A STUDY OF ATMOSPHERIC n-ALKANES AND PAHs AND THEIR DISTRIBUTIONS BETWEEN THE GASEOUS AND PARTICULATE PHASES

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A dissertation submitted to the faculty
of the Oregon Graduate Institute
of Science and Technology
in partial fulfillment of the
requirements for the degree
Doctor of Philosophy
in
Environmental Science and Engineering

December 1989

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DEDICATION

To my

Mother & Father

and

Deborah, Kendra & Levi

ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor, Jim Pankow, for providing the opportunity to work on my this research project. His support (spiritual and financial), enthusiastic teaching, tremendous patience, and incredible editing ability were above and beyond the call of duty. THANX!

The guidance and advice from Jim Huntzicker is also greatly appreciated. His many helpful discussions, office space (vertical and horizontal), and insight into local politics were all very helpful.

I would also like to thank the other two members of my examination committee, Rick Johnson and Bob O'Brien, for providing valuable constructive criticism and their signatures.

Even though "I didn't write anything down", I still managed to learn a tremendous amount from Lorne Isabelle (most of which can't be repeated here). Whether it was discussing Finnigan software or fixing "the beast", I am deeply indebted to Lorne for all of his help.

The best thing you can say about friends is they are there when you need them. Whether it was making or fixing equipment, talking shop, "drowning sorrows", or all of the above, the help of the following people is greatly appreciated: Mike Anderson, Wild Bill Asher, Jerry Boehme, Don Buchholz, Bob Cary, Nancy Christie, Steve and Shirley Crawford, Bob Dalluge, Dan Danks, Paul

Davis, Doug Davis, Margaret Day, Rick DeCesar, Dave Duncan, Mike Elovitz, Bill Fish, Gordon Frost, Bill and Mary Gambill, Su Ge, Carol Hendrickson, Jim Hurst, Judi Irvine, Walter Krieck, J. MacPherson, Carl Miller, Bill Pengelly, Matt Perrot, Donna Reed, Mike Rosen, Stewart Rounds, Allan and Barbara Ryall, Mike Schlender, Greg Schwind, Laura Scott, Maureen Sloan, John Storey, Fred Thone, Bruce Tiffany, Barb Turpin, Bob Turpin, Dennis Turri, Julie Wilson, Jan and Gary Woodruff, and Mike Zimmerman.

I am grateful to the Oregon Department of Environmental Quality for allowing us to sample at their S.E. Lafayette site and providing various sampling equipment. I would like to especially thank Dennis Duncan and his co-workers who helped in various aspects of sampling at S.E. Lafayette. I would like to thank Alltech Associates of Deerfield, Illinois for the donation of the Tenax-TA used in this study and ERT of Boston, MA for the donation of the high volume air sampling shells.

Many thanks go to Walter Giger for providing support and friendship while I finished writing my dissertation at EAWAG (ostensively working for him as a postdoc). I am deeply indebted to Christian and Marielotte Leuenberger for providing support and friendship in making our move and stay in Switzerland a wonderful experience.

I would like to thank my loving wife and children for providing new challenges and understanding my widely vacillating mood swings.

Finally, I would like to thank my mother and father who have provided tremendous support throughout my "career" as a "professional student". Without their support and understanding, none of this would have been possible.

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ABSTRACT

A Study of Atmospheric n-Alkanes and PAHs and Their Distributions Between the Gaseous and Particulate Phases

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The extent to which a compound is removed from the atmosphere and transported to other compartments will depend in part on how that compound is distributed between the gaseous and particulate phases. Recent theoretical advances indicate that a compound's vapor pressure and the ambient temperature will play large roles in determining the extent to which the compound partitions to atmospheric particulate matter. However, the testing of such theory requires artifact free values of the gas and particulate phase concentrations. A field study designed to minimize sampling artifacts was conducted in Portland, OR during 1988. During this study, the concentrations of n-alkanes (C16 through C31) and eleven polynuclear aromatic hydrocarbons (PAHs) were measured in the gas and particulate phases over a range of ambient temperatures (7 - 31°C).

Two air samplers were built to collect gas and particulate phase samples. One of the samplers utilized two quartz fiber filters (QFFs) in series and followed by two polyurethane foam sheets (PUFSs). The second sampler utilized a Teflon membrane filter (TMF) followed by a QFF and two PUFSs. Gas phase adsorption to the QFFs, as measured on the backup QFFs, was found to be a significant artifact for all of the more volatile n-alkanes as well as some of the PAHs studied. It was also determined that the QFF behind the TMF provided the best estimate of the extent of gas phase adsorption to the QFFs.

Atmospheric partitioning was examined in the context of an equilibrium distribution constant K and a compound's temperature corrected subcooled liquid vapor pressure (p°_L). The parameter K is defined as A(TSP)/F where A and F are the gas and particulate phase concentrations (ng/m^3), respectively, and TSP is the total suspended particulate matter concentration (µg/m^3). As predicted by equilibrium adsorption theory, the correlation between log K vs. log p°_L was generally quite high. When the gas and particulate phase concentrations were corrected for gas phase adsorption to the QFFs, the correlation (r^2) between log K and log p°_L increased from ~0.74 to ~0.90.

CHAPTER 1. INTRODUCTION

The transport and cycling of both natural and anthropogenic chemicals in the environment is an extremely dynamic process that is important for the well being of all earth's inhabitants. Knowledge of the transport and fate of a chemical in the environment is important in determining the beneficial or deleterious effects to an ecosystem. The fate of a chemical is dependent on where and in what physical state the chemical is emitted and on how it partitions between various compartments in the environment. The atmosphere plays a major role in the transport and cycling of chemicals, especially those that are volatile or semi-volatile in nature. For example, atmospheric sources of semi-volatile polychlorinated biphenyls (PCBs) to the Great Lakes constitutes >80% of the total PCB input to that ecosystem (Eisenreich et. al., 1981). Atmospheric input to ecosystems can be broken down into its two primary constituents; input from the gas phase and input from the particulate phase. Thus, the extent to which compounds are removed from the atmosphere and become available to other compartments depends in part on how a chemical is distributed between the gaseous and particulate phases.

The fate of chemicals in the environment has become a topic of increasing importance since many anthropogenic chemicals have recently been found to be harmful at low levels. Many atmospheric trace organic compounds are at least partially anthropogenic in origin. It is surprising that little research has been completed on atmospheric trace organic compounds and their distribution between the gas and particulate phases. The major reason for this is that analytical methodologies have only recently been developed to the state where differentiation is now possible between the gas and particulate phases.

Due to the complexity and sheer number of trace organic compounds in ambient air, experimental measurements of the concentrations in the gas and particulate phases and of the corresponding partition coefficients between the two phases for all compounds is beyond the scope any single research project or even many combined research projects. However, it should be possible to obtain an understanding of atmospheric partitioning by developing predictive correlation equations and parameterizations for those selected trace organic compounds that can be studied. These predictive equations can then be applied to compounds that have not been examined experimentally to estimate the extent to which they will partition between the phases. Partition coefficients obtained in this manner can then be used as primary inputs for various compartmental models to predict chemical fate in the environment.

1.1 Objectives

The goal of this research was to determine which factors influence the partitioning of atmospheric trace organic compounds between the gaseous and particulate phases. In support of this, a number of related topics were also investigated, including 1) artifact free sampling and analytical methodologies; and

2) predictive parameterizations based on equilibrium theory and linear Langmuir isotherms for gas/particle partitioning.

A general review of sampling and analytical techniques for atmospheric SOCs is given in Chapter 2. The analytical methods that were used in this study, along with concentrations that were found in both phases are given in Chapter 4. Partitioning theory based on linear Langmuir adsorption theory is examined in detail in Chapter 3. Organic and elemental carbon concentrations from the filters are examined in Chapter 5. In Chapter 6, the concentrations from both the gas and particulate phases are examined within the theoretical framework described in Chapter 3. Finally, in Chapter 7, the conclusions and topics for future study are presented.

1.2 Selection of Target Compounds

To assess the impact of trace organic compounds on the environment, it would be helpful to know how all organic pollutants are distributed between the gaseous and particulate phases. It also would be helpful to be able to predict how some of the natural and anthropogenic compounds that are beneficial to an ecosystem will partition between the various compartments in the environment. Therefore, a group of n-alkanes was chosen to represent a class of compounds that are beneficial to an ecosystem (as a carbon source for lower organisms). A group of polycyclic aromatic hydrocarbons (PAHs) was chosen to represent a potentially toxic class of compounds. The selected target compounds as well as other similar atmospheric trace organic compounds will be referred to here collectively as semi-volatile organic compounds (SOCs).

A group of 16 n-alkanes ranging from $C_{16}H_{34}$ to $C_{31}H_{64}$ was selected four reasons: 1) they are representative of a beneficial class of compounds; 2) they are relatively inert under typical atmospheric sampling, extraction, concentration, and analysis conditions; 3) they are at ambient concentrations that are relatively easy to determine analytically; and 4) they have subcooled liquid vapor pressures (p°_L) that span ≈6 orders of magnitude (Table 1.1). Relatively volatile compounds ($p^\circ_L > 10^{-4}$ torr) will exist primarily in the gas phase and the less volatile compounds ($p^\circ_L < 10^{-8}$ torr) will exist primarily in the particulate phase. Compounds in the intermediate volatility range will exist, in significant fractions, in both the gas and particulate phases.

In addition to the 16 n-alkanes, two isoprenoids (pristane and phytane) were chosen as they are only a result of natural production. Thus, they provide a measure of the influence of natural emissions on the air parcels collected. In contrast, both the n-alkanes and the PAHs result from both natural and anthropogenic emissions.

The 11 PAHs studied were chosen because they are known or have been implicated as carcinogens and/or mutagens (Mabey et. al., 1982). These PAHs have been studied extensively in several environmental compartments. In fact, atmospheric gas/particle partitioning for a few of the PAHs has been studied in some detail. By monitoring these PAHs along with the n-alkanes from Table 1.1, comparisons can be made between the partitioning behavior of the target SOCs for typical atmospheric conditions in Portland, OR and that in other cities.

The subcooled liquid vapor pressures (p°_L) and aqueous solubilities (S) of the target compounds are given in Table 1.1. The structures of the target compounds along with the name abbreviations that will be used throughout this document are given in Figure 1.1. Subcooled liquid vapor pressures will be used in this document rather than solid vapor pressure (p°_S). The vapor pressure of a compound over a pure solid is lower than that over an indifferent surface (e.g. particulate matter) since the latter does not have the stability of a crystal lattice. Thus, physical adsorption of gas phase molecules to atmospheric particulate matter is expected to be controlled by p°_L, rather than p°_S. This approach is consistent with partitioning theory that will be presented in Chapter 3 and with experimental partitioning results (Bidleman and Foreman, 1987; Bidleman, 1988; Pankow, 1987; Ligocki and Pankow, 1989). The interconversion between the two vapor pressures can be approximated by a form of the Clausius-Clapeyron equation, namely

$$\ln p^\circ_L / p^\circ_S = \Delta S_f \, (T_m - T)/RT \qquad 1.1$$

where ΔS_f = the entropy of fusion (kcal/mol)

T_m = melting point (°K)

T = ambient temperature (°K)

R = gas constant

For SOCs, 6.79 is often used as an average value of $\Delta S_f /R$ (Mackay et. al., 1986; Bidleman and Foreman, 1987).

Table 1.1. Solubilities and Subcooled Liquid Vapor Pressures of Target Compounds at 25°C.

Compound	S (mg/L)	ref	p°_L (torr)	ref
n-Alkanes				
Hexadecane	na		6.81×10^{-4}	a
Heptadecane	na		5.32×10^{-4}	a
Octadecane	na		1.92×10^{-4}	a
Nonadecane	na		4.34×10^{-5}	a
Eicosane	1.9×10^{-3}	b	1.42×10^{-5}	a
Heneicosane	na		6.54×10^{-6}	a
Docosane	na		2.04×10^{-6}	a
Tricosane	na		6.52×10^{-7}	a
Tetracosane	na		2.04×10^{-7}	a
Pentacosane	na		6.52×10^{-8}	a
Hexacosane	1.7×10^{-3}	c	2.04×10^{-8}	a
Heptacosane	na		6.52×10^{-9}	a
Octacosane	na		2.04×10^{-9}	a

Table 1.1 (cont'd.). Solubilities and Subcooled Liquid Vapor Pressures of Target Compounds at 25°C.

Compound	S (mg/L)	ref	p°_{L} (torr)	ref
Nonacosane	na		$6.52\text{x}10^{-10}$	a
Triacontane	na		$2.04\text{x}10^{-10}$	a
Hentriacontane	na		$6.52\text{x}10^{-11}$	a
PAHs				
Acenapthene	4.5	c	$1.10\text{x}10^{-2}$	d
Fluorene	1.85	c	$3.10\text{x}10^{-3}$	e
Phenanthrene	1.28	c	$5.35\text{x}10^{-4}$	e
Anthracene	$4.5\text{x}10^{-2}$	e	$5.03\text{x}10^{-4}$	e
Fluoranthene	$2.4\text{x}10^{-1}$	c	$5.27\text{x}10^{-5}$	e
Pyrene	$1.4\text{x}10^{-1}$	c	$3.40\text{x}10^{-5}$	e
Benz(a) Anthracene	$1.1\text{x}10^{-2}$	c	$1.91\text{x}10^{-6}$	e
Chrysene	$1.8\text{x}10^{-3}$	a	$1.76\text{x}10^{-6}$	e
Benzo(b&k) Fluoranthene	$1.1\text{x}10^{-3}$	c	$1.60\text{x}10^{-7}$	e

Table 1.1 (cont'd.). Solubilities and Subcooled Liquid Vapor Pressures of Target Compounds at 25°C.

Compound	S (mg/L)	ref	p°_L (torr)	ref
Benzo(e) Pyrene	$6.2\text{x}10^{-3}$	c	$9.59\text{x}10^{-8}$	e
Benzo(a) Pyrene	$1.5\text{x}10^{-3}$	g	$9.19\text{x}10^{-8}$	e

na = not available; a) Duce and Gagosian, 1982; b) Mackay and Shiu, 1981; c) Pearlman et. al., 1984; d) Foreman, 1986; e) Yamasaki et. al., 1982.

