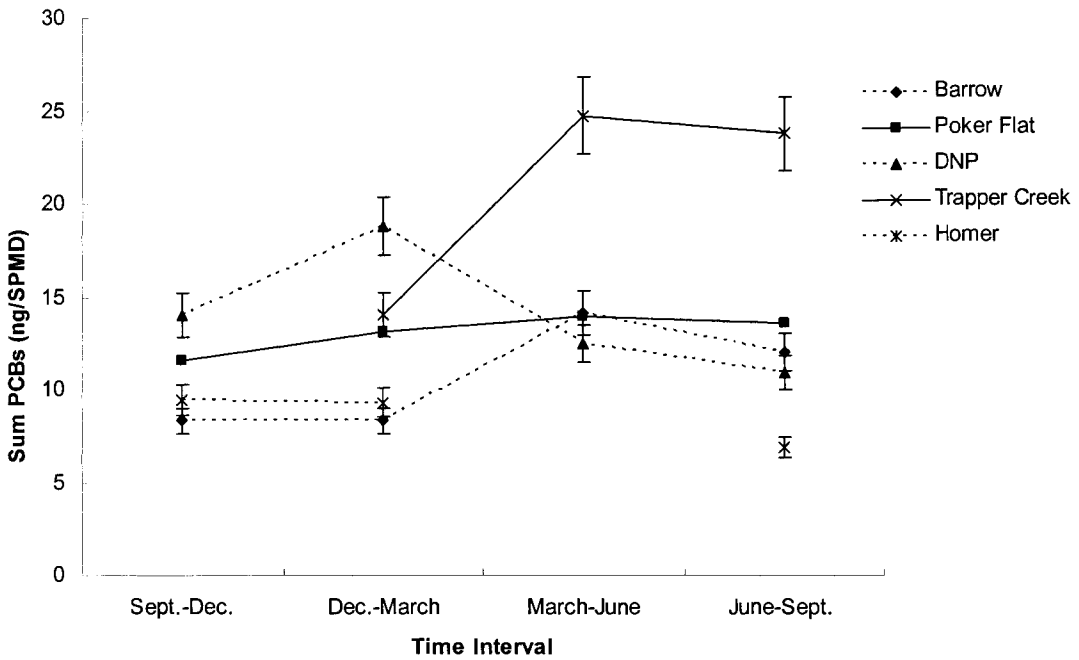


Figure 4.19. Summation of PCB levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

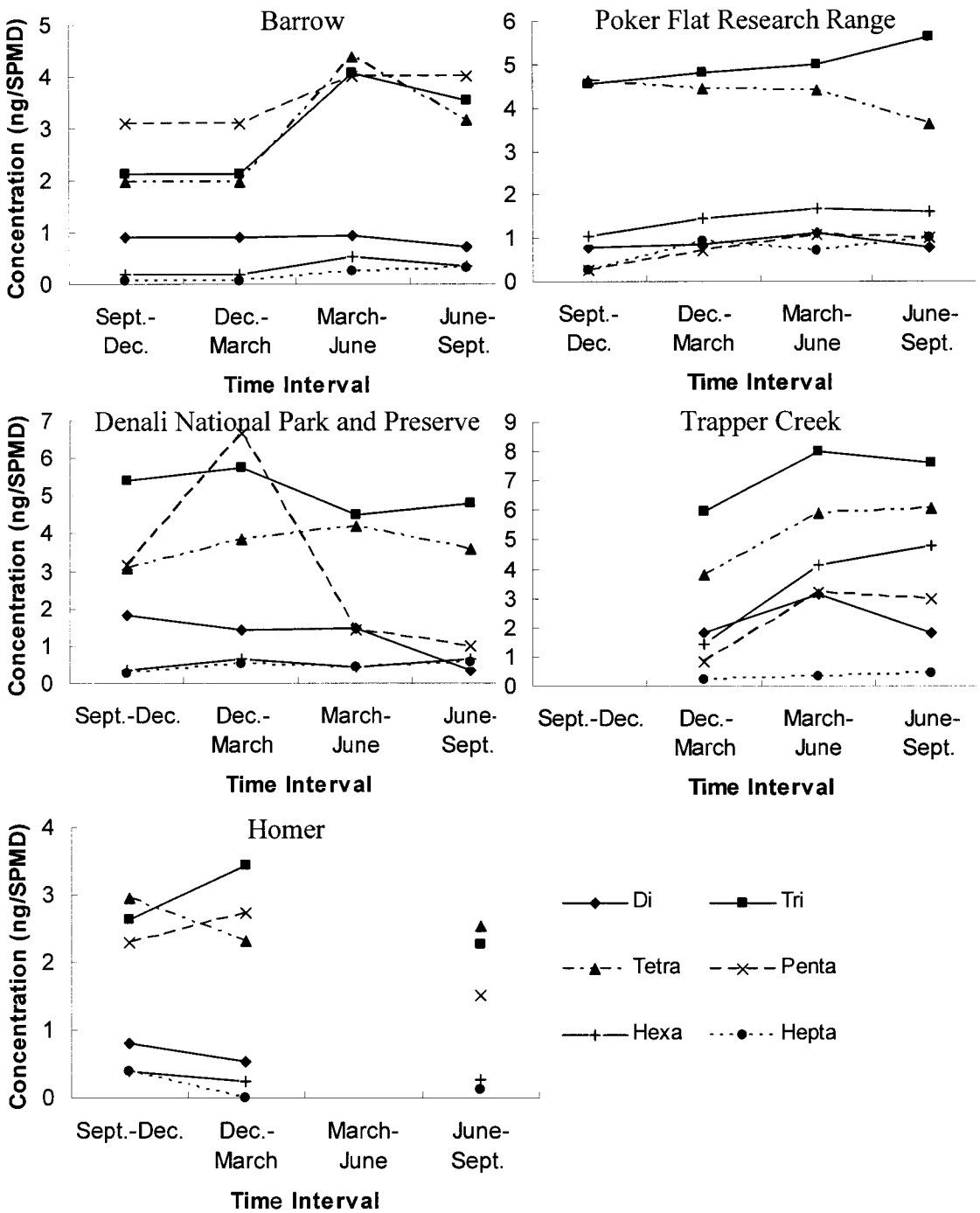


Figure 4.20. Summation of PCB levels separated by degree of chlorination detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

4.9. Polyaromatic hydrocarbons measured in SPMDs

The sum of PAH levels showed Homer had the highest concentration of PAHs, approximately 350 ng/SPMD, during the September to March sampling time (Figure 4.21). The summation of the different types of PAHs detected at all sites and sampling periods in SPMDs showed phenanthrene to be at the highest concentration at 1μg/SPMD. The Barrow samples showed a slight increase in total PAH concentrations during the colder periods.