Figure 1.1. Formulas, Structures (carbon-carbon bonds only), and Name Abbreviations of Target Compounds.

Compound	Formula	Structure	Abbreviation
n-Alkanes			
Hexadecane	$C_{16}H_{34}$		C16
Heptadecane	$C_{17}H_{36}$		C17
Octadecane	$C_{18}H_{38}$		C18
Nonadecane	$C_{19}H_{40}$		C19
Eicosane	$C_{20}H_{42}$		C20
Heneicosane	$C_{21}H_{44}$		C21
Docosane	$C_{22}H_{46}$		C22
Tricosane	$C_{23}H_{48}$		C23
Tetracosane	$C_{24}H_{50}$		C24
Pentacosane	$C_{25}H_{52}$		C25
Hexacosane	$C_{26}H_{54}$		C26
Heptacosane	$C_{27}H_{56}$		C27
Octacosane	$C_{28}H_{58}$		C28

Figure 1.1 (cont'd.). Formulas, Structures (carbon-carbon bonds only), and Name Abbreviations of Target Compounds.

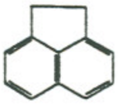
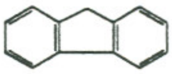
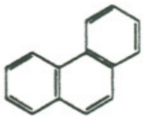
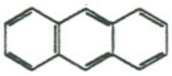
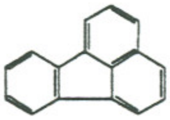
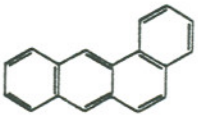
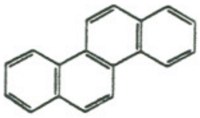
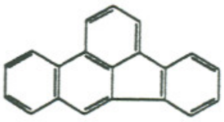
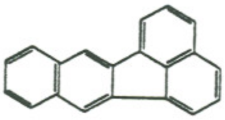
Compound	Formula	Structure	Abbreviation
Nonacosane	$C_{29}H_{60}$		C29
Triacontane	$C_{30}H_{62}$		C30
Hentriacontane	$C_{31}H_{64}$		C31
PAHs			
Acenapthene	$C_{12}H_{10}$		ACE
Fluorene	$C_{13}H_{10}$		FLU
Phenanthrene	$C_{14}H_{10}$		PHE
Anthracene	$C_{14}H_{10}$		ANT
Fluoranthene	$C_{16}H_{10}$		FLA
Pyrene	$C_{16}H_{10}$		PYR

Figure 1.1 (cont'd.). Formulas, Structures (carbon-carbon bonds only), and Name Abbreviations of Target Compounds.

Compound	Formula	Structure	Abbreviation
Benz(a) Anthracene	$C_{18}H_{12}$		BaA
Chrysene	$C_{18}H_{12}$		CHR
Benzo(b) Fluoranthene	$C_{20}H_{12}$		BFL
Benzo(k) Fluoranthene	$C_{20}H_{12}$		BFL
Benzo(e) Pyrene	$C_{20}H_{12}$		BeP
Benzo(a) Pyrene	$C_{20}H_{12}$		BeP

Chapter 2. Atmospheric Semivolatile Organic Compounds

2.1. Distribution of Semivolatile Organic Compounds between the Gaseous and Particulate Phases.

Atmospheric SOCs will always be present, to some extent, in both the gas and particulate phases. The partitioning of a compound between the phases depends on the ambient temperature, the saturation vapor pressure of the compound, and the amount and type of particulate material present. The compound-dependent fraction that is associated with the particulate phase has come to be referred to symbolically as ϕ. Junge (1977) developed an equilibrium expression for ϕ based on a linear Langmuir isotherm

$$\phi = \frac{c_J\theta}{p + c_J\theta} \qquad 2.1$$

where c_J = a constant that is dependent on the compound and ambient temperature (torr-cm^3/cm^2)

θ = aerosol surface area concentration (cm^2/cm^3 air)

p = saturation vapor pressure (torr)

The value of ϕ can be experimentally determined according to

$$\phi = \frac{c_p}{c_p + c_g} \qquad 2.2$$

where c_p = particulate phase concentration (ng/m^3)

c_g = gas phase concentration (ng/m^3)

While Junge's ϕ (equation 2.1) is useful in predicting the general trend of the extent of association with the particulate phase, it is only an approximation. In particular, the constant c_J is compound and temperature dependent. Also, the aerosol surface area concentration θ, is dependent on the concentration, type, and origin of the particulate material. The aerosol surface area concentration is an extremely difficult parameter to measure in ambient air. For non-porous particles, it can be approximated using the particle size distribution.

While equation 2.1 describes nonspecific physical adsorption at equilibrium, it may be expected that the extent to which a compound partitions to the particulate phase will depend on the form in which it was introduced into the atmosphere. For example, PAHs are emitted to the atmosphere primarily from combustion sources. A fraction of a compound's particulate phase concentration that was formed as a result of combustion processes might be trapped inside the particulate matter and may not be able to exert its full thermodynamic activity. Therefore, equation 2.1

may sometimes predict a lower fraction in the particulate phase than might be present in the ambient atmosphere.

A linear Langmuir isotherm was also used by Yamasaki et. al. (1982) to investigate gas/particle partitioning. They examined the dependence of PAH partitioning in Tokyo on the ambient temperature (T) and the total suspended particulate matter (TSP) using the expression

$$\log K = \frac{A(TSP)}{F} = \log \frac{A}{F/TSP} = \frac{m}{T} + b \qquad 2.3$$

where K = equilibrium distribution coefficient (ng/µg)

A = concentration collected on sorbent bed (ng/m^3)

F = concentration collected on filter (ng/m^3)

TSP = total suspended particulate matter (µg/m^3)

T = degrees K

If there are no sampling artifacts, then $A = c_g$ and $F = c_p$. The parameter K can be thought of as an equilibrium distribution coefficient. It is a ratio of a compound's activity in the gas phase (ng/m^3) to that in/on the particulate matter (ng/µg). As T increases, the gas phase will tend to be preferred over the particulate phase. The slope (m) in a plot of log K vs. 1 / T will therefore, be negative. The slope and intercept (b) are compound dependent.

2.2. Measurement of Atmospheric Semivolatile Organic Compounds

2.2.1. Review of Sampling Methods for the Particulate Phase

The collection of particulate phase trace organic compounds is usually carried out by drawing a large volume of air through a fibrous or membrane filter. Both experimental (Lockhart et. al., 1964) and theoretical (Friedlander, 1977) work has demonstrated that these filters are extremely efficient (>99.99%) in collecting atmospheric particles. Even the particles for which the collection efficiency is at a minimum (0.3 µm) are collected at greater than 99.99% efficiency. Particles larger than 0.3 µm tend to be collected by direct impaction and particles smaller than 0.3 µm tend to be collected by diffusion (Friedlander, 1977). John and Reischl (1978) conducted experiments on a variety of filters using urban dust and a particle counter. They determined that for membrane filters with a pore size of <0.3 µm, the collection efficiency was similar to that of fibrous filters.

If no sampling artifacts are present, the concentration as measured on a filter will be representative of the particulate phase concentration in the atmosphere. Unfortunately, a variety of mechanisms can lead to artifacts in atmospheric trace organic sampling. Two of the most important artifact mechanisms in particulate phase sampling are volatilization losses ("blow off") from particle laden filters and adsorption from the gas phase to the filters themselves. Depending on the sampling conditions, both artifacts can be important and will need to be addressed. The magnitudes of these artifacts are dependent on the changes in the sampling temperature, composition of the air that is being sampled, and the physical and chemical characteristics of the particulate phase.

Early investigators believed that loss by volatilization was the primary source of sampling artifacts. Two basic types of studies led to this conclusion. Firstly, ambient particulate material was collected on a glass fiber filter (GFF). Either clean air or a pure inert gas was then passed through the particle laden filter. A sorbent bed was used to collect the amount of material that "volatilized" (Rondia, 1965; Broddin et. al., 1980; Koing et. al., 1980; Schwartz et al., 1981, Van Vaeck et. al., 1984; Van Vaeck and Van Cauwenberghe, 1985). It should be kept in mind that a portion of the amount of material found on the sorbent bed could have originated as adsorbed gases on the filter. Thus, what "volatilized" from the particulate phase may have been an overestimation of the actual losses from the particles.

With this caveat in mind, the above results indicate that volatilization losses from a particle laden filter can be significant for relatively volatile compounds. In particular, if sampling of a relatively cleaner air parcel of air follows the sampling of a relatively more contaminated parcel, then volatilization losses will occur. Volatilization losses can also be magnified by temperature increases during the sampling event. These conclusions have serious implications for sampling of atmospheric SOCs.

The second type of experiment used the results from the above experiments as a starting point. Believing that volatilization was the most important sampling artifact, several researchers adopted the use of replacing the filter several times during a sampling event (Van Vaeck et. al., 1984; Cautreels and Van Cauwenberghe, 1978; Appel et. al., 1979). The idea behind this was to minimize volatilization by reducing the volume of air that comes in contact with the particles collected on each filter. This also has the advantage of minimizing temperature and air parcel fluctuations for each filter.

Unfortunately, the results obtained using multiple filters can often have multiple interpretations. For example, Appel et. al. (1979) found there was 21% more total carbon in seven two hour samples than in one 14 hour sample. While these results support the volatilization assumption, an alternative conclusion can be reached by looking at gas phase adsorption to the filter. Indeed, a compound in the gas phase will partition not only to atmospheric particulate matter but also to the filter. By repeatedly exposing clean filters to ambient gas phase concentrations, there is the potential that the higher concentration measured using multiple filter may have been due to sorption on the filters. In the above example, the 21% increase could actually correspond to a 3% adsorption artifact for each of the seven filters.

Another complicating factor is the potential for chemical reactions on a particle laden filter to be interpreted as volatilization losses. For example, certain PAHs have been found to undergo nitration and epoxidation reactions under ambient sampling conditions (Pitts et. al., 1978; Pitts et. al., 1980; Lee et. al., 1980). However, the magnitude of this effect may be quite variable. While, for some of the more reactive PAHs this effect could be significant, its magnitude for the less reactive PAHs and for the n-alkanes is not significant (Konig et. al., 1980).

The potential artifact of gas phase adsorption to a filter has received much less attention. From the limited amount of data available on this subject it is clear that under certain circumstances, gas phase adsorption to a filter can be a significant artifact. For example, inorganic gas phase sulfate and nitrate have been found to sorb onto a particle laden filter causing as much as a 10 fold increase in the amount collected in the particulate phase (Spicer and Schumacher, 1977; Coutant, 1977; Witz and Went, 1981). For organic carbon, Cadle et. al. (1983) have reported that an average of 15% collected on quartz fiber filters (QFFs) is from adsorbed gas. Eichman et. al. (1979) reported that for the more volatile n-alkanes (C_9 - C_{17}), gas phase adsorption can account for up to 20% of the measured particulate phase concentration. Ligocki and Pankow (1989) have reported that gas phase adsorption of some PAHs and n-alkanes can account for anywhere from 5-70% of the amount found on primary filter in a configuration with two filters in series.

McDow and Huntzicker (1989) studied the effects of face velocity (volumetric flow rate / filter surface area) on gas phase adsorption of organic carbon to quartz and Teflon membrane filters and combinations of the two. They used a series of side by side samplers consisting of a QFF followed by another

QFF, and another sampler that was equipped with a Teflon membrane filter (TMF) followed by a QFF. They hypothesized that if physical adsorption is the most important artifact, then the amount of adsorption will be dependent on the surface area of the filter. They observed that the measured concentration of aerosol organic carbon was found to exhibit a significant decrease with increasing face velocity. They also found that concentration of organic carbon on the QFF behind the TMF was approximately twice that of the QFF behind a QFF, under the same sampling conditions. Thus, by placing a QFF behind a TMF as opposed to a QFF (a TMF has ~7 times less surface area than a QFF), a better estimate of the amount of gas phase adsorption to a primary filter can be determined than obtained with a QFF/QFF combination.

From the above series of experiments, McDow and Huntzicker (1989) concluded that: 1) volatilization or outgassing from the filter itself was not responsible for the organic carbon concentrations measured on the backup QFFs; and 2) under typical sampling conditions, gas phase adsorption was the dominant artifact for organic carbon measured on QFFs. The magnitude of this artifact was found to be significant (>20%) in typical ambient air. While these results were obtained using a method that did not distinguish between different compounds on the filter, similar results are expected for atmospheric compounds that have a significant concentration in the gas phase.

Based on the above discussion, it may be concluded that when sampling atmospheric particulate matter, both gas adsorption to the filter and volatilization from the particulate matter need to be considered in order to obtain a realistic estimate of the atmospheric, particulate phase-associated concentration. Depending on the design of the experiment, the magnitudes of the two artifacts discussed above can either be corrected for, or minimized. One way to accomplish this is to minimize the sampling time so as to minimize the fluctuations in temperature and also the potential for sampling air parcels of different compositions (Cadle et. al., 1983). In conjunction with this approach, using QFF and TMF filters to estimate the contribution of gas adsorption as described by McDow and Huntzicker (1989) will provide a system that addresses the major artifacts associated with sampling.

2.2.2. Review of Sampling Methods for the Gas Phase

The most common method for sampling gas phase SOCs in ambient air is to use some type of sorbent that traps the analytes of interest. The ideal properties of a sorbent for gas phase sampling of SOCs are ones that will permit relatively high volumetric flow rates (up to 1.5 m^3/min) while quantitatively collecting the analyte of interest. These sorbents must also allow easy recovery of the trapped analytes and have relatively low blank levels. The type of sorbent used depends on the chemical and physical properties of the target compounds as well as the concentration range of the compounds of interest. Concentrations in the atmosphere generally decrease with decreasing volatility. Since the more volatile compounds are present at relatively higher concentrations, small bed volumes (<10 cm^3) and volumetric flow rates of <600 ml/min are used to collect them. For the less volatile compounds, much larger bed volumes (<635 cm^3) are used with volumetric flow rates of up to 1.5 m^3/min. The increased bed volumes and flow rates are needed to obtain enough sample so that compounds that are at very low concentrations in ambient air can be determined.

The collection efficiency of sorbents beds can be examined in the context of chromatographic theory (Tanaka, 1978; Brown and Purnell, 1979; Bertoni et. al., 1981; Krost et. al., 1982; Bidleman et. al., 1984; Feng and Bidleman, 1984; Pankow, 1988; Pankow, 1989). Sorbent beds can be thought of as short chromatographic columns. Sampled analytes are initially trapped at the head of the sorbent bed. As the sampling continues, the analytes will continue to migrate through the bed by a series of desorptions and readsorptions. The compounds will begin to elute off of the bed in large amounts when breakthrough volumes of the analytes are approached. Breakthrough volumes depend on the affinity of the analyte for the sorbent bed, the volume of the sorbent bed, and the ambient temperature.

A variety of sorbents have been used to sample the more volatile constituents in ambient air. Activated carbon was one of the first sorbents used. However, it did not permit quantitative recovery for many compounds (West et. al., 1958). Chromatographic packing materials (e.g. Porapak Q and S, Chromsorb, and Tenax) were next studied for a variety of compounds (Williams and Umstead, 1968;

Dravnieks et. al., 1971). Tenax-GC, a 2,6-diphenyl phenylene oxide porous polymer was found to be very useful in trace gas analysis as it exhibits low blank levels and high thermal stability (Zlatkis et. al., 1973; Bertsch et. al., 1974; Pellizari et. al., 1975a,b). Several years later, Tenax-TA became available as specially processed Tenax-GC that offered even lower blank levels and a higher specific surface area for adsorption. Tenax-GC has continued to be highly popular. Crisp (1980) has reviewed solid sorbent samplers and most of the chromatographic packing materials used in these samplers. While most of the above sorbents are effective at low sample volumes, compounds with relatively high vapor pressures ($p^\circ > 10^{-1}$ torr) exhibit significant breakthrough for large sample volumes. For example, Brown and Purnell (1979) determined that at 20 °C, the 1% breakthrough volume for acetone ($p^\circ = 10^{1.88}$ torr) was 515 mL for 0.13g of Tenax-GC, sampling at 50 mL/min.

As noted above, for measurement of compounds that are present in the atmosphere at relatively low concentrations, large volumes of air need to be sampled. While large Tenax-GC and -TA traps could be used, the cost of these traps is prohibitively expensive and the pressure drop through these sorbent beds is not compatible with sampling at the flow rates needed to obtain a large sample volume. As an alternative, polyurethane foam (PUF) has been successfully applied to a large variety of compounds in the atmosphere (Bidleman and Olney, 1974; Turner and Glotfelty, 1977; Lewis, 1977; Ligocki and Pankow, 1985). PUF has many advantages for sampling atmospheric SOCs: it is inexpensive, easy to handle, easy to clean prior to sampling, and once collected, the trapped analytes are easy to recover. These features make PUF very attractive for compounds where large volumes must be sampled. It is unfortunate that the more volatile SOCs exhibit low breakthrough volumes on PUF.

In order to quantitatively determine compounds in the gas phase with a wide range of volatilities, an integrated approach using both Tenax-TA for the more volatile compounds and PUF for the less volatile compounds should be used. An advantage of this type of system is that there is sufficient overlap of compounds of intermediate volatility that each method can be used as an independent check on the other to determine the sampling efficiencies of the sorbents. While Bidleman and Olney (1974) were the first group to report this sampling approach, others were quick to follow (Cautreels and Van Cauwenberghe, 1978; Thrane and Mikalsen, 1978; Yamasaki et. al., 1982; Keller and Bidleman, 1984).

Samplers that have integrated both particulate and gas phase measurements have enjoyed limited success in light of the artifacts associated with sampling the particulate phase. In the studies using integrated samplers, the only artifact that was investigated, if any, was volatilization. However, as noted above, one needs to minimize the magnitudes of both volatilization and gas adsorption to the QFFs to truly understand the partitioning process. Therefore, an integrated sampler that uses both QFF/QFF and TMF/QFF combinations, with high enough volumetric flow rates so that temperature and air parcel fluctuations are minimized, will provide the best estimates of the concentrations in both the gas and particulate phases. These filters should then be followed by a gas sampling train that includes PUF in parallel with a low flow rate Tenax-TA sampling train.

2.2.3. Review of Analytical Methods

2.2.3.1. General

After collection, the target compounds need to be transferred from the sampling matrix to the analytical instrument. There are three basic methods for isolation of the SOCs: supercritical fluid extraction, solvent extraction, and thermal desorption. Supercritical fluid extraction has received much attention, however many uncertainties still remain concerning its applicability to a wide range of compounds and matrices (e.g. Hawthorne et. al., 1989).

2.2.3.2. Solvent Extraction

Solvent extraction of porous polymers, PUF, QFFs, and TMFs is typically limited to less volatile compounds that will not suffer appreciable losses during the extraction and subsequent concentration steps. Solvent extraction usually involves either Soxhlet extraction or sonication to promote the transfer of the target compounds into the solvent (Billings and Bidleman, 1980; Leuenberger and Pankow, 1984; Ligocki, 1986).

Once the analytes have partitioned into the solvent, solvent extracts must often be concentrated so that the analytes will be at a detectable level in the analytical determination step. Kuderna-Danish (K-D) apparatus is most commonly used for this solvent concentration step. It involves a selective distillation of the solvent while leaving the target compounds behind. This step is usually followed by a column clean-up step to separate the analytes of interest from other compounds that were extracted with the target compounds and might interfere with the analytical determination. The next step involves concentrating the solvent down for analytical detection (e.g. to ~200 µL) by passing an inert gas over the extract and removing a majority of the solvent. There is a great potential for the loss of the more volatile analytes during the blowdown step, especially when approaching the final volume of 200 µL. This has been addressed by Hart and Pankow (1987) for PCB congeners. They reported quantitative recoveries by skipping the blowdown step and injecting up to 1 mL of extract from the K-D step onto a glass wool / Tenax cartridge, selectively volatilizing the solvent, then thermally desorbing the analytes directly onto the head of a capillary column.

2.2.3.3. Thermal Desorption

Thermal desorption directly from Tenax for relatively volatile compounds has been studied extensively (Pellizzari et. al., 1975a,b; Pankow et. al.; 1982a,b; Pankow and Kristensen, 1983; Ligocki et. al., 1985; Hart and Pankow, 1987;

Pankow et. al., 1988). For such compounds, thermal desorption has many advantages over solvent extraction. For example, it allows a sample to be obtained and processed with minimal handling. It also allows the analysis of the complete sample, not a fraction as when solvent extraction is used to recover the analytes.

In addition to using it to recover analytes from Tenax, thermal desorption has also been applied to particle laden filters with some success (Greaves et. al., 1985; McDow, 1986; Turpin and Huntzicker, 1988). However, incomplete desorption of the less volatile analytes along with the desorption of some compounds that degrade the performance of the analytical chromatography column are problems that need to be addressed before thermal desorption of filters can become a mainstream technique.

After extraction and concentration by whatever method (i.e. supercritical extraction, solvent extraction, or thermal desorption), the analytes need to be separated from each other and other interfering compounds in order for them to be identified. Gas chromatography (GC) or high performance liquid chromatography (HPLC) are the most widely used methods for separating complex mixtures into their components. For most nonpolar SOCs (e.g. n-alkanes and PAHs), GC is the method of choice since a wide variety of specific detectors can be coupled to a GC column. HPLC is typically reserved for compounds that are not easily gas chromatographable, e.g. polar and thermally labile compounds. Although, a wide variety of detectors are available for the GC, the most widely used detector for complex samples is the mass spectrometer (MS). There are many advantages of a coupled GC/MS system including adequately low detection limits (~0.5 ng), a linear dynamic range of ~10^3, and mass information for each fragment of each compound. This technique has been used extensively in the determination of a variety of compounds in complex environmental matrices (e.g. Eichelberger et. al., 1974; Cautreels and Van Cauwenberghe, 1978; Ligocki, 1986).

Chapter 3. Partitioning Theory and Gaseous/Particulate Phase Distributions

3.1. Langmuir Isotherm

The Langmuir model for sorption assumes that a certain finite number (S) of sorption sites are present (Langmuir, 1918). If S_o equals the number moles of sites that are unoccupied and S_1 equals the number that are occupied, then

$$S = S_o + S_1 \tag{3.1}$$

For gas/solid sorption, when evaporation and sorption are at equilibrium, then

$$k_1\ S_1 = k_2\ p\ S_o \tag{3.2}$$

where k_1 and k_2 are desorption and sorption rate constants (s^{-1}), respectively, and p is the gas phase partial pressure (atm) of the compound of interest. If θ_L is the fraction of sites occupied at equilibrium, then

$$\theta_L = \frac{S_1}{S} = \frac{b_L p}{1+b_L p} \tag{3.3}$$

where $b_L = k_2 / k_1$. Pankow (1987) derives the expression for b_L (atm^{-1}) as

$$b_L = \frac{N_o s_o (1.013\text{x}10^6 \text{ gcm}^{-1}\text{s}^{-2}/\text{atm}) t_o e^{Q1/RT}}{(2\pi MRT)^{1/2}} \qquad 3.4$$

where N_o = Avogadro's number (6.02 x 10^{23} mol^{-1})

s_o = surface area per sorption site (cm^2)

t_o = characteristic molecular vibration time (10^{-13} - 10^{-12} s)

Q_1 = enthalpy for desorption directly from the surface (kcal mol^{-1})

R = gas constant

T = temperature (°K)

M = molecular weight (g mole^{-1})

Equation 3.4 can be rewritten as $b_L = b_{O,L}e^{Q1/RT}$, where b_L is a strong function of temperature .

As described by Pankow (1987), focussing on 1 cm^3 of air, we have

$$\theta_L = \frac{S_1/V}{S/V} = \frac{S_1/V}{\theta_J N_s} \qquad 3.5$$

where S_1/V represents the concentration of occupied sites and $\theta_J N_s$ represents the concentration of total sites available for adsorption. From equation 2.1, θ_J is the aerosol surface area concentration (cm^2/cm^3) and N_s is the number of moles of sorption sites/cm^2 on the particulate matter. N_s will depend not only on the identity of the sorbing compound but also on the chemical and physical properties of the particulate matter. Thus, for Langmuirian sorption, the particulate-associated concentration of a sorbing compound in the atmosphere in units of mol/cm^3 will be given by

$$c_{p,m} = S_1/V = \theta_L \theta_J N_s \tag{3.6}$$

By the Ideal Gas Law,

$$c_{g,m} = n/V = p/RT \tag{3.7}$$

where n/V is mole/cm^3 in the gas phase. From equations 3.3-3.7,

$$\phi = \frac{b_L RT \theta_J N_s}{1+b_L p+b_L RT \theta_J N_s} \tag{3.8}$$

When $b_L p \ll 1$, the isotherm can be linearized, leading to

$$\phi = \frac{b_L RT \theta_J N_s}{1+b_L RT \theta_J N_s} \tag{3.9}$$

3.2. BET Isotherm

As discussed by Brunauer et. al. (1938) and summarized by Adamson (1982) and Pankow (1987), multilayer sorption can be described by simultaneous sorption / desorption equilibria. Junge (1977) began with the BET equation in the following form:

$$\mathbf{n/n_{\infty}} = \frac{b_B p}{(p_o - p)(1 + (b_B - 1)p/p_o)} \qquad 3.10$$

where **n** = surface concentration of the sorbed species (g cm^{-2})

n_{∞} = surface concentration for a monolayer (g cm^{-2})

b_B = dimensionless constant

p = gas phase partial pressure of compound (atm)

p_o = saturation vapor pressure at temperature of interest (atm)

When the entropy of desorption from the surface is approximately equal to the entropy of vaporization of the liquid (Q_v), then

$$b_B \approx e^{(Q1-Qv)/RT} \qquad 3.11$$

When p is very low relative to p_o, the extent of coverage is low and few sites are occupied and $n/n_\infty \approx \theta_L$ (i.e. the fractional coverage predicted from BET theory is approximately equal to the fraction of the sorption sites occupied that is predicted from linear Langmuirian adsorption theory). From equations 3.4 and 3.11

$$b_L = b_{O,L} b_B e^{Qv/RT} \tag{3.12}$$

Pankow (1987) has shown that when the surface is completely covered by the liquid sorbate (i.e. $p = p_o$), b_L is related to b_B by the following expressions

$$b_{O,L} = 1/p_o \tag{3.13}$$

$$b_L = b_B/p_o \tag{3.14}$$

The derivation of Junge's equation for ϕ starts with a form of the BET equation and immediately makes the assumption that the sorption is linear in nature. Namely, when $b_B >> 1$, $p << p_o$, and there is low coverage ($\theta_L < 1$), then linear Langmuirian adsorption is assumed. Using these assumptions in equation 3.10, along with equations 3.9 and 3.14, ϕ can be expressed as a function of b_B and p_o (torr)

$$\phi = \frac{760 b_B R T \theta_J N_s}{p_o + 760 b_B R T \theta_J N_s} \tag{3.15}$$

By comparing equation 2.1 with 3.15, Pankow (1987) has shown that

$$c_J = 760 b_B RTN_s = 760 RTN_s e^{(Q1-Qv)/RT} \qquad 3.16$$

If $N_s e^{(Q1-Qv)/RT}$ is relatively constant from compound to compound and for a given sample particulate matter, then c_J will likewise be constant.

3.3. Application of Adsorption Theory to Gas/Particle Partitioning

Yamasaki et. al. (1982) and Bidleman et. al. (1984) have applied a linear Langmuir isotherm to the equilibrium distribution coefficient, K. From Langmuirian adsorption theory, Pankow (1987) derives

$$K = \frac{A(TSP)}{F} = \frac{990(2\pi MRT)^{1/2}}{N_s A_{tsp} N_o s_o t_o RTe^{Q1/RT}} \qquad 3.17$$

where A_{tsp} = specific surface area of TSP (cm²/µg)

$$\log K = m / T + b \qquad 3.18$$

From equations 3.17 and 3.18

$$m = \frac{Q_1}{2.303R} + \frac{T_{amb}}{4.606} \qquad 3.19$$

$$b = \log \frac{2.75x10^5(M/T)^{½}}{A_{tsp}t_o} - \frac{1}{4.606} \qquad 3.20$$

With M = 175 g/mol, T_{amb} = 293 °K, A_{tsp} = 0.025 $cm^2/\mu g$, and $t_o = 10^{-12.5}s$, using equation 3.20 Pankow (1987) obtains an estimate for b of 19.2. Experimental values of b for PAHs has been estimated to be 21.4 ± 2.0 respectively (Yamasaki et. al. 1982; Bidleman et. al. 1986). The experimental and predicted values of b are surprisingly close given the potential for a wide range of both atmospheric conditions and the physical and chemical compositions of the particulate matter. This is especially true given that the b values are often based on samples taken throughout the year where seasonal influences on the nature of the particulate matter might be expected to be large.