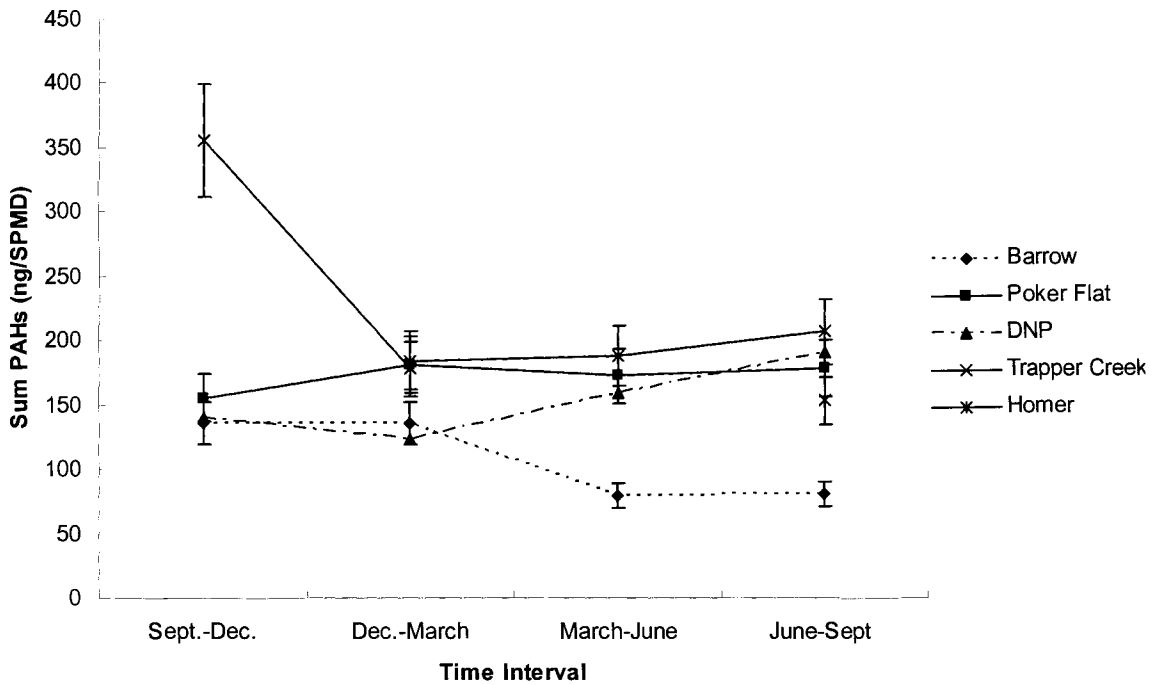


Figure 4.21. Summation of PAH levels detected in SPMDs at five locations in Alaska during different time intervals. The values shown in the first two time intervals (September-December and December-March) in the Barrow plot are the six-month sampling concentrations divided by two to account for the accidentally doubled sampling duration. The Trapper Creek September-December and Homer March- June levels are missing because of damage to vials during shipment.

The ratios of select PAHs have been examined for use in source identification (Yunker *et al.*, 2002). Multiple ratios are useful in comparing different sources, due to overlaps in characteristic PAH patterns from each source and the selective decay of more labile PAHs. A single ratio may not be definitive in determining sources. The ratios of phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (Fl/Py) were plotted against each other for a source determination of the PAHs in the SPMDs at the five locations (Figure 4.22). The Ph/An ratios ranged from approximately 10 to 70 with a majority of the ratios centered around 10 to 20. Less variability was seen in the Fl/Py ratios (ranging from ≅1.1 to 2.3) measured in the SPMDs. The Fl/(Fl +Py) ratios ranged from 0.53 to 0.70. PAH ratios used to determine potential sources are listed in Table 4.29.

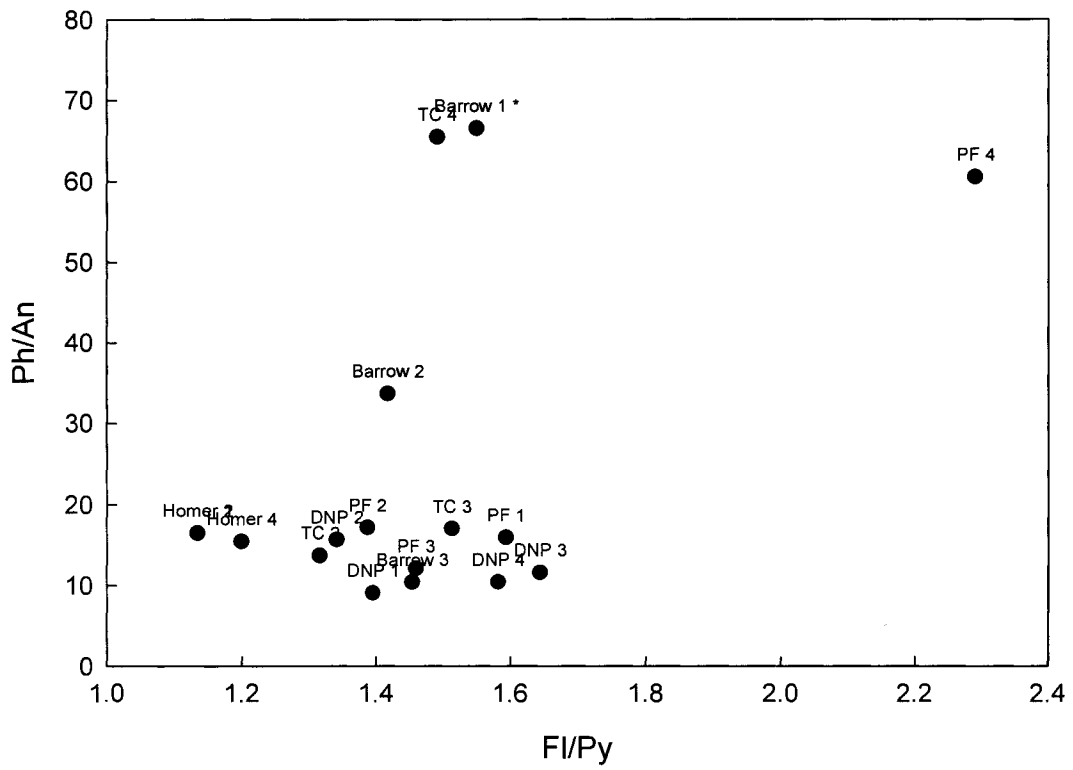


Figure 4.22. The ratios of phenanthrene to anthracene (Ph/An) plotted against fluoranthene to pyrene (Fl/Py) detected in SPMDs at five locations (PF= Poker Flat Research Range, TC= Trapper Creek and DNP= Denali National Park and Preserve) in Alaska during different time intervals (1= September-December, 2= December-March, 3= March-June, and 4= June-September). The Barrow 1* is a measurement from Sept.-March. Trapper Creek (September-December) and Homer (March- June) ratios are missing because of damage to vials during shipment.

Table 4.29. PAH ratios used to determine potential sources.

	Indication of Source		
Ratio	Petrogenic	Pyrogenic	Reference
Ph/An	> 25	<10	Budziski *et al.*, 1997
Fl/Py	<1	>1	Yunker *et al.*, 1999
Fl/(Fl +Py)	<0.40	0.40-0.50 combustion of liquid fossil fuel; > 0.5 grass, wood & coal	Yunker *et al.*, 2002

Chapter V
Discussion

5.1. Using SPMD in Alaska

Passive air sampling is becoming more prevalent for monitoring of semi-volatile organic contaminants. A variety of passive air samplers are being utilized in a wide range of geographical locations to monitor organic pollutants. However, these samplers are not frequently utilized in locations where they would be the most beneficial, like the Arctic. The fact that POPs can migrate into the Arctic, coupled with the remoteness and size of the area, makes passive sampling very attractive. Having samplers with no maintenance requirements, low cost and easy deployment is advantageous in the Arctic.