Rather than examining m and b data obtained from a potentially wide range of atmospheric conditions, it may be more useful to look at a class of similar compounds for a particular sampling event as a function of saturation vapor pressure. One of the advantages of examining K as a function of p is that the fluctuations in atmospheric conditions and composition of particulate material can be reduced by focussing on sorption to particulate matter collected over a single sampling interval. The expression derived by Pankow (1987) for the equilibrium distribution coefficient using equations 3.4, 3.13, and 3.17 is

$$K = \frac{10^6 p_o}{N_s A_{tsp} R T e^{(Q1-Qv)/RT}} \tag{3.21}$$

Thus

$$\log K = \log C + \log p_o \tag{3.22}$$

$$\text{where} \quad C = \frac{10^6}{N_s A_{tsp} R T e^{(Q1-Qv)/RT}} \tag{3.23}$$

Using values of $N_s \approx 4\text{x}10^{-10}$ mole/cm^2, $A_{tsp} \approx 0.025$ cm^2/µg, and T = 293°K, equation 3.21 becomes (Pankow, 1987)

$$K \approx (5.6)^{-j}(5.5\text{x}10^9)p_o \tag{3.24}$$

where $j = Q_l - Q_v$ (kcal/mol)

If $N_s e^{(Q1-Qv)/RT}$ is relatively constant from compound to compound, a plot of log K vs. log p_o at a given temperature will have a constant slope equal to +1.

The y-intercept will give an estimate of the difference between desorption energies from the surface of the particulate material to that of the pure liquid. Limited experimental evidence suggests that this difference is ~3 kcal/mole for PAHs (Yamasaki et. al., 1982; Ligocki and Pankow, 1989 and Bidleman et. al., 1986). Based on these measurements and equation 3.20, at 20°C, $b \approx 7.50$ for PAHs.

3.4. Nonexchangeable Material

In gas/particle partitioning, non-equilibrium conditions can result when a compound is not able to exert its full thermodynamic activity in the particulate phase. This would occur whenever some of the compound is bound within the particulate phase as nonexchangeable material. The bound material would not be available for equilibrium partitioning and would lead to a lower ratio of gas phase to particulate phase concentrations than would be expected at full equilibrium. This would cause the value of log A(TSP)/F to be lower than expected and the fraction associated with particulate matter (ϕ) to be higher than expected.

In a manner that is consistent with the above discussion, detailed investigations of equation 3.22 and plots of log A(TSP)/F vs. log p_o have indicated that the more volatile compounds can exhibit lower values of log A(TSP)/F than would be expected for full equilibrium. In fact, both Ligocki and Pankow (1988) and Foreman and Bidleman (1988) have shown that for compounds with relatively high vapor pressures, significant negative deviations from a linear relationship between log A(TSP)/F and log p_o occurs.

An expression has been formulated by Pankow (1988) to predict the magnitude of this nonexchangeable effect. Let x be the percentage of compound that is nonexchangeable. The value of x will depend on the compound of interest and also the physical and chemical characteristics of the particulate matter. At equilibrium (denoted by subscript eq), the gas phase concentration can be determined from equation 3.22

$$A_{eq} = F_{eq} C p_o \,/\, (TSP) \qquad 3.25$$

where A_{eq} = gas phase concentration at equilibrium (ng/m^3)

F_{eq} = particulate phase concentration at equilibrium (ng/m^3)

Let A_T and F_T be the total amount of compound in the gas and particulate phases, respectively, expressed as percentages. Thus

$$A_T + F_T = 100\% \qquad 3.26$$

where $A_T = A_{eq}$ and $F_T = x + F_{eq}$. Therefore, expressions can be written for A_{eq} and F_{eq} as

$$F_{eq} = \frac{100\text{-}x}{1+Cp_o\ /(TSP)} \qquad 3.27$$

$$A_{eq} = \frac{(100\text{-}x)Cp_o\ /(TSP)}{1+Cp_o\ /(TSP)} \qquad 3.28$$

The expressions for the distribution coefficient (equation 3.22) and fractions associated with the particulate phase (equation 2.1) can be modified by the above expressions to yield

$$\log \frac{A_T(TSP)}{F_T} = \log C + \log p_o + \log \frac{100\text{-}x}{100+Cp_o x\ /(TSP)} \qquad 3.29$$

and

$$\phi = \frac{\dfrac{(100\text{-}x)}{[1+Cp_o\ /(TSP)]} + x}{100} \qquad 3.30$$

The significance of equation 3.29 to gas/particle partitioning has been reviewed by Pankow (1988). In particular, he notes that:

1) equation 3.29 reverts back to equation 3.22 when x=0;

2) the direction of the deviation from the line described by equation 3.29, as a function of log p_o, will always be negative;

3) increasing x will always increase the deviation;

4) the magnitude of the deviation increases as p_o increases; since the value of log $A_T(TSP)/F_T$ cannot be increased beyond the constant value of log $[(100-x)(TSP)/x]$, even when full equilibrium conditions would result in exceedingly large values of this ratio;

5) increasing TSP for constant x and p_o will decrease the deviation since doing so increases the amount of material associated with the particulate matter anyway; and

6) when the value of $Cp_ox/(TSP)$ is small relative to 100, then the negative deviation becomes constant and independent of p_o and equal to $\log((100-x)/100)$.

The presence of even as small a fraction as 0.01% can have a profound effect on the partitioning and hence transport of compounds in the environment. This might be especially true for compounds formed during fossil fuel combustion (e.g. PAHs and alkanes), where some of the more volatile compounds could be trapped in/on organic soot particles as those particles cool.

3.5. Measurement of Gas/Particle Partitioning in the Atmosphere

As described in Section 2.2.1, measurement of atmospheric gas/particle partitioning of SOCs has traditionally been accomplished by passing a volume of air through a filter followed by an adsorbent. The SOCs are then extracted from the filter and sorbent with solvent and analyzed by GC/MS. This approach has been used extensively to measure the concentration of SOCs in a variety of locations. However, there has been far more research completed on measuring the concentrations in the particulate and gas phases (especially the particulate phase), than on the factors that actually influence the partitioning between the phases.

Particulate phase concentrations have been determined in marine air (Duce and Gagosian, 1982; Masclet et. al., 1988; Sicre et. al., 1987a,b; Eichman et. al., 1979 and 1980; Halkiewicz et. al., 1987), urban air (Bidleman et. al, 1986; Farmer and Wade, 1986; Yamasaki et. al., 1982; Greaves et. al., 1987; Coutant et. al., 1988; Van Vaeck et. al., 1978; Cautreels and Van Cauwenberghe, 1978; Ligocki and Pankow, 1989), and remote air (Simoneit, 1984; Doskey and Andren, 1986; McVeety and Hites, 1988).

Gas phase concentrations of SOCs have been determined in marine air (Eichmann et. al., 1979 and 1980; Masclet et. al., 1988; Duce and Gagosian, 1982), urban air (Bidleman et. al, 1986; Farmer and Wade, 1986; Yamasaki et. al., 1982; Greaves et. al., 1987; 1988; Van Vaeck et. al., 1978; Cautreels and Van Cauwenberghe, 1978; Ligocki and Pankow, 1989), and remote air (Doskey and

Andren, 1986; McVeety and Hites, 1988). Particulate and gas phase concentrations can be used to help predict the fluxes into or out of an ecosystem.

While many of the studies cited above measured the concentrations of SOCs in both the gas and particulate phases, generally, little attention was paid to monitoring the atmospheric conditions during sampling. Also, as very few studies measured TSP or the ambient T, the possibility of sampling artifacts was usually not considered. It is therefore of little use to apply Langmuirian adsorption theory to these data sets.

The study by Yamasaki et. al. (1982) in Tokyo was the first to examine partitioning of PAHs as a function of ambient temperature and TSP (equation 2.3). Bidleman et. al. (1986, 1987a,b) examined PAHs and organochlorines compounds in Columbia SC, Denver CO, New Bedford MA, and Stockholm Sweden and found that equation 2.3 is obeyed in those cities as well. Ligocki and Pankow (1988) obtained similar results for PAHs in Portland, OR. These results have led to the conclusion that the sorption properties of urban particulate matter are similar and are only weak functions of season and location. This is rather surprising as the physical and chemical composition of particulate matter would seem to have the potential to vary significantly from city to city.

3.6. The Role of Partitioning in Environmental Fate Calculations

3.6.1. Precipitation Scavenging

It has been estimated that atmospheric input of PCBs to the Great Lakes ecosystem accounts for >80% of the input from all sources, including direct industrial discharges to the lakes (Eisenreich, 1981). Atmospheric removal of SOCs by precipitation scavenging accounts for at least 50% of the input for each of the PAHs and organochlorines studied by Murphy (1981), Andren and Strand (1981), Bidleman et. al. (1981), and Strachan and Eisenreich (1986). The magnitude of the effect of precipitation scavenging can be estimated by the washout ratio W. Pankow (1987) developed an expression for W as

$$W = W_g(1-\phi) + W_p\phi \tag{3.31}$$

$$\text{where} \quad W_g = RT/H = \frac{[\text{dissolved, rain}]}{[\text{gaseous, air}]} \tag{3.32}$$

and

$$W_p = \frac{[\text{particulate, rain}]}{[\text{particulate, air}]} \tag{3.33}$$

and W_g = gas scavenging washout ratio

W_p = particle scavenging ratio

H = Henry's Gas Law constant (atm-m^3/mol)

[ ] = concentration (e.g. ng/m^3)

The first term in equation 3.31 describes the removal due to gas scavenging and the second term describes removal by particle scavenging.

The flux from precipitation scavenging can be estimated by

$$F_{wet} = [air]\ W\ P \qquad 3.34$$

where F_{wet} is in g/(m^2 yr), and P is the precipitation rate in m/yr. Therefore, in order to obtain accurate values of the washout ratios and fluxes for SOCs, accurate estimates of a compound's concentrations in the gas and particulate phases are needed.

3.6.2. Gas Exchange

All compounds in the gas phase have the potential to undergo direct exchange with bodies of water. Since water covers ~75% of the earth's surface, there is the potential for gas exchange to make a significant contribution to the cycling of such compounds. This is especially true for compounds that are soluble or slightly soluble in water. A two film model has been used to describe the steady state flux (mol/m^{2}h) into or out of a body of water (Liss and Slater, 1974)

$$F_{gas} = k_g(c_g - c_{g,I}) = k_l(c_l - c_{l,I}) \qquad 3.35$$

where k_g and k_l are mass transfer coefficients for the gas and liquid phases, respectively and the subscript I denotes interfacial layer. When $c_{g,I}$ and $c_{l,I}$ are in equilibrium with one another, then (Mackay and Leinonen, 1975)

$$F_{gas} = k_{OL}(C - p/H) \qquad 3.36$$

$$\frac{1}{k_{OL}} = \frac{\ }{k_L} + \frac{RT}{Hk_G} \qquad 3.37$$

where k_{OL} = overall mass transfer coefficient (m/h)

C = solute concentration in liquid phase (mol/m^3)

p = solute partial pressure (atm)

Accurate dissolved and gas phase concentration values are needed in order to predict flux rates from gas exchange.

For compounds whose transport is dominated by liquid phase resistance ($H \geq 5 \times 10^{-3}$), equation 3.36 reduces to

$$F_{gas} = k_L(c\text{-}p/H) \tag{3.38}$$

Conversely, for compounds whose transport is dominated by gas phase resistance ($H \leq 5 \times 10^{-6}$), equation 3.36 becomes

$$F_{gas} = \frac{k_G(cH\text{-}p)}{RT} \tag{3.39}$$

For neutral SOCs, that are at least slightly soluble in water, equation 3.38 will be the most applicable form of the gaseous exchange flux equation.

3.6.3. Dry Deposition

Direct deposition of particulate matter to the earth's surface can make a significant contribution to atmospheric flux of SOCs. For example, Eisenreich et. al. (1981) estimated that the atmospheric inputs of PCBs to the Great Lakes ecosystem from dry deposition exceeded wet deposition by a factor of 2.5 . The flux from dry deposition may be parameterized according to

$$F_{dry} = c_p \; v_{d,p} \tag{3.40}$$

where $v_{d,p}$ = particle dry deposition velocity (cm/s)

Dry deposition velocities are strongly influenced by the size distributions of the particles being removed. Like atmospheric particulate filtration, the smaller particles are removed at the surface by Brownian diffusion and the larger particles are removed by impaction. Very large particles are removed by gravitational settling. Most researchers studying dry deposition are working towards obtaining accurate estimates of $v_{d,p}$ for both hygroscopic and non-hygroscopic surfaces. Thus, accurate values of both c_p and $v_{d,p}$ are needed to accurately predict the importance of F_{dry} to an ecosystem.

Chapter 4. Air Sampling for SOCs

4.1. Experimental Procedure

4.1.1. Sampling Apparatus

An air sampler was developed which can concurrently sample both the gas and particulate phases for SOCs. This sampler is of the high volume (HI-VOL) type. It utilizes 20 x 25 cm quartz fiber filters (QFFs) or Teflon membrane filters (TMFs) followed by two parallel gas sampling channels (Figure 4.1). In an effort to determine the magnitude of gas phase adsorption of SOCs to filters, two identical samplers were built (Figure 4.2). The first HI-VOL utilized a QFF followed by another QFF. This sampler will be referred to as the quartz sampling train. The second sampler utilized a TMF followed by a QFF, and will be referred to as the Teflon sampling train. The terms quartz sampling train and Teflon train will be used throughout the remainder of the document. The HI-VOLs were designed to reduce volatilization losses by minimizing the sampling time. This was achieved by using 20 x 25 x 1.27 cm rectangular PUF sheets (PUFSs) operating at a volumetric rate of ~1.4 m^3/min. Since the collection of SOCs on sorbents can be thought of in terms of chromatography theory, the mass or volume of the sorbent is the factor controlling retention volume, not the shape of the bed. Thus, two sorbent beds with identical sorbents having different geometric shapes, but the same

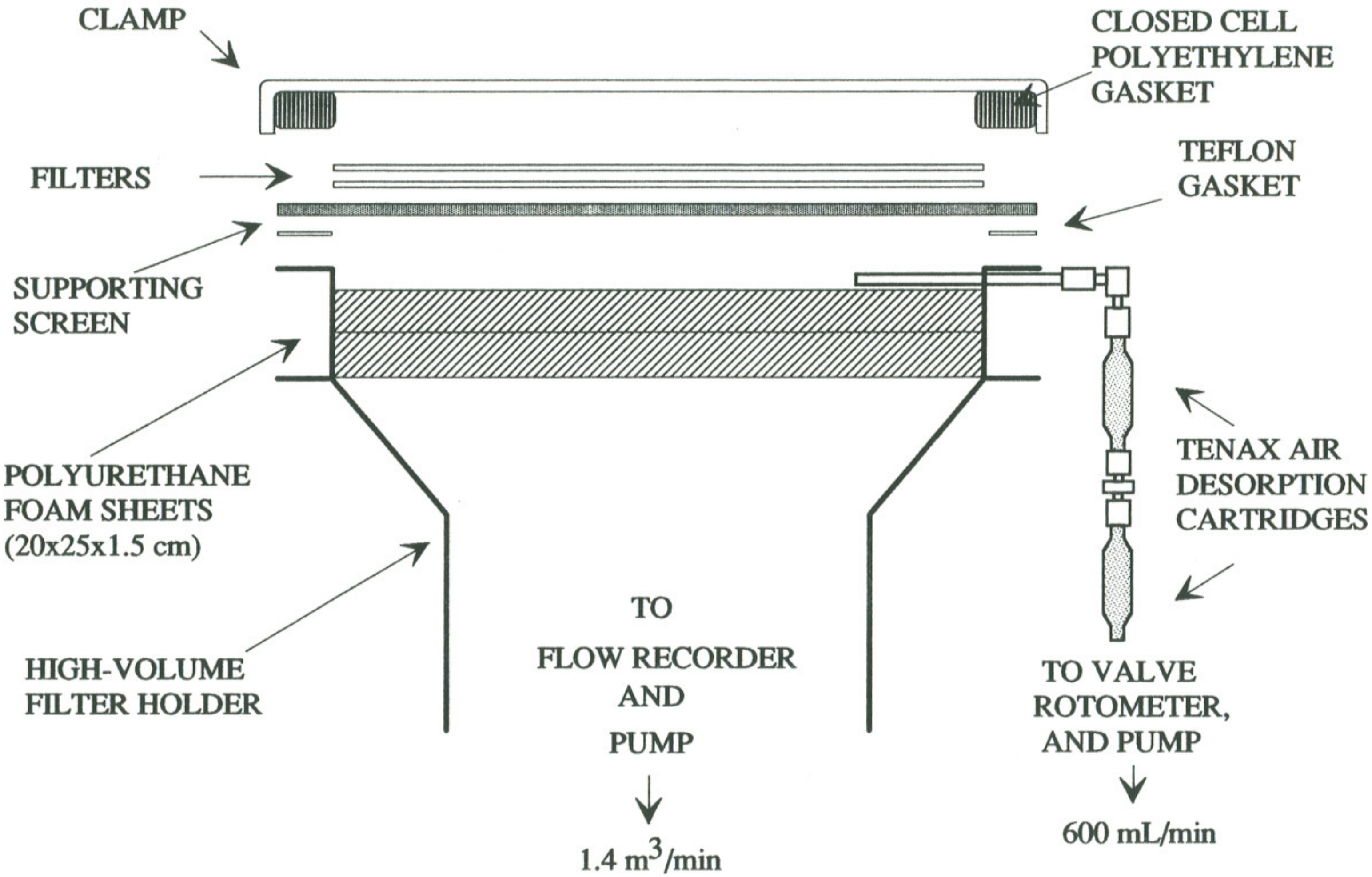


Figure 4.1. Exploded view of HI-VOL air sampler used to concurrently sample particulate and gas phase SOCs.

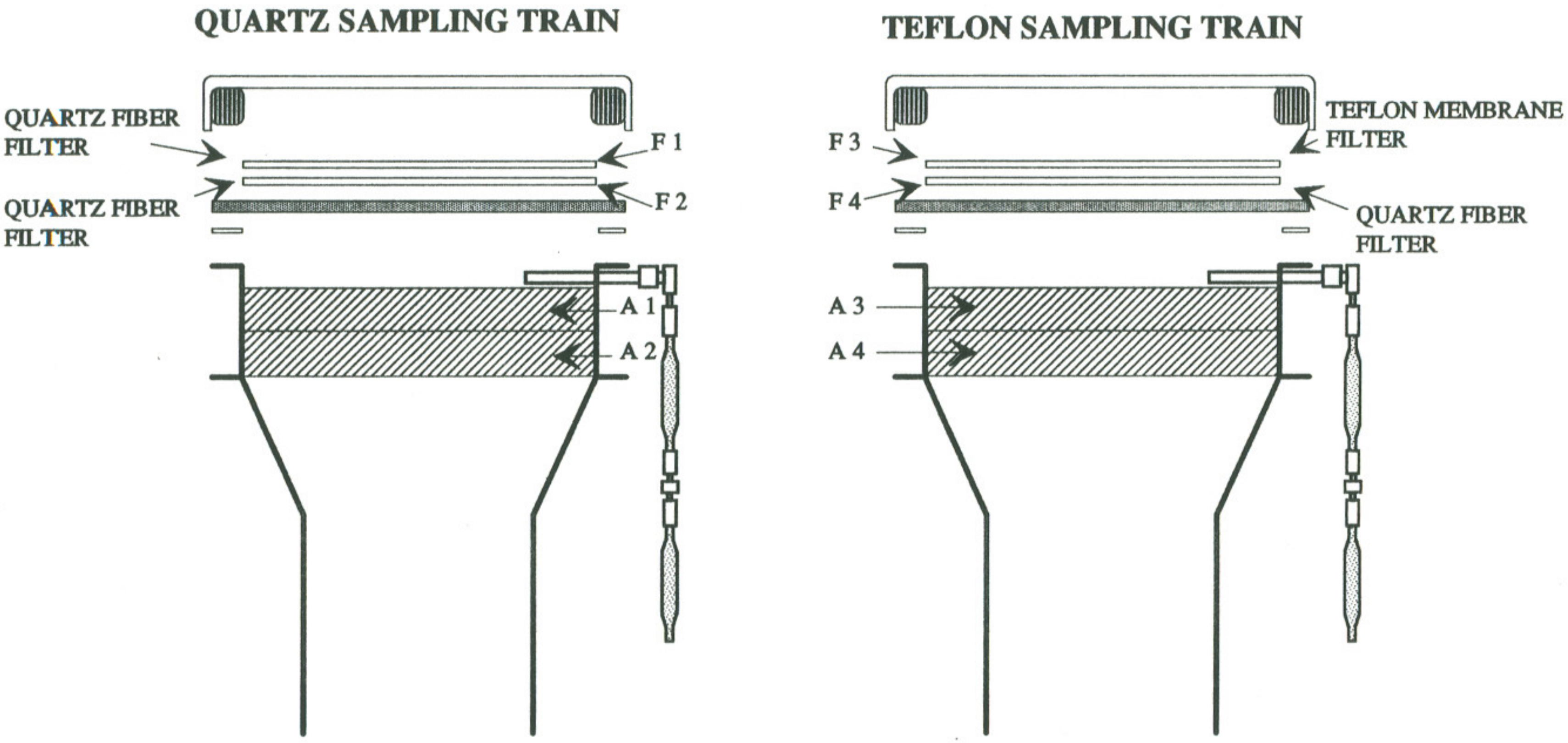


Figure 4.2. Exploded view of the HI-VOL air samplers. a) quartz sampling train. b) Teflon sampling train. F1) quartz/quartz primary filter (QQP). F2) quartz/quartz backup filter (QQB). A1) primary PUFS behind the quartz filter train (PQP). A2) backup PUFS behind the quartz filter train (PQB). F3) Teflon/quartz primary filter (TQP). F4) Teflon/quartz backup filter. A3) primary PUFS behind the Teflon sampling train. A4) backup PUFS behind the Teflon sampling train.

mass or volume of sorbent will theoretically have the same collection efficiencies. Thus, rather than use the more common 7.5 x 7.5 cm o.d. PUF plug for which the maximum flow rate is ~0.2 m^3/min, a rectangular PUF bed system was developed.

A 20 x 25 cm stainless steel box was welded onto a seamless stainless steel HI-VOL filter holder (Anderson Samplers, Atlanta, GA) to hold the PUFSs. The less volatile SOCs were collected by the PUFSs, while the more volatile compounds were collected on Tenax-TA air desorption cartridges (ADCs). A Gast 1031 oil-less carbon vane pump (Gast Manufacturing Corp., Benton Harbor, MI) provided a flow rate of ~600 mL/min through the Tenax cartridges, while a General Metal Works model 2000 blower (Ann Arbor, MI) provided the flow for the PUFSs. The Gast pump, a programmable timer, and a recording thermograph were housed in a box ~6 m downwind of the HI-VOLs. The flow rate for the HI-VOLs was measured with a top loading orifice flow calibrated pressure transducer (Anderson Samplers, Atlanta, GA), while the ADC flow rates were measured with a laboratory-calibrated rotameter (Dwyer Instruments, Michigan City, IN).

The ADC bodies were constructed of 1.1 cm o.d. x 8.0 cm long Pyrex tubing. Each 5.7 cm^3 bed volume was packed with 0.79 g of 35/60 mesh Tenax-TA and was held in place by silanized glass wool. The ends of the cartridges were constructed of precision 0.64 cm o.d. Pyrex tubing and were sealed with Teflon ferrules in 0.64 cm stainless steel Swagelok (Crawford Fitting Co., Solon, OH) fittings for sampling and storage.

4.1.2. Sampling Site

Fourteen samples were collected at the Oregon Department of Environmental Quality's (ODEQ) air monitoring station located at 5824 S.E. Lafayette. The station is in an urban/residential area of southeast Portland. The samplers were located on the ~10 m high roof of the ODEQ air monitoring station and were on opposite corners of a 8 x 8 m platform. Sampling days were chosen to coincide with ODEQ's measurements of TSP and PM-10 (concentration of particulate material <10 μm, in μg/m^3). The samplers were operated by a programmable timer starting at 0600 and ending at 1200 hr for each sampling event.

4.1.3. Materials

The 20 x 25 cm QAOT-UP QFFs were obtained from Pallflex Corp. (Putnam, CT). The 2 μm pore size, 20 x 25 cm Teflon backed Teflon membrane filters (TMFs) (Zefluor) were obtained from Gelman Inc. (Ann Arbor, MI). Polyether type polyurethane foam with a density of ~0.022 g/m^3 was purchased from Beaverton Packaging Co. (Beaverton, OR) in precut 22 x 26 x 1.3 cm sheets. Tenax-TA was obtained from Alltech Associates (Deerfield, IL). Glass distilled methylene chloride was purchased from EM Science (Cherry Hill, NJ). Perdeuterated fluoranthene and perylene were purchased from MSD Isotopes (Los Angeles, CA). Pristane and phytane were purchased from Analabs (North Haven, CT). The other alkanes and PAHs were purchased from Chem Service (West Chester, PA).

4.1.4. Preparation of Sampling Materials

Prior to sampling, PUFSs and TMFs were cleaned by separate Soxhlet extractions for 24 hr with methylene chloride. They were dried under a stream of prepurified nitrogen. The QFFs were baked in a muffle furnace at 600 °C for 4 hr., then allowed to cool in the furnace. The filter heads were cleaned with Alconox detergent (New York, NY), rinsed with deionized water, and baked at 250 °C for 24 hr prior to sampling. The filter heads were then assembled in the laboratory and wrapped in muffle-furnace-baked aluminum foil for transport to the sampling site.

Packed ADCs were cleaned by passing 4 L of 60:40 acetone:hexane through a series of 12 cartridges at a rate of ~4 mL/min with a Waters HPLC pump (Millford, MA). The ADCs were dried with a stream of ultrapure helium, then conditioned by heating at 320 °C for 4 hr under a flow of ultrapure helium (~50 mL/min). After conditioning, the ADCs were capped with pre-cleaned brass Swagelok caps equipped with Teflon ferrules. All of the Swagelok fittings and ferrules were precleaned by sonication in 60:40 acetone:hexane and air dried. They were then baked at ~200 °C under vacuum (20 μm Hg) for 4 hr prior to assembly. The capped cartridges were stored and transported in clean Pyrex culture tubes.

4.1.5. Recovery Studies

Recovery studies of the target compounds from QFFs, TMFs, and PUFSs were completed prior to the first sampling event and after the last one. Absolute and surrogate relative recoveries were obtained by spiking the filters and PUFSs with a mixture of target compounds in methylene chloride. The spiked filters and PUFSs were then subjected to the entire extraction, concentration, clean-up, and analysis procedure used for all samples. Recoveries were determined after each step and the product of the recoveries for these steps was used to calculate an overall recovery for the procedure.

4.1.6. Analysis of Samples

After sampling, the filter head was immediately wrapped in muffle-furnace-baked aluminum foil and brought back to the laboratory. A 47 mm diameter punch was taken from each of the QFFs, placed in aluminum foil lined petri dishes, and stored at 0 °C. Within two months of collection, the punches were analyzed for elemental and organic carbon using a thermo-optical carbon analyzer. The remaining portions of filters and PUFSs were Soxhlet extracted within 1 hr of the end of sampling and the extracts were analyzed within two months. The sealed ADCs were immediately stored at 5 °C and then thermally desorbed within two months of collection.