In this study, SPMDs were evaluated for use in Alaska. Unlike other locations where SPMDs have been deployed in the atmosphere, Alaska has some unique environmental conditions that are associated with its location in the Arctic. These conditions include temperatures that can reach below -40°C during the winter and 24 hour sunlight during summer periods. Although these conditions can have direct influences on atmospheric POP concentrations, they may also alter relationships between concentrations measured in SPMDs and the sampled air.

Contaminant concentrations measured in the blanks were lower than in the actual samples; however, higher values of the more volatile compounds, like naphthalene, were seen in the blanks and should be addressed. Absorption of these compounds likely occurred during transport of the SPMDs to their respective locations and not during storage in the laboratory, since they stored at -40°C in the lab and are different from site blank to site blank. Compounds detected in the blank from Barrow were lower than in a blank that travel to the other locations; this is likely because of the lower contaminant levels in general for the Barrow site. Placing the SPMD containers on ice during transport should help reduce the contaminant levels detected in the blanks during future studies because the colder temperatures reduce uptake of contaminants into SPMDs.

The reproducibility in the SPMDs in this study was similar to others reported in the literature. The RSD% for PAHs reported by Bartkow *et al.* (2004) ranged from 34% to 3%, with most < 20% and was similar to RSD% in PAHs reported here. Good reproducibility has also been seen in polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs) and PAHs in other studies like Lohmann *et al.* (2001). However in Lohmann *et al* (2001), concentration differences for PCDD/Fs between the SPMDs increased slightly with increasing chlorination and it was suggested that these heavier compounds would have been largely particle associated, leading to quantification differences. That was not the case with the PCBs in this study. No distinct pattern of decreasing reproducibility, represented by RSD%, with increasing chlorination was seen and large increases in RSD% were likely the result of the low concentrations measured, which adds to the relative quantification errors.

Although SPMDs are mainly used to sample for vapor-phase organic contaminants, it is speculated that contaminants adhered to particles that are absorbed onto the membrane or lipid on the exterior of the SPMD may diffuse into the triolein of the SPMD. The possibility of sampling particulate-bound contaminants was examined by exposing SPMD to filtered and non-filtered air. No signification differences (α= 0.05) were seen between the different SPMDs for OC and PAH measurements. However, there were significant differences in the PCBs measurements, even with the fact that the surface of the membrane was cleaned prior to chemical analysis. The difference in concentrations suggests that the PCBs bound to the surface of particulates eventually transfer into the triolein. PCBs with more substituted chlorine atoms were measured at higher concentrations and more frequently in SPMDs exposed to non-filtered air as opposed to filtered air. The percentage of PCBs in the particulate phase has been shown to increase with chlorine substitutes for PCBs in samples taken from Chicago air (Harner and Bidleman, 1998).

It is suspected that a significant difference between the OCs and PAHs measured in the filtered and non-filtered air was not seen here because of flow rate differences between the canisters for the two experimental setups. The flow rate was measured at the

beginning of the study, but not continuously throughout the study. If an increase in the flow rate for the filtered air occurred during the six month sampling period, the uptake of gas phase PAHs and OCs would have increased, since uptake of contaminants is positively correlated to turbulence around the SPMD (Söderstrom and Bergqvist, 2004). Thus, even if more particulate OCs and PAHs are detected in the SPMD exposed to non-filtered air, the SPMD exposed to filtered air could have sampled the same compounds in the gas phase at a higher rate resulting in no difference between the two measurements. Evidence for the higher sampling rates because of increased flow rates can be seen in the more volatile PAHs, which are expected to have much higher concentrations in the gas phase. Here levels of naphthalene, 2-methylnaphthalene and 1-methylnaphthalene were approximately a factor of 2 greater in concentration in the SPMD exposed to filtered air. These higher concentrations were measured in the filtered air experimental setup due to the increased air flow.

Other explanations for not seeing significant differences between OC and PAH concentrations measured in the filtered and non-filtered air could be due to increased temperature, which could caused OCs and PAHs trapped particulates on the SPMDs to desorbed, or a very clean air mass that could cause the contaminants to desorbed. These two explanations are probably unlikely, since the canisters housing the SPMDs were set up in a laboratory with a controlled room temperature and sampling occurred over a heavily used parking lot at UAF. In addition, the high triolein to air partitioning coefficient will likely prevent contaminants from desorbing to the air when exposed to clean air masses.

The reasoning for significant differences for PCBs, even with inconsistent air flows, can be explained by low vapor pressure of highly chlorinated PCBs. Even with increased flow rates for the SPMD exposed to filtered air, the lack of gas phase PCBs associated with more substituted chlorine atoms will not result in increased concentrations because of the filtering process. PCB 194, 195, 206 and 207, which contain eight and nine chlorine atoms, were not detected in the SPMD with filtered air, but trace levels of these compounds were detected in the SPMD exposed to non-filtered

air. These highly chlorinated PCBs were likely associated with particulates and filtered out by the Teflon filter prior to reaching the SPMD. Measurements from Harner and Bidleman (1998) showed the average particulate percentage associated with octa-chlorine substituted PCBs to be 79.5% in air measurements.

Photodegradation represents a critical transformation pathway for some POPs, particularly many PAHs (Niu *et al.*, 2003 and 2004). During the summer months the Arctic environment is exposed to prolonged sunlight. While photodegradation is an important element in the removal of contaminants present in the air, photodegradation could alter the POP concentrations already measured by SPMDs and make comparisons of levels from other locations and times difficult without compensating for the lost POPs. The long sampling times, large variability in sunlight exposure and different degradation rates for each compound can make compensating for the contaminants lost within the SPMD difficult or nearly impossible. To decrease some of the exposure to sunlight a deployment unit was developed here and comparisons were made to determine if the deployment unit help minimize degradation of POPs by sunlight.

The experimental results lead to the same conclusion as Alvarez *et al* (2005). where SPMDs spiked with perdeuterated PAHs and exposed to sunlight showed that after 28 days SPMDs not fully protected from sunlight had significantly decreased PAH concentrations compared to protected SPMDs. In this study, higher concentrations of PAHs were also seen in a SPMD protected from sunlight as opposed to a SPMD not fully protected from sunlight. Although a glass cover was used to partially protect the SPMD, Figure 4.1 showed partial transmittances of UV-B and A were permitted to allow photolysis to occur. It should be noted that only a small amount (approximate range of 0-20% transmittance) of the UV-B radiation was allowed through the glass cover and a larger portion of UV-A (approximate range of 20-85% transmittance) was allowed through the cover. There are three likely scenarios by which photolysis reactions could occur inside the deployment unit and lead to decreased PAH levels measured in the sunlight-exposed SPMD: 1) photodegradation of airborne PAHs within the deployment unit before the compounds enter the SPMD, 2) photodegradation of PAHs on the surface

of the SPMD, and/or 3) photodegradation within the triolein. All scenarios would lead to decreased PAH concentrations in the sun-exposed SPMD.