4.1.6.1. Extraction of Filters and PUFSs

Prior to extraction, the QFFs, TMFs, and PUFSs were each spiked with 100 µL of a surrogate solution containing fluoranthene-d_{10}, eicosane-d_{42}, and perylene-d_{12} each at 40 ng/µL. The surrogate standards were used to monitor losses of the target compounds during the entire analytical procedure. Before each sampling event, all of the extraction glassware was washed with Alconox detergent and either baked in a muffle furnace at 450 °C for 24 hr, or soaked in a chromic acid bath overnight, rinsed with deionized water, and baked at 200 °C for 4 hr.

Each of the filters, including the blank QFFs and TMFs, were Soxhlet extracted with 125 mL of methylene chloride for 4 hr (~20 cycles). The PUFSs, including a blank, were Soxhlet extracted with 350 mL of methylene chloride for 4 hr (~15 cycles). Hot water baths, at 50 °C, provided the heat for the modified round bottom flasks used for the Soxhlets. The Soxhlet extraction apparatus used is shown in figure 4.3. To minimize transfer losses and avoid contamination from the laboratory, the extracts were concentrated to ~2 mL directly in the round bottom flasks used in the extractions. This was carried out using a miniature Kuderna-Danish (K-D) apparatus attached to the top of each flask.

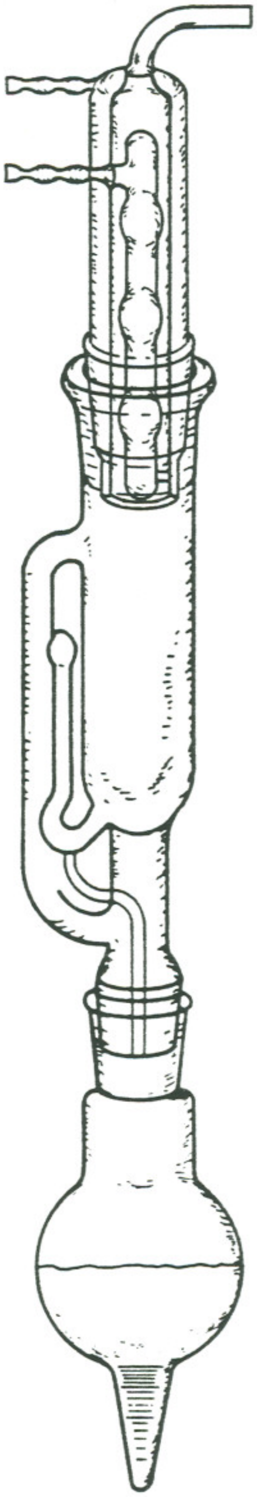


Figure 4.3. Soxhlet extraction apparatus used to extract the target SOCs.

4.1.6.2. Concentration and Cleanup of the Extracts

Highly polar compounds, such as carboxcyclic acids, ketones, and aldehydes, were found to seriously degrade the lifetime of the GC analytical column. The concentrated extracts were therefore quantitatively transferred to clean-up columns containing Na_2SO_4 and silica gel. The 1 x 15 cm clean-up columns contained 0.50 g of each Na_2SO_4 and silica gel. Prior to packing in the column, the latter had been deactivated to 3% after baking. The extracts were eluted with 10 mL (~10 bed volumes) of solvent, collected in 3 mL mini-vials (Alltech Associates), and concentrated to 2 mL by inert gas blowdown. To counteract evaporative cooling, the vials were placed in a heated aluminum block at 40 °C. The extracts were stored at 5 °C until they were analyzed by GC/MS. In addition to removing polar compounds from the extracts, the clean-up columns also removed particulate material and water.

4.1.6.3. GC/MS Analysis of QFF, TMF, and PUFS Extracts

Prior to analysis, the volume of each extract was reduced to 200 µL by blowdown with ultrapure helium. A 5 µL aliquot of an internal standard solution containing 400 ng/µL of decaflurotriphenylphosphine, 2,2',5-tribromobiphenyl or 2,2',5,5'-tetrabromobiphenyl was added just before analysis. All of the extracts were analyzed by on-column injection capillary column gas chromatography/mass spectrometry. A 30 m, 0.32 mm i.d., 0.25 µm film DB-5 fused silica capillary column (J&W Scientific, Rancho Cordova, CA) mounted in a Hewlett Packard 5790A GC was used to separate the compounds.

The capillary column was interfaced directly into the source of a Finnigan 4000 MS/DS (Sunnyvale, CA) (Pankow and Isabelle, 1984). The helium carrier gas linear velocity was 40 cm/s at 60 °C with a head pressure of 6 psi. The column was held at 60 °C for 1 min after a 1 µL injection, then programmed to 300 °C at 10 °C/min. The MS was operated in the electron impact mode, scanning from 50-450 amu in 0.5 s with the electron multiplier set at ~-1600 volts. The transfer line, ion source, and manifold temperature were maintained at 250, 250, and 100 °C, respectively.

4.1.6.4. Identification and Quantification Procedure for Target Compounds

The target compounds were identified and quantified by comparing retention times, mass spectra, and mass intensities with those observed for those compounds from injections of internal and external standard solutions. This involved a five part process:

1) external standard solutions were prepared over concentration ranges bracketing the expected concentrations in the sample extracts;
2) retention times and mass spectra were recorded for the target compounds, surrogate standards, and internal standards;

3) a response curve was generated for each compound using the external standards;
4) a response factor (RF) relative to the appropriate surrogate standard was calculated by the GC/MS/DS software according to

$$\mathrm{RF} = \frac{(\text{area})(\text{surrogate standard amount})}{(\text{surrogate standard area})(\text{amount})} \qquad 4.1$$

5) a sample extract was run (under the same GC/MS conditions); the retention times and spectra in the sample were compared to those observed for the external standard runs. A program (THRECR) was used in Finnigan's operating system to do this automatically (Appendix 1). Positive identification was considered accomplished if a sample peak had the same retention time, masses, and ratio of masses observed for the same compound in an external standard run; and
6) peaks in the sample extracts that were positively identified were integrated using a program (QUSLRN) in Finnigan's operating software (Appendix 1). The concentrations were calculated by rearrangement of equation 4.1, i.e.

$$\text{amount} = \frac{(\text{area})(\text{surrogate standard amount})}{(\text{surrogate standard area})(\mathrm{RF})} \qquad 4.2$$

4.1.6.5. Analysis of ADCs

ADCs were analyzed by thermal desorption capillary GC/MS/DS. Prior to desorption, a 1 µL aliquot of a surrogate standard solution containing fluoranthene-d_{10} at 10 ng/µL was injected onto the head of each cartridge. The cartridge was then placed in a desorption apparatus (Pankow et. al., 1988; Ligocki 1986) and purged with a head pressure of 5 psi for 10 min at a flow rate of 15 mL/min. This step removed any oxygen in the cartridge along with most of the solvent. With the GC oven at -30 °C, the flow was reversed and the compounds were thermally desorbed for 30 min at 250 °C with a head pressure of 30 psi. After the desorption, the head pressure was reduced to 5 psi and the oven was programmed at 10 °C/min to 250 °C. The MS parameters used are described in Section 4.1.6.3.

4.1.6.6. Method Quantitation limits

For the purposes of this study, a conservative method was used to estimate the method quantitation limit. The method quantitation limit was defined here as the amount of substance needed to generate an area for the quantitation ion of >200 counts above an average of the baseline in the chromatographic region of interest. While this criterion was used for the quantitation ion, three other major characteristic fragment ions were required to be present (but not necessarily > 200 counts) in the correct ratios in the peak in order for a compound to be quantitated. For the GC/MS conditions utilized in this study, this typically corresponded to ~0.5 ng for the external standard solutions, and therefore atmospheric concentrations of ~0.2 ng/m^3.

4.2. Atmospheric Concentrations of Target SOCs

4.2.1. Results from Recovery Studies

4.2.1.1. Extraction Efficiencies of Target SOCs from QFFs

Methylene chloride (MeCl$_2$) has many properties needed in an extraction solvent. As a result, MeCl$_2$ has been used in many studies involving SOCs (Simoneit, 1984; Sicre et. al., 1987; Masclet et. al., 1988; Doskey and Andren, 1988). Firstly, MeCl$_2$ has a low boiling point (39.75 °C). Since many analytes of interest have boiling points much higher than this (e.g. for $C_{16}H_{34}$, b_p = 287 °C), they will not be lost in the extraction and concentration steps. This reduces the potential for volatilization of the higher boiling compounds. Secondly, MeCl$_2$ is relatively dense (1.326 g/mL). Therefore, solvent removal in a K-D apparatus is relatively quick because the fractionating bulbs are very buoyant. Thirdly, MeCl$_2$ is moderately polar which makes it an efficient solvent for some of the more polar PAHs.

In an effort to simulate atmospheric concentrations, recovery studies were carried out at an equivalent atmospheric concentration of 3 ng/m^3 and a typical sample volume of 500 m^3. The absolute and surrogate standard relative recoveries (SSRRs) of the target SOCs from QFFs are presented in Table 4.1. The average absolute recovery was 79% for n-alkanes with a range of 73-85%. The PAH recoveries averaged 87%, with a range of 82-92%. The average SSRR for the n-alkanes was 91% with a range of 82-102%. The average SSRR for the PAHs was 98% with a range of 93-103%. The average standard deviations for the n-alkanes and PAHs SSRRs were 10% and 11%, respectively. This is indicative of good analytical precision since the precision of on-column injections of the external standard solutions were rarely lower than ~6% at the low ng/µL level.

An extraction time of 4 hr was chosen based on three preliminary experiments. In the first, a 2 hr extraction of QFFs, TMFs, and PUFS, yielded recoveries that were less than quantitative (<50%) for both the surrogate and the external standards. The second experiment yielded semi-quantitative (>75%) recoveries for 4 hr extractions. The third experiment demonstrated that significant quantities of solvent were lost after an extraction time of 5 hr. In an effort to minimize solvent and analyte evaporation through the ground glass joint between the condenser and Soxhlet, a dual walled, high efficiency condenser was designed. The inner wall acted as a cold finger and kept the solvent from ever reaching the ground glass joint. While further attempts to optimize the extraction time were not

Table 4.1. Recoveries of Target SOCs from QFF Extraction and Analysis Procedure.

Compound	Absloute Recovery (%)[a]	Relative Recovery (%)[b]
Alkanes[c]		
Hexadecane	73 ± 5	82 ± 7
Heptadecane	75 ± 6	86 ± 6
Pristane	73 ± 4	84 ± 5
Octadecane	78 ± 8	89 ± 9
Phytane	80 ± 9	92 ± 10
Nonadecane	77 ± 8	88 ± 8
Eicosane	85 ± 15	102 ± 10
Heneicosane	78 ± 9	92 ± 7
Docosane	77 ± 7	90 ± 4
Tricosane	78 ± 8	90 ± 9
Tetracosane	80 ± 9	93 ± 7
Pentacosane	80 ± 10	90 ± 12
Hexacosane	85 ± 13	95 ± 15
Heptacosane	84 ± 13	95 ± 15
Octacosane	83 ± 13	94 ± 15
Nonadecane	80 ± 10	90 ± 13
Triacontane	79 ± 9	89 ± 12
Hentriacontane	84 ± 13	94 ± 15

Table 4.1 (cont'd.). Recoveries of Target SOCs from QFF Extraction and Analysis Procedure.

Compound	Absolute Recovery (%)[a]	Relative Recovery (%)[b]
PAHs[d]		
Acenapthene	85 ± 8	96 ± 9
Fluorene	91 ± 9	102 ± 11
Phenanthrene	90 ± 6	101 ± 9
Anthracene	82 ± 6	93 ± 8
Fluoranthene	83 ± 11	94 ± 12
Pyrene	89 ± 7	100 ± 10
Benz(a) Anthracene	86 ± 15	97 ± 16
Chrysene	91 ± 9	102 ± 12
Benzo(b&k) Fluoranthene	82 ± 7	93 ± 8
Benzo(e) Pyrene	92 ± 11	103 ± 13
Benzo(a) Pyrene	88 ± 9	99 ± 12

a) ± 1s based on five replicate samples. b) Absolute recoveries are based on internal standard 2,2',5-tribromobiphenyl or 2,2',5,5'-tetrabromobiphenyl. c) Relative recoveries are based on surrogate standard eicosane-d_{42}. d) ± 1s based on three replicate samples.

made, it was felt that 4 hr was a good compromise between recovery and extraction time.

4.2.1.2. Extraction Efficiencies of Target SOCs from TMFs

Extraction efficiencies of the target SOCs from TMFs were investigated as described in Section 4.2.1.1. As with the QFFs, methylene chloride was used in the Soxhlet extractors (Figure 4.3) to extract the target compounds from TMFs. The absolute recoveries of n-alkanes from TMFs ranged from 68-88% and averaged 75% (Table 4.2). The absolute recoveries of the PAHs averaged 79%, and ranged from 67-85%. The SSRRs for the n-alkanes averaged 96% and ranged from 87-112%. The SSRRs for the PAHs averaged 107% and ranged from 92-117%. The average standard deviations for the SSRRs were 9 and 12%, for the n-alkanes and PAHs, respectively. Although, the average SSRR for the PAHs was >100%, it was not significantly different from 100% at the 95% confidence level.

4.2.1.3. Extraction Efficiencies of Target SOCs from PUFS

Petroleum ether and acetone/hexane mixtures have been used with good success for the extraction of SOCs on PUF (Bidleman et. al., 1974; Ligocki and Pankow, 1989). However, methylene chloride was investigated here as a solvent for use with PUF so as to minimize the number of solvents being used at one time.

Table 4.2. Recoveries of Target SOCs from TMF Extraction and Analysis Procedure.