While sunlight is an issue for photodegradation of PAHs in SPMDs during the summer periods in the Arctic and sub-Arctic, it is less of a concern during the winter periods. The uptake of contaminants by passive sampling media has been shown to be largely controlled by the air-side mass transfer coefficient and based on molecular diffusivity (Shoeib and Harner, 2002a). Molecular diffusivity is considered a weak function of temperature and calculations suggest over a 20°C temperature change the diffusivity will only increase by the small factor of 1.13 (13%). A study in water showed sampling rates increased by a factor of 3 over the temperature range of 2°C to 30°C (Booij *et al.*, 2003). The uptake rates for these studies are true for temperate temperatures, but at lower temperature one must take into account the restriction in the membrane.

Although molecular diffusivity does not change much with temperature, a reduction in the polymer chain movement at lower temperatures can occur and limit the uptake of contaminants into the triolein. The uptake results at different temperatures showed a decrease in POP concentrations in SPMDs with decreased temperatures. The calculated uptake rates for the three compounds tested (lindane, DDE and DDT) dropped factors of 5, 14 and 26, respectively, as the temperature range dropped from 10°C to -8°C. These results suggest greater steric hindrance in the diffusion of these compound in the membrane in the following order DDT >DDE >lindane (DDT has the greatest steric hindrance). This supports findings by Saleem *et al.* (1989), where diffusion coefficients of various compounds in low density polyethylene decrease with increasing compound size, decreased temperature and a more rigid shape. Permeation through the membrane will therefore be the rate limiting step in the uptake of POPs into SPMDs at lower temperatures because the size and the shape of the compounds allowed through the LDPE membrane is more restricted.

The calculated air concentrations used in developing the uptake rates at the three different temperatures must be somewhat correct for the decrease to be certain, since

uptake rates were calculated based on the ratio of the concentrations measured in the SPMD to the calculated air concentration generated and multiplied by the number of days (equation 6). The contaminant concentrations in the SPMDs have more certainty than the air concentrations, since they were directly measured. The air concentrations have less certainty than the SPMD concentrations since they were based on gravimetric loss of contaminants from permeation tubes, air flow rates and loss of contaminant into upstream SPMD(s). These air concentrations are more likely to be overestimated than underestimated, since decreases in contaminant air concentrations are more probable in the system than gains. Two possible mechanisms for decreased air concentrations include leakage from sealed canisters and/or adhesion of compound onto the surface of the canisters. If air concentrations were overestimated, then there would be an increase in the uptake rates and less of a change between the different temperature ranges, which is not the case here. The air flow needed to generate contaminant air concentrations in the canisters caused turbulence around the membranes that likely increased the uptake of contaminants into the membranes, thus these calculated uptake rates are not applicable for the field calculations where deployment units were used to minimized wind exposure. But, for a relative comparison of POPs sequestration at different temperatures in the laboratory, these uptake rates are useful, since the turbulence is likely to be the same for the laboratory control studies.

The difference in the air sampling rates for DDE and DDT indicate that ratios of similar compounds may not be directly related to atmospheric ratios at lower temperatures. These differences are attributed to changes in the calculated air sampling rates because of more steric hindrance by the larger parent compound (in DDT case is the addition of a chlorine atom) at lower temperatures and differences in the triolein to air partition coefficient for the compounds measured. The increased resistance of the parent compound would lead to lower DDT to total DDT ratios and decreased DDT to DDE rations. The results here then suggest that the field ratios for DDT to DDE are biased toward higher DDE levels and lower DDT levels at lower temperatures.

Good agreements have been seen in the literature between calculated air concentrations from passive air samples and air concentrations from active air samplers during simultaneous sampling (e.g. Gouin *et al.*, 2005a; Bartkow *et al.*, 2004). Agreements were within a factor of 3. The results from this study were slightly higher for the PAH comparisons and agreements were within a factor of 6.5. The longer deployment times and lack of air sampling rates at Arctic temperatures can influence the concentration comparisons. The air sampling rates used for the calculations were taken from the literature where measurements were made at 22°C as opposed to being measured at the average air temperature measured (-14°C) during the study. The higher temperature air sampling rates likely resulted in underestimated air concentrations derived from the SPMD measurements at lower average temperatures. In addition, concentrations from the active air sampler were reported as gas and particulate-bound concentrations while the SPMDs were only used to sample gas phase contaminants.

5.2. POPs detected in Alaska using SPMDs

The results of the present study using SPMDs for air monitoring demonstrate the presence of a wide range of trace POPs in the ambient Alaska air at all locations sampled. Sources of these POPs can be attributed to local sources, distant sources, or a mixture of both. The POPs could be from a recent release or an aged past release that is still lingering in the area. Although these contaminants are assumed to be not widely utilized in Alaska, continued increases in human population and military facilities in Alaska have resulted in the use of these chemicals in Alaska (Table 5.1).

A variety of persistent organic contaminants have been identified in aboitic and biotic samples in Alaska. Specific organic contaminants measured include: PAHs in spruce needles (Howe *et al*, 2005); OCs in ring seals and polar bears (Kucklick *et al.*, 2002); and OCs and PCBs in eggs of common and thick-billed murres (Vander Pol *et al.*, 2004). Measured concentrations of these contaminants can be highly variable depending on the sampling medium and location.

Table 5.1. Areas in Alaska where local sources of POPs are of concern (Table is modified from AMAP, 2004).

Site	Possible POPs of concern	Reference
Adak Island (Aleutian Islands)	Solvents	1,3
King Salmon Air Station	Solvents	1,3
Pribilof Islands	Fuel	1,3
St. Lawrence Island	Fuel	1,3
Cape Romanzof Long Range Radar Site	Solvents	1,3
Umiat (former Air Force Base on Colville River)	Solvents	2,3
Operable Unit D, Fort Richardson	Solvents	1,3
Dutch Harbor, Unalaska	Fuel	2,3
Yakutat Airport	Fuel	2,3
Barter Island (Kaktovik)	PCBs	2,3
Wildwood AFS	Dioxins	2,3

1 www.state.ak.us/dec/spar/csp; 2 www.poa.usace.army.mil/fuds; 3 www.akaction.net/pages/mapping

Because of the lack of air sampling rates for individual POPs into SPMDs at various temperatures, no transformations of the concentrations of specific POPs in SPMDs for the field samples were made during the evaluations of measurements at the five locations. Thus, the values reported in the results section are considered semi-quantitative for discussion purposes.

The numerous compounds screened for in this study can be difficult or time consuming to relate. Multivariate analysis was useful in making the task less complicated and more visual. By normalizing all the POP concentrations measured the relationships between compounds could be visualized with principal component analysis. Correlations between parent and daughter compounds are expected in some degree but correlations between unrelated compounds may be less apparent but potentially provide useful information. For example, chlordane and HCH are not directly related structurally, but along PC1 (Figure 4.8) they are negatively correlated. After further evaluation, it is apparent that higher concentrations of chlordane, a more hydrophobic and less volatile compound was measured in the Interior samples compared to the coastal samples from Barrow and Homer. While HCH, a less hydrophobic and more volatile compound, was

measured at higher concentrations in the coastal SPMD samples than the Interior samples. In addition, total POP concentrations were higher in Interior samples than coastal samples.

The one common feature between the two coastal samples is the close proximity to a large body of water. However, during the winter and spring months in Barrow ice covers the majority of the coastal area and open water is not the case. During these sampling periods the colder temperatures are likely the cause of lower POP concentrations measured by the SPMDs compared to Interior samples. On the other hand, decreased POP concentrations for the Barrow summer samples and Homer samples may be due to processes occurring over the oceans. It has been shown that biogeochemical processes in the ocean, such as phytoplankton uptake and vertical fluxes of particles, play a critical role in the global dynamics and ultimate sinks of POPs (Dachs *et al.*, 2002). These processes are more important for hydrophobic compounds, because the less hydrophobic chemicals, such as the low chlorinated PCBs, do not interact strongly with organic matter. Observations of POP concentrations at both of the coastal sites showed lower concentrations of hydrophobic compounds than in the Interior samples. In addition, samples from Homer had far fewer highly substituted chlorinated PCBs than the Interior samples.

The spatial distribution of the SPMD samples at different locations and sampling periods with the principal component analysis (Figure 4.7) in conjunction with data evaluation suggests different patterns of POPs are being sampled. The different patterns can be attributed to different air masses being sampled by the SPMDs. The Barrow samples, which are from an Arctic site were distinct from sub-Arctic samples. In addition, the Homer sample from September to December was different from the rest of the samples. Homer is located in a maritime zone of southern Alaska, where the weather is usually moderated by the ocean and large variability in wind patterns could account for the larger seasonal variability in the POP concentrations. Smaller seasonal variability was seen in the Poker Flat and Denali National Park samples as compared to the other samples and may be due to the positioning of the sites between the Brooks and Alaska

mountain ranges. These mountain ranges can change the dynamics of the wind patterns. The Trapper Creek samples had higher seasonal variability in comparison to the Interior samples. The site was south of the Alaska Range and more exposed to southerly wind.

The ratios of the relative concentrations of isomers in SPMD should not deviate drastically between actual air samples and other media, since these chemicals should have very similar triolein to air partitioning coefficients and any restrictions caused by the membrane at colder temperature should be similar because there are no additional atoms incorporated into the molecule. These isomeric ratios are potentially useful in giving information about potential sources, due to isomeric differences in degradation rates and expected source emission ratios. For example, ratios of α to γ-HCH have been used to evaluate the sources and use history of HCHs (Oehme and Mano, 1984). The α to γ-HCH ratios measured in this study were similar to those reported by Holoubek *et al.* (2000) in pine needles (0.1) in the Czech Republic and in air (0.4–1.0) in west Sweden in 1990 (Brorstrom-Lunden *et al.*, 1994). The average ratios in the Alaska samples were 0.2 (Figure 4.13). The lower ratios of α to γ-HCH in Alaska indicates the presence of an γ-HCH source in Alaska.

Two chlordane species, trans-chlordane (TC) and cis-chlordane (CC), are routinely reported to examine sources. The expected ratio of technical chlordane for TC/CC in ambient air after a recent application to an agricultural field is expected to be approximately 1.7 (Bidleman *et al*, 1990). The TC isomer is relatively less stable than the CC isomer and more susceptible to degradation by microorganisms in soil (Beeman and Matsumura, 1981). A TC/CC ratio of greater than 1 is an indication of a recent release or the slower degradation of TC in the Arctic. At Alert, Canada, for periods where TC/CC ratios were greater than 1 in the atmosphere, five-day back trajectories showed a stronger than normal influence from the Eurasian sector which has high chlordane usage (Hung et al., 2002). A noticeable 36% drop in the ratio of TC to CC during the March to June Barrow sample (Figure 4.14) was measured using SPMD during this study. During this time the polar sunrise occurred and the drop suggests an increase in oxidizing chemicals (Platt and Hönninger, 2003). In addition, the presence of UV radiation could result in an

increased degradation of TC. Ratios measured in SPMD were typically greater than 1 (Table 5.2).

Table 5.2. Ratio of trans-chlordane (TC) to cis-chlordane (CC) measured in SPMDs at the five locations in Alaska during the sampling periods.

	September-December	December-March	March-June	June-Sept.
Barrow	← 1.1 →		0.7	1.1
Poker Flat	1.2	1.2	1.2	1.2
Denali National Park	1.3	1.3	1.2	1.2
Trapper Creek	Missing	1.2	1.2	1.2
Homer	1.3	1.1	Missing	1.1

Although DDT has been banned or highly restricted in many countries, it is still being used in others, especially those where vector control is needed to control the spread of diseases. Technical DDT is a mixture of approximately 80% p,p'-DDT and 20% p,p'-DDE (Ramesh *et al.*, 1989). In Arctic locations during summertime, DDT to DDE ratios were on the order of 1 to 1.5 in Alert, Canada, and around 3 in Amderma, Russia from 1999 to 2000. Higher DDT to DDE ratios have also been measured at Tagish in Western Canada and are associated with trans-Pacific transport from Asia (Bailey et al., 2000). Trans-Pacific transport of trace gases and particles from Asia to North America has been reported from ground-based stations (Parrish *et al.*, 1992; Jaffe *et al.*, 1999; Cahill, 2003; Weiss-Penzias *et al.*, 2004).

As mentioned earlier, laboratory findings suggested that the ratio of DDT to DDE is biased towards DDE at lower temperatures, so winter time DDT to DDE ratios are underestimated. An underestimated value should occur more frequently in the Barrow samples (September-March and March to June) because of the colder temperatures. The results here typically showed higher ratios of DDT to DDE (Table 5.3) in several Interior Alaska samples. These results suggest that there is a fresher input of DDT into the Interior of Alaska or aged DDT is lingering in higher concentrations in comparison to the coastal samples.

Table 5.3. Ratio of DDT (p,p'-and o,p'-DDT) to DDE (p,p'-and o,p'-DDE) measured in SPMDs at the five locations in Alaska during the sampling periods.

	September-December	December-March	March-June	June-Sept.
Barrow	← 0.1 →		0.2	0.2
Poker Flat	0.4	0.8	1.4	2.6
Denali National Park	2.0	1.8	0.3	2.5
Trapper Creek	missing	1.3	0.8	0.3
Homer	0.3	0.7	Missing	0.2

Polyaromatic hydrocarbons are ubiquitous in the environment and the results came to the same conclusion given that some of the highest POP concentrations measured by SPMD are PAHs. Measurements of selected PAH ratios have been made in sediments to distinguish between the two main types of PAH sources: petrogenic (petroleum sources) and pyrogenic (high temperature combustion-derived). However, unlike sediments where the PAH distribution patterns are better preserved, gas phase PAHs are more susceptible to degradation by photolysis and reactive gases. Different partitioning rates into the water phase between air and soil and different microbial degradation rates of PAHs will result in changes in the ratio observed in the air and sediment. The majority of the samples suggest pyrogenic sources with the exception of four samples. The Ph/An ratio for the four samples (Barrow September-March and March-June, Trapper Creek June-September and Poker Flat June-September)suggests petrogenic sources due to the Ph/An ratios being greater than 25 (based on Table 4.29). However, the Fl/Py ratio indicates pyrogenic sources for the four samples. The abnormally low anthracene is likely a result of faster decay of photolabile anthracene than relatively stable phenanthrene in the atmosphere and measurements taken during prolong sunlight.