Compound	Absolute Recovery (%)[a]	Relative Recovery (%)[b]
Alkanes[c]		
Hexadecane	68 ± 3	87 ± 5
Heptadecane	73 ± 2	94 ± 6
Pristane	68 ± 5	87 ± 7
Octadecane	76 ± 2	99 ± 9
Phytane	88 ± 9	99 ± 10
Nonadecane	73 ± 4	94 ± 4
Eicosane	88 ± 9	112 ± 10
Heneicosane	79 ± 6	100 ± 8
Docosane	75 ± 8	97 ± 4
Tricosane	73 ± 3	94 ± 5
Tetracosane	75 ± 5	96 ± 7
Pentacosane	73 ± 3	95 ± 11
Hexacosane	75 ± 4	97 ± 12
Heptacosane	75 ± 3	95 ± 11
Octacosane	74 ± 5	96 ± 11
Nonadecane	71 ± 3	92 ± 9
Triacontane	71 ± 4	92 ± 12
Hentriacontane	76 ± 7	99 ± 15

Table 4.2 (cont'd.). Recoveries of Target SOCs from TMFs Extraction and Analysis Procedure.

Compound	Absolute Recovery (%)[a]	Relative Recovery (%)[b]
PAHs[d]		
Acenapthene	67 ± 5	92 ± 8
Fluorene	80 ± 6	109 ± 12
Phenanthrene	85 ± 9	117 ± 10
Anthracene	81 ± 6	107 ± 11
Fluoranthene	80 ± 6	105 ± 14
Pyrene	82 ± 9	111 ± 10
Benz(a) Anthracene	79 ± 13	104 ± 22
Chrysene	86 ± 8	113 ± 11
Benzo(b&k) Fluoranthene	80 ± 7	110 ± 12
Benzo(e) Pyrene	76 ± 10	104 ± 14
Benzo(a) Pyrene	77 ± 8	105 ± 13

a) ± 1s based on five replicate samples. b) Absolute recoveries are based on internal standard 2,2',5-tribromobiphenyl or 2,2',5,5'-tetrabromobiphenyl. c) Relative recoveries are based on surrogate standard eicosane-d_{42}. d) ± 1s based on three replicate samples.

The Soxhlet apparatus for the PUFSs was a larger version of the filter Soxhlets. In preliminary studies, as in the filter extractions, it was found that 4 hr extractions provided a good compromise between extraction efficiency and extraction time (see Section 4.2.1.1). The results of the recovery studies are presented in Table 4.3. The absolute recoveries for the n-alkanes averaged 85% with a range of 75-93%. The absolute recoveries for the PAHs ranged from 79-92% and averaged 84%. The SSRRs for both the n-alkanes and PAHs was much higher. The n-alkanes averaged 104% and ranged from 93-113%, while the PAHs averaged 105% and ranged from 99-115%.

4.2.1.4. Comparison of Extraction Efficiencies for Target SOCs from QFFs, TMFs, and PUFSs

The recovery studies were designed so that extraction efficiencies from the filters and the PUFSs could be compared under identical conditions. Average surrogate standard relative extraction efficiencies for n-alkanes and PAHs were first compared to 100% recovery via student's t-tests (Table 4.4). The surrogate standard relative extraction efficiencies for all of the target SOCs from the filters and PUFSs were found to be significantly different from 100% at the 95% confidence level. Nevertheless, the recoveries (91-107%) were very close to 100% and were adequate for the purposes of this study.

The average SSRRs for the filters and the PUFSs were also compared

Table 4.3. Recoveries of Target SOCs from PUFS Extraction and Analysis Procedure.

Compound	Absloute Recovery (%)[a]	Relative Recovery (%)[b]
Alkanes[c]		
Hexadecane	75 ± 13	93 ± 12
Heptadecane	79 ± 6	96 ± 11
Pristane	79 ± 3	97 ± 7
Octadecane	89 ± 2	109 ± 9
Phytane	89 ± 3	108 ± 7
Nonadecane	89 ± 5	109 ± 6
Eicosane	89 ± 3	109 ± 5
Heneicosane	86 ± 5	103 ± 8
Docosane	85 ± 9	104 ± 7
Tricosane	83 ± 5	101 ± 3
Tetracosane	88 ± 4	105 ± 7
Pentacosane	83 ± 3	101 ± 6
Hexacosane	89 ± 4	108 ± 9
Heptacosane	78 ± 3	96 ± 7
Octacosane	93 ± 3	113 ± 5
Nonadecane	88 ± 3	107 ± 3
Triacontane	89 ± 2	108 ± 6
Hentriacontane	81 ± 7	98 ± 11

Table 4.3 (cont'd.). Recoveries of Target SOCs from PUFS Extraction and Analysis Procedure.

Compound	Absloute Recovery (%)[a]	Relative Recovery (%)[b]
PAHs[d]		
Acenapthene	79 ± 4	99 ± 6
Fluorene	91 ± 5	115 ± 8
Phenanthrene	81 ± 6	102 ± 9
Anthracene	84 ± 5	103 ± 8
Fluoranthene	83 ± 3	100 ± 9
Pyrene	85 ± 7	107 ± 8
Benz(a) Anthracene	86 ± 8	105 ± 14
Chrysene	81 ± 7	102 ± 9
Benzo(b&k) Fluoranthene	84 ± 7	106 ± 12
Benzo(e) Pyrene	92 ± 10	116 ± 12
Benzo(a) Pyrene	82 ± 6	103 ± 8

a) ± 1s based on six replicate samples. b) Absolute recoveries are based on internal standard 2,2',5-tribromobiphenyl or 2,2',5,5'-tetrabromobiphenyl. c) Relative recoveries are based on surrogate standard eicosane-d_{42}. d) ± 1s based on four replicate samples.

Table 4.4. Results of a t-Test Comparison of Average Extraction Efficiencies vs. 100% Recovery for Target SOCs from QFFs, TMFs, and PUFSs.

	t-test[a]	
	Alkanes[b]	PAHs[c]
QFF	-8.36	-2.26
TMF	-3.11	4.60
PUFS	2.83	3.54

a) $t = x - \mu/(s/(n)^{1/2})$; b) $t_{(0.025,17)} = 2.11$; c) $t_{(0.025,10)} = 2.23$.

among one another (Table 4.5). At the 95% confidence level, the recoveries from the TMFs and PUFSs were significantly higher than the recoveries from the QFFs for both the n-alkanes and PAHs. The recoveries from the PUFS were significantly higher than the TMFs only for the n-alkanes. While the extraction efficiencies for the target SOCs generally increased from QFFs to TMFs to PUFSs, from a practical point of view, the differences among the three were very small. Therefore, the subsequent concentrations that are reported will be calculated by taking the recovery of the surrogate standard to be 100%.

4.2.2. Results From Filter Artifact Studies

All of the extracts from the filters and the PUFSs were analyzed in duplicate by GC/MS. As shown in Table A2, the analytical precision of these measurements averaged ±10%. The precision associated with the volume of air sampled was also ±10%. Thus, by standard propagation of error techniques, the coefficient of variation (CV) associated with each concentration measurement (ng/m^3) was ±14%. This is the precision estimate that will be used for all calculations in which concentration data are used.

Table 4.5. Comparison of Average Extraction Efficiencies for the Target SOCs Between QFFs, TMFs, and PUFSs.

	t-test[a]	
	QFF	TMF
n-Alkanes[b]		
QFF		
TMF	-2.98	
PUFS	-7.31	-4.18
PAHs[c]		
QFF		
TMF	-4.00	
PUFS	-3.28	0.75

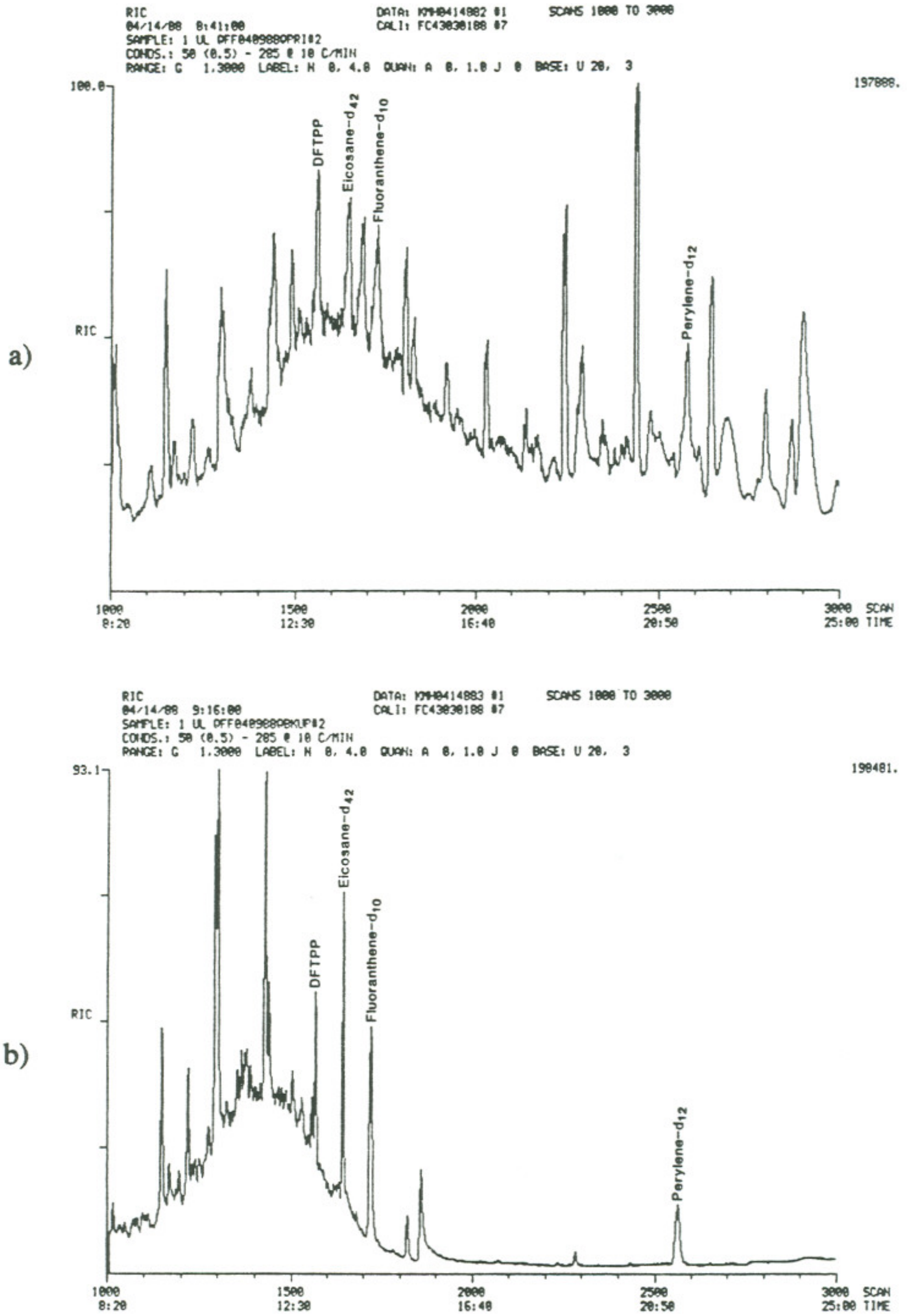
a) $t = (x_1 - x_2)/(s_1^2/n_1 + s_2^2/n_2)^{1/2}$; b) $t_{(0.025,\infty)} = 1.96$; c) $t_{(0.025,17)} = 2.11$.

4.2.2.1. Adsorption of Gases to QFFs

Gas adsorption to QFFs was examined for the target n-alkanes and PAHs by examining the concentration of analytes on the backup QFFs (QQB and TQB). Since concentrations on the backup filter are a result of gas adsorption only (Section 2.2.1), the backup QFF data provides measures of the compound-dependent extent of gas adsorption on a QFF.

Chromatograms of extracts from typical QQP, QQB, TQP, TQB and blank QFF and TMF filters obtained during ambient sampling in Portland, OR are presented in Figures 4.4, 4.5, and 4.6. For all of the events sampled, a large unresolved hydrocarbon hump occurred in the QFF extracts. The elution times of the maxima of the unresolved hydrocarbon humps, as a function of chromatogram elution time or MS scan number, was as follows: QQP ≥ TQB > QQB. The unresolved hydrocarbon humps for the TMF extracts were much smaller than the humps for the QFFs and sometimes not discernable from the baseline.

Compounds in the gas phase partition to filters much like they partition to atmospheric particulate matter. Since QFFs have a higher surface area than TMFs, compounds in the gas phase will partition to QFFs to a much greater extent than they do to TMFs. However, if filter surface area is the only factor in determining the amount found on the QQBs and TQBs, then the chromatograms for both types of backup filters should be the same. This is clearly not the case. It appears that compounds in the gas phase have a higher relative affinity for the initial QFF in



```
RIC                                     DATA: KMH0414882 #1      SCANS 1000 TO 3000
04/14/88  8:41:00                       CALI: FC43030188 #7
SAMPLE: 1 UL DFF0409880PRI#2
CONDS.: 50 (0.5) - 285 @ 10 C/MIN
RANGE: G   1.3000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

```
RIC                                     DATA: KMH0414883 #1      SCANS 1000 TO 3000
04/14/88  9:16:00                       CALI: FC43030188 #7
SAMPLE: 1 UL DFF040988PBKUP#2
CONDS.: 50 (0.5) - 285 @ 10 C/MIN
RANGE: G   1.3000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 4.4. a) Typical QQP chromatogram from Portland, OR in 1988. b) Typical QQB chromatogram from Portland, OR in 1988.