PAH ratios at other sites from the literature using SPMDs were calculated in Table 5.3. In Thailand, ratios of Ph/An at rural locations ranged from 29 to 70 and in more urban sites ratios ranged from 12 to 16 (Söderstrom and Bergqvist, 2003). The Fl/Py

ratios at the same locations in Thailand ranged from 1.3 to 2.8, with the higher values coming from the rural sites and were similar to the ratios reported here. The rural locations suggest the predominance of pyrogenic sources. PAH ratios obtained from SPMDs in Australia and England showed more variability. The ratios obtained in this and other studies suggest that different decay rates for PAHs in air complicate assessing possible sources and the routinely used ratios must be further examined.

Table 5.3. Ratios of PAHs in air calculated from SPMDs reported in the literature at various sites suggest large variability.

Ratio	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
Ph/An	34.2	29.3	9.8	28.6	12.0	14.6	54.7	22.5	29.1	74.5	6.6	5.0	70.0	29.1	13.0	16.4	13.3	11.7
Fl/Py	2.0	2.8	1.8	2.1	1.6	1.5	2.2	1.4	3.1	2.0	2.2	2.4	2.9	2.0	1.5	1.3	2.3	1.7
Fl/(Fl+Py)	0.67	0.74	0.64	0.67	0.62	0.61	0.68	0.59	0.75	0.67	0.68	0.71	0.74	0.66	0.60	0.57	0.69	0.63

A = field station, semirural

B = coastal (Morecambe Bay/Irish Sea), near Blackpool

C = down wind motorway

D = rural

E = rural, mushroom farm in area

F = city residential area

G = industrial

H = coastal (Morecambe Bay), industrial harbor

I = coastal (Irish Sea), small village

J = coastal (Morecambe Bay)

K = South Brisbane Australia next to M1 motorway

L = Springwood Australia suburb

M = > 1km from rural area, background air

N = rural area, background/ rural air

O = semi-urban area < 5 m from moderate traffic

P = urban area < 50 m from heavy traffic

Q = urban area < 5 m from heavy traffic

R = urban area < 5 m from heavy traffic

A-K = Northwest England (Nov.-Dec.) (Lohmann *et al.*, 2001)
M, N = Australia (April) (Bartkow *et al.*, 2004)
O-R = Thailand (April-March) (Söderström and Bergqvist 2003)

Chapter VI
Conclusion and future research ideas

The work described in the thesis examines the use of SPMD for air monitoring of non-polar aromatic pollutants classified as POPs (OCs, PCBs, and PAHs) in arctic and sub-arctic conditions in Alaska. Conclusions from the work were based on answering hypotheses stated in chapter 3 and suggestions for further research are listed below.

Hypothesis 1:

H_0: There is no difference in POP concentrations in sun-exposed and non-exposed SPMDs (sun = no sun).

The null hypothesis was rejected. Lower levels of PAHs were seen in the sun-exposed SPMD. Additional research on the photodegradation of compounds being sampled by the SPMD should examine how much sunlight gets into the deployment unit and to what degree the photodegradation is actually occurring within the SPMD.

Hypothesis 2:

H_0: There is no difference in POP concentrations between SPMDs in filtered air and non-filtered air (filtered air = non-filtered).

No difference in OC and PAH concentrations were measured. However, PCB measurements did reject the null hypothesis and suggest SPMDs are capable of sampling for particulate-bound PCBs. More samples are needed to confirm the results and better ways to maintain flow in the system are required to prevent changes in the air sampling rates.

Hypothesis 3:

H_0: There is no difference in POP concentrations in SPMDs for different temperatures ($Temperature_1 = Temperature_2 = Temperature_3$).

The null hypothesis was rejected. There are differences in air sampling rates at difference temperatures for POPs into SPMDs. A decrease in air sampling rates was seen with decreasing temperature. Three compounds (lindane, DDE and DDT) decreased by factors of 5, 14 and 26, respectively, when the temperature dropped from 10°C to -8°C. More POPs are needed to examine the differences in sampling rates caused by size and shape for these temperature ranges. Humidity changes should also be tested to determine if changes in atmospheric water vapor influence air sampling rates.

Hypothesis 4:

H_0: There is no difference in POP concentrations between calculated SPMD concentrations and concentrations determined from active air sampler (SPMD = Active).

There was a difference between PAH derived air concentrations measured with passive sampling and PAH air concentrations measured with active sampling. PAH measured air concentrations of phenanthrene, anthracene, fluoranthene and pyrene were approximately 3 to 7 times higher in samples collect through active sampling than PAH derived air concentrations collected through SPMDs. Studies with more POPs are needed at relevant air sampling rate temperatures to make better comparisons in the Arctic.

Hypothesis 5:

H_0: There is difference in POP concentrations at the five locations in Alaska measured by SPMDs. (Barrow = Poker Flat = Denali National Park = Trapper Creek = Homer)

Principal component analysis and evaluation of the data suggest that three distinct groups are depicted in principal component 2 with the Barrow samples and the Homer

September-December sample separated from the other samples. The separation suggests different pattern of POP concentrations impacting each of the three groups.

Passive air samplers are unique because of their simplicity. The simplicity and relatively cheap cost make them very attractive for multiple sample deployments. The study here focused on using SPMDs in remote areas for monitoring persistent organic pollutants. However, more information can be obtained in future studies by deploying samples in areas like agricultural fields, military facilities, urban areas, etc. where chemical are released. Larger variability in the concentrations in these areas in comparison to background air is more likely to be captured. While one may agree that active samplers would be more appropriate, the cost, set up and maintenance requirements of active samplers still make passive sampling attractive even with electrical resources available. Passive samplers can be sent to schools worldwide. The students can deploy them as science projects because of their simplicity and learn about air pollution.

The issues associated with differences in air sampling rates for passive samplers can be dealt with for future studies. A small motorized fan power by a battery can be inserted at the bottom of the deployment units to induce air flow. The flow will reduce the thin boundary layer around the passive sampler and increase air sampling rate of the passive sampler. The fans should be consistent in speed, so air sampling rates are the same between deployment units. Comparison of deployment units with fans and without fans can be made to examine the differences in concentrations between the two deployment units. In addition multiple samples in deployment units with fans should be deployed in close proximity to examine their reproducibility. The restriction of compounds at lower temperatures by the membrane can be dealt with by using passive air sampler mediums that eliminates the membrane. Other recent passive air samplers like polyurethane foam and styrene-divinylbenzene copolymer have no membrane to restrict the compounds from entering at colder temperatures.

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Appendix A. Physical-chemical properties of some persistent organic pollutants.

Table A-1. Physical-chemical properties used to assess long-range transport of some persistent organic pollutants.

CAS #	NAME		Log air 1/2 life values (hrs)		physico-chemical properties (Log Value)				
		MW	mean	max	H	VPl	Koa	Sol	Kow
91-20-3	Naphtalene	128.18	1.21	1.47	1.63	1.57	5.10	1.49	3.37
118-74-1	Hexachlorobenzene	250.32	4.31	4.57	2.12	-0.61	6.80	-2.30	5.50
120-12-7	Anthracene	178.24	0.06	0.23	0.60	-1.11	7.34	-1.35	4.54
129-00-0	Pyrene	202.26	0.13	0.31	-0.04	-1.92	8.61	-0.88	5.18
13029-08-8	PCB-4	223.1	2.48	2.61	1.77	-0.22	6.74	-0.37	4.72
206-44-0	Fluoranthene	202.26	1.05	1.31	-0.19	-2.06	8.60	-0.59	5.22
208-96-8	Acenaphthylene	152.2	-0.14	0.10	0.92	0.62	6.85	1.21	4.00
2437-79-8	PCB-47	291.98	3.01	3.16	1.24	-2.70	8.06	-1.76	5.94
319-84-6	a-HCH	290.82	1.71	1.97	-0.06	-1.00	7.26	0.00	3.80
33284-50-3	PCB-7	223.1	2.48	2.61	1.66	-0.60	7.17	-0.21	5.15
37680-65-2	PCB-18	257.54	2.72	2.86	1.96	-0.66	7.26	-0.75	5.33
37680-73-2	PCB-101	326.42	3.33	3.46	1.55	-2.46	8.24	-2.10	6.09
38380-02-8	PCB-87	326.42	3.33	3.46	1.39	-2.64	8.50	-2.14	6.23
38444-81-4	PCB-26	257.54	2.72	2.86	1.79	-1.77	7.55	-0.72	5.65
3844-93-8	PCB-40	291.98	3.01	3.16	1.34	-2.70	7.65	-1.36	5.67
50-29-3	p,p'-DDT	354.48	1.99	2.25	0.37	-3.87	9.93	-2.26	6.19
57-74-9	Chlordane	409.76	1.45	1.71	0.47	-2.58	8.70	-1.25	6.00
58-89-9	y-HCH	290.82	1.71	1.97	-0.83	-1.56	8.08	0.86	3.70
608-93-5	Pentachlorobenzene	305.96	3.78	4.04	1.93	-0.02	6.50	-0.19	5.00
72-54-8	p,p'-DDD	320.04	1.99	2.25	-0.19	-3.16	9.81	-1.30	5.50
72-55-9	p,p'-DDE	319.03	1.99	2.25	0.90	-2.43	9.45	-1.40	5.70
76-44-8	Heptachlor	373.3	0.73	0.99	2.55	-0.57	8.87	-1.25	5.27
83-32-9	Acenaphthene	154.22	0.68	0.94	1.09	0.18	7.66	0.58	3.92
85-01-8	Phenanthrene	178.24	1.04	1.30	0.51	-0.95	7.45	0.04	4.57
86-73-7	Fluorene	166.23	1.57	1.83	0.90	-0.15	6.68	0.28	4.18
92-52-4	biphenyl	154.22	1.77	2.04	1.73	0.57	6.23	0.64	4.12

Values were obtained from Gramatica *et al.* (2000).

Appendix B. Data used for PCA.

Table B-1. POP Concentrations used in the PCA.

	Barrow 2	Barrow 3	PF 1	PF 2	PF 3	PF 4	DNP 1	DNP 2	DNP 3	DNP 4	TC 2	TC 3	TC 4	Homer 1	Homer 2	Homer 3
1245 TCB	10.45	1.99	2.30	2.96	1.82	2.37	2.43	1.82	1.66	1.18	4.09	3.13	4.73	4.42	9.15	2.39
1234 TCB	0.37	0.33	0.24	0.38	0.00	0.00	0.37	0.40	0.35	0.00	0.93	1.04	0.70	0.32	0.53	0.00
PentaCB	1.07	2.18	1.64	1.75	0.00	0.53	0.88	1.38	0.95	0.49	1.11	1.21	0.64	0.60	1.54	0.56
Alpha-HCH	2.50	3.51	1.83	1.28	0.78	1.12	1.06	0.94	0.94	0.88	0.69	0.93	0.90	1.85	2.14	1.55
HCB	13.13	11.70	2.49	5.02	1.84	2.12	3.42	3.22	4.00	2.49	2.44	3.64	2.64	2.72	7.51	3.45
Pentachloroaniso	1.91	1.22	1.73	1.36	1.87	2.72	1.94	1.41	1.78	4.72	1.38	1.72	3.08	1.54	1.85	1.83
Gamma-HCH	28.25	42.11	5.22	5.51	3.09	3.98	5.20	5.61	4.32	5.29	4.67	4.82	4.28	42.25	6.52	17.54
Octachlorostyren	0.21	0.16	0.15	0.05	0.02	0.06	0.02	0.03	0.04	0.03	0.00	0.03	0.03	0.03	0.07	0.04
Oxychlordane	0.15	0.17	0.68	0.41	0.06	0.19	0.17	0.11	0.17	0.09	0.07	0.23	0.10	0.05	0.27	0.06
o,p'DDE	1.40	2.32	0.63	0.90	0.65	0.92	0.64	0.93	0.74	0.80	0.92	1.28	1.09	1.33	0.62	0.91
p,p'DDE	7.94	11.51	6.67	2.79	4.96	2.76	1.97	5.17	11.39	7.81	9.09	184.00	173.87	6.00	2.25	6.22
o,p'DDD	0.02	0.03	0.88	0.04	0.06	0.04	0.01	0.17	0.02	0.00	0.03	0.02	0.02	0.00	0.09	0.00
p,p'DDD	0.00	0.00	0.28	0.26	0.00	0.84	0.40	0.76	0.20	1.50	1.51	8.55	3.85	0.00	0.00	0.00
o,p'DDT	0.50	0.59	0.77	0.78	0.92	1.63	0.70	0.78	0.72	0.61	1.45	2.37	1.45	0.46	0.59	0.33
p,p'DDT	1.39	1.61	2.44	2.35	6.82	7.88	4.48	10.37	2.62	20.66	12.01	142.30	44.97	1.53	1.37	1.33
Photomirex	0.02	1.74	2.77	4.57	0.04	2.71	4.84	4.49	3.02	4.05	1.12	1.43	2.46	2.44	2.37	0.00
C	1.34	1.45	0.28	2.28	2.12	2.26	2.48	2.88	2.12	2.55	2.11	2.81	2.47	0.93	1.54	0.91
Heptachlor	0.37	0.50	0.28	0.74	0.45	0.75	0.51	0.53	0.56	0.59	0.80	0.72	0.73	0.47	0.51	0.00
U1	0.19	0.18	0.22	0.28	0.30	0.36	0.28	0.28	0.32	0.29	0.33	0.36	0.39	0.00	0.28	0.00
C1A	0.34	0.50	0.75	1.02	0.80	0.88	0.78	1.27	0.75	0.96	0.87	1.05	1.05	0.36	0.52	0.35
U3	0.02	0.00	0.03	0.07	0.08	0.10	0.07	0.03	0.07	0.05	0.08	0.10	0.04	0.03	0.02	0.00
Trans-Chlordane	0.96	2.14	3.19	4.25	3.20	3.79	3.32	5.11	3.18	4.06	4.05	4.59	4.54	1.61	2.18	1.50
C5	1.00	2.15	0.48	0.67	0.57	0.69	0.48	0.70	0.55	0.60	0.69	0.96	0.81	0.98	0.46	0.68
C3	0.15	0.12	0.00	0.13	0.16	0.25	0.13	0.17	0.13	0.14	0.16	0.19	0.16	0.00	0.00	0.00
Cis-Chlordane	1.34	1.93	2.67	3.41	2.71	3.24	2.59	4.05	2.65	3.27	3.42	3.87	3.90	1.27	2.00	1.37
Trans-Nonachlor	0.60	0.80	0.73	1.08	0.88	0.94	0.87	1.30	0.95	0.98	1.30	1.42	1.37	0.44	0.66	0.41
Cis-Nonachlor	0.22	0.26	0.25	0.27	0.21	0.41	0.15	0.05	0.23	0.06	0.08	0.09	0.09	0.13	0.18	0.13
Toxaphene 2	1.12	0.97	0.00	0.47	2.00	5.25	0.00	0.45	0.89	0.45	0.53	0.58	0.57	0.00	2.20	0.00

Table B-1. (continued)

	Barrow 2	Barrow 3	PF 1	PF 2	PF 3	PF 4	DNP 1	DNP 2	DNP 3	DNP 4	TC 2	TC 3	TC 4	Homer 1	Homer 2	Homer 3
PCB4/10	0.24	0.26	0.33	0.33	0.30	0.32	0.50	0.41	0.39	0.34	1.11	1.23	0.97	0.24	0.26	0.16
PCB18	0.44	0.73	0.36	0.34	0.43	0.40	1.28	0.70	0.66	0.30	0.40	0.55	0.41	0.00	0.34	0.00
PCB17	0.25	0.30	0.00	0.26	0.32	0.30	0.37	0.29	0.31	0.25	0.32	0.38	0.31	0.00	0.24	0.00
PCB26	0.83	0.63	0.24	0.29	0.31	0.34	0.00	0.00	0.00	0.00	1.63	2.08	2.08	0.50	0.58	0.60
PCB25	2.02	1.87	3.30	3.49	3.26	3.50	3.36	4.47	2.84	3.94	2.87	4.07	3.58	1.65	2.29	1.67
PCB52	0.69	0.97	0.48	0.47	0.49	0.55	0.00	1.04	0.83	0.84	0.50	0.58	0.47	0.00	0.00	0.00
PCB70/76	0.40	0.25	0.24	0.32	0.42	0.49	0.61	0.62	0.50	0.42	0.44	0.56	0.42	0.26	0.23	0.00
PCB84/89	1.22	1.62	0.00	0.32	0.44	0.40	0.06	0.08	0.13	0.16	0.40	0.56	0.50	0.72	0.20	0.54
PCB101	0.76	0.37	0.18	0.17	0.21	0.17	0.34	0.43	0.32	0.34	0.16	0.20	0.18	0.26	0.20	0.20
PCB141	0.04	0.00	0.11	0.18	0.11	0.13	0.00	0.05	0.04	0.00	0.14	0.18	0.14	0.04	0.00	0.00
PCB180	0.04	0.11	0.10	0.12	0.30	0.56	0.07	0.08	0.08	0.10	0.00	0.00	0.12	0.00	0.00	0.00
Naphthalene	9.80	1.86	15.08	40.22	16.72	9.18	5.58	13.88	14.36	13.86	34.58	28.18	26.02	13.86	6.93	3.98
2-Methylnaphtha	9.02	2.64	18.50	21.82	16.24	9.48	9.20	13.82	14.58	14.66	36.46	33.56	26.40	21.48	10.74	7.30
1-Methylnaphtha	7.50	3.20	16.98	22.36	13.48	7.94	9.70	13.04	13.06	13.36	28.18	24.28	18.80	23.68	11.84	7.52
Biphenyl	2.00	5.88	5.88	8.24	3.58	2.32	7.78	4.58	4.58	4.84	3.20	2.98	2.64	7.04	3.52	3.26
Acenaphthylene	0.52	0.41	1.20	2.56	1.04	0.70	5.04	1.12	1.08	1.42	0.90	0.88	0.92	8.46	4.23	2.98
Acenaphthene	1.70	1.10	3.02	2.32	4.16	5.76	2.20	2.72	3.24	3.54	2.04	2.12	2.12	5.50	2.75	3.98
Fluorene	5.14	27.28	7.96	18.22	12.04	13.40	13.76	9.04	15.32	17.12	6.32	6.18	8.28	34.30	17.15	20.12
Phenanthrene	30.28	24.30	54.20	38.26	65.06	84.64	52.80	39.98	57.92	84.16	39.12	57.60	78.52	150.18	75.09	68.08
Anthracene	0.90	2.34	3.42	2.24	5.40	1.40	5.84	2.56	5.02	8.12	2.86	3.40	1.20	9.14	4.57	4.42
C2 Fluorene	0.00	0.00	4.70	6.94	3.08	11.06	9.32	4.68	7.66	11.48	6.34	0.00	12.48	9.28	4.64	4.48
Benzo(a)anthrace	0.78	1.12	2.20	1.80	1.10	1.00	0.92	1.04	1.66	0.94	1.52	1.72	0.98	1.42	0.71	0.88
45-Methylenephe	1.44	1.44	3.08	1.90	3.74	4.20	2.58	1.82	9.08	3.26	1.86	2.24	3.90	11.70	5.85	4.64
Fluoranthene	6.04	5.44	11.54	8.16	13.52	18.70	8.88	8.64	6.58	7.88	11.72	14.62	14.56	24.50	12.25	10.90
Pyrene	4.26	3.74	7.24	5.88	9.26	8.16	6.36	6.44	4.00	4.98	8.90	9.66	9.76	21.58	10.79	9.08
Retene	0.52	0.44	0.66	0.58	4.04	1.02	0.46	0.48	0.38	0.46	0.50	0.38	0.58	13.48	6.74	1.58

Appendix B-2. Parameters used for PCA models.

Software: Unscrambler ® version 8.0.5

Calibration Method: PCA

Validation Method: Cross validation

Weights: All 1/SD

Mode: Full, center data, issue warnings

Number of PCs calculated: 4

Sample size: 16 see table A-1

Variable size 66 see table A-1

Samples: Locations and time intervals at the five locations in Alaska

Variables: Concentrations of POPs detected in SPMDs

Transformation: None

Appendix C. Concentrations in active air samples.

Table C-1. Polyaromatic hydrocarbon levels (pg/m^3) in the atmosphere of Barrow measured with active air sampler.

	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
8/16/2002	30.5	226.3	13.08	15.8	52.5
8/31/2002	109.3	355.3	16.58	28	66.6
9/6/2002	14.8	121	4.23	8.8	7
10/10/2001	30.8	82.9	3.4	5.8	17.2
10/17/2002	67	125.8	10.3	35	51.7
10/24/2002	64	155.8	8.19	22.4	31.7
11/1/2002	131	76.1	3.42	18.2	15.2
11/6/2002	86.5	39.6	1.7	8.2	6.8
11/15/2002	89.9	19.7	1.18	6.1	3.9
11/23/2002	189.9	78	4.14	42.9	32.5
11/29/2002	186.7	78.7	3.65	39.6	26.5
12/5/2002	233.9	118.6	3.34	72.3	37.8
12/26/2002	268.2	197.3	6.23	138.3	91.3
1/3/2003	187.5	137.4	3.49	44.7	22.5
1/17/2003	516.3	127.9	2.29	95.6	57.8
1/24/2003	364.1	82.9	2.33	57.8	39.4
1/31/2003	822.5	215.9	4.9	157.4	98.3
2/24/2003	249.5	123.1	2.0	78.6	39.6
Average	202.4	131.2	5.2	48.6	38.8