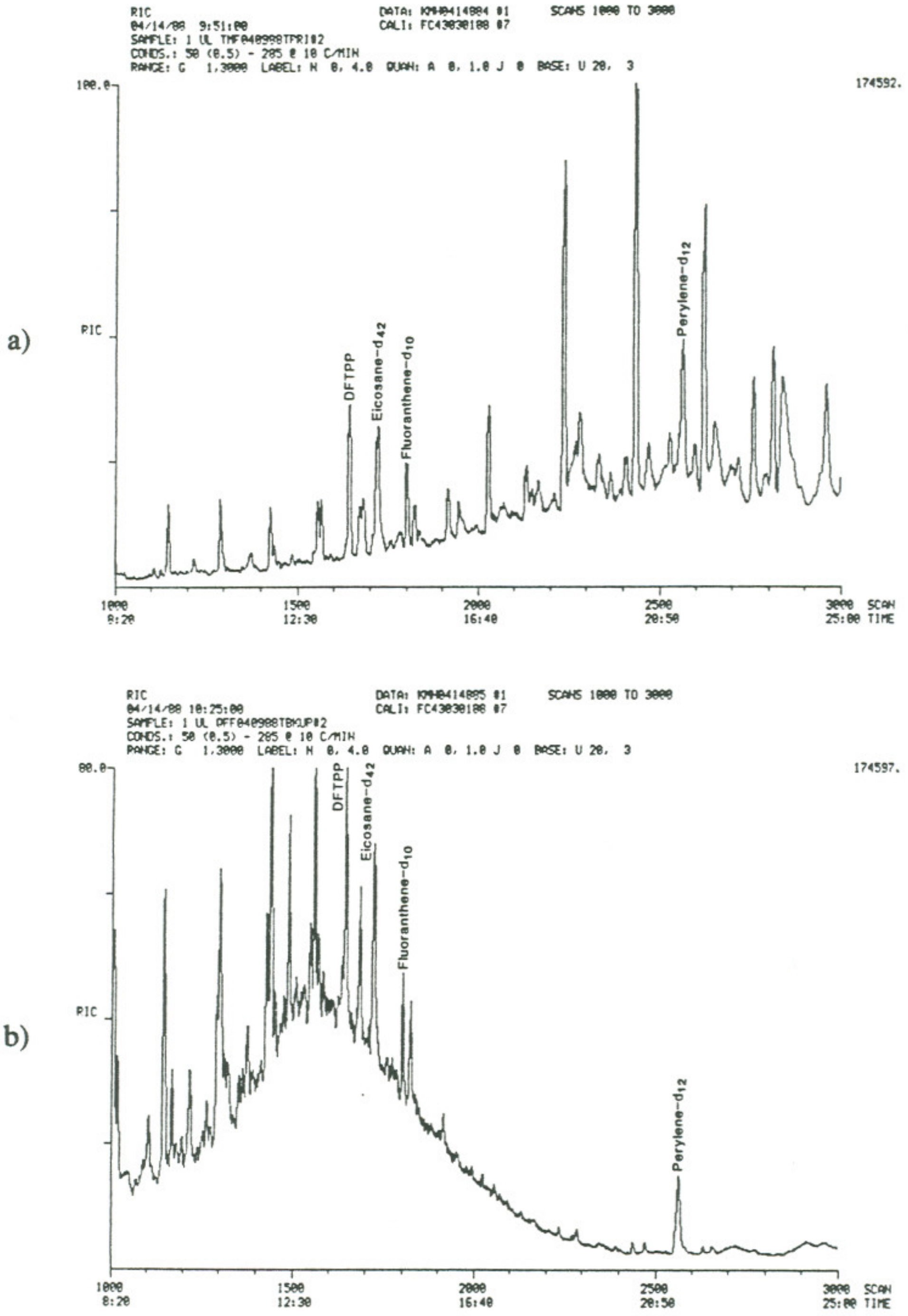


Figure 4.5. a) Typical TQP chromatogram from Portland, OR in 1988. b) Typical TQB chromatogram from Portland, OR in 1988.

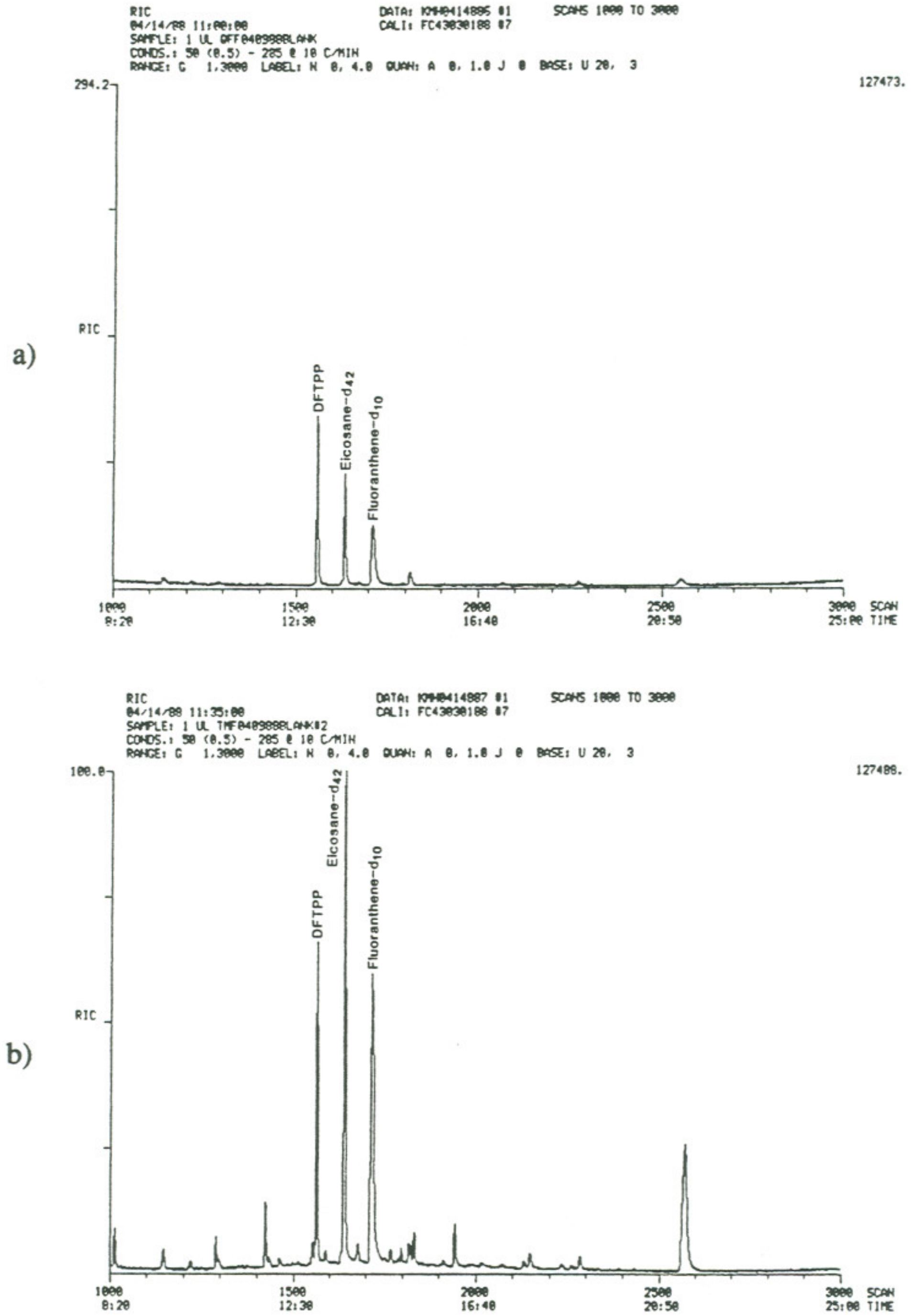


Figure 4.6. a) Typical blank chromatogram of a QFF from Portland, OR in 1988. b) Typical blank chromatogram of a TMF from Portland, OR in 1988.

each sampling train. This could be due to preferential adsorption of compounds to the initial QFF surface which might alter the sorption characteristics of the filter. If this is the case, then it might lead to a depletion of the compounds that were responsible for the preferential adsorption to the initial QFFs. This would change the gas phase concentration profile that is seen by the QQB filters. These results will be discussed in more detail in Section 4.2.5.

While a visual examination of the chromatograms along the above lines is useful, a more quantitative approach must be taken in order to determine the effects of gas adsorption to the filters. A t-test was therefore used to compare the amounts of the target n-alkanes and PAHs on the QQB and TQB filters. For the n-alkanes, from C16 to ~C21, no significant differences at the 95% confidence level were obtained between the concentrations on the QQB and TQB filters (Table 4.6). From ~C22 to C26, the TQB concentrations were significantly higher than those on the QQB in ~70% of the events sampled. There were no significant differences between the concentrations in the remaining 30%. In instances where a significant difference existed between QQB and TQB concentrations, ~90% of the time the concentration measured on the TQB was greater than the concentration measured on the QBB. In most cases within this volatility range, a concentration greater than the minimum quantitation limit was only observed on the TQB filters. For the n-alkanes larger than ~C27, detectable concentrations were not observed on either the QQBs or TQBs.

The target PAHs demonstrated a trend that was similar to that observed for

Table 4.6. Results of t-tests at the 95% Confidence Level for Target Compound Concentration Differences Between Quartz/Quartz Backup Filters and Teflon/Quartz Filters in for Samples Collected in Portland, OR in 1988.

	Temperature °C											
	13	13	14	22	31	19	19	20	18	8	9	11
mo	2	3	4	7	7	8	8	8	8	11	11	11
day	27	16	9	20	26	1	7	19	31	17	23	29
n-Alkanes												
C16	-[a]	-	-	-	-	-	T[b]	-	-	-	-	T
C17	-	-	-	-	-	-	-	-	-	-	-	-
C18	-	-	-	-	-	-	-	-	Q[c]	-	Q	-
C19	-	-	T	-	-	-	-	-	-	-	Q	-
C20	T	T	T	-	-	-	-	-	-	Q	-	-
C21	-	T	T	-	-	-	-	-	-	T	T	-
C22	T	T	T	-	T	T	T	-	T	T	T	T

Table 4.6 (cont'd.). Results of t-tests at the 95% Confidence Level for Target Compound Concentration Differences Between Quartz/Quartz Backup Filters and Teflon/Quartz Filters for Samples Collected in Portland, OR 1988.

	Temperature °C											
	13	13	14	22	31	19	19	20	18	8	9	11
mo	2	3	4	7	7	8	8	8	8	11	11	11
day	27	16	9	20	26	1	7	19	31	17	23	29
C23	-	T	T	-	T	T	T	T	T	T	nd	T
C24	T	nd	nd	T	T	nd	T	T	T	T	nd	nd
C25	nd	nd	T	T	nd	nd	T	nd	nd	T	nd	nd
C26	nd	nd	nd	T	nd	nd	nd	nd	nd	nd	nd	nd
C27	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C29	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 4.6 (cont'd.). Results of t-tests at the 95% Confidence Level for Target Compound Concentration Differences Between Quartz/Quartz Backup Filters and Teflon/Quartz Filters for Samples Collected in Portland, OR 1988.

	Temperature °C											
	13	13	14	22	31	19	19	20	18	8	9	11
mo	2	3	4	7	7	8	8	8	8	11	11	11
day	27	16	9	20	26	1	7	19	31	17	23	29
C31	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PAHs												
ACE	na	na	na	-	-	-	-	-	-	-	Q	-
FLU	na	na	na	-	-	-	-	-	-	-	-	-
PHE	na	na	na	-	-	-	-	-	-	-	-	-
ANT	na	na	na	-	-	-	-	-	-	-	-	-
FLA	T	-	-	-	-	-	-	-	-	-	-	-
PYR	na	na	na	T	-	-	-	-	-	-	-	-

Table 4.6 (cont'd.). Results of t-tests at the 95% Confidence Level for Target Compound Concentration Differences Between Quartz/Quartz Backup Filters and Teflon/Quartz Filters for Samples Collected in Portland, OR 1988.

	Temperature °C											
	13	13	14	22	31	19	19	20	18	8	9	11
mo	2	3	4	7	7	8	8	8	8	11	11	11
day	27	16	9	20	26	1	7	19	31	17	23	29
BaA	nd	T	nd	-	-	-	-	-	Q	T	T	-
CHR	na	na	na	-	-	-	-	T	-	T	T	T
BFL	na	na	na	T	-	-	-	T	T	nd	nd	nd
BeP	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd
BaP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

a) - = no statistically significant difference between the concentrations on the QQB and TQB. b) T = TQB significantly higher concentration than QQB. c) Q = QQB significantly higher concentration than TQB. d) nd = not detected at a statistically significant level on at least one of the filters. e) na = not analyzed.

the n-alkanes. Indeed, no significant differences existed between the concentrations on the QBB and TQB filters for acenaphene through pyrene. For benz(a)anthracene through benzo(b&k)fluoranthene, when a significant difference existed between the QQB and TQB filters, the concentration on the TQB filter was greater than the QQB filter in ~99% of the cases. No PAHs less volatile than benzo(b+k)fluoranthene were detected at significant levels on either backup filter.

4.2.2.2. Adsorption of Gases to TMFs

An effort was made to test the assumption that gas adsorption to the TMF was negligible. This was examined by using a TMF followed by a TMF in the Teflon sampling train. The primary TMF in this experiment will be called "TTP" and the backup TMF will be called "TTB". Two sampling events were chosen to test the assumption, 12/5/88 and 12/11/88. These events were characterized by ambient temperatures of 7 and 10°C, respectively. As seen in Table 4.7, for the more volatile n-alkanes, the concentrations of the target SOCs on the TTB filters were significantly greater than those on the QQB filters. However, no significant differences were seen in the concentrations of target PAHs on the QQB and TTB filters. Both of these results were rather unexpected.

In Section 4.2.2.1 it was concluded that while chromatograms of the QQB and TQB extracts were qualitatively different, the concentrations for most of the target SOCs on the QQB and TQB filters were not different. However,

Table 4.7. Results of t-tests at the 95% Confidence Level for the Comparison Between QQB and TTB Concentrations in Portland OR, in 1988.

	Date	
Compound	12/5/88	12/11/88
n-alkanes		
C16	T[a]	T
C17	T	T
C18	T	T
C19	T	T
C20	-[b]	-
C21	-	-
C22	T	T
C23	nd[c]	nd
C24	nd	nd
C25	nd	nd
C26	nd	nd
C27	nd	nd
C28	nd	nd
C29	nd	nd
C30	nd	nd
C31	nd	nd

Table 4.7 (cont'd.). Results of t-tests at the 95% Confidence Level for the Comparison Between QQB and TTB Concentrations in Portland, OR in 1988.

	Date	
Compound	12/5/88	12/11/88
PAHs		
ACE	-	-
FLU	-	-
PHE	-	-
ANT	T	-
FLA	-	-
PYR	-	-
BaA	-	-
CHR	Q[d]	nd
BFL	nd	nd
BeP	nd	nd
BaP	nd	nd

a) - = no significant difference between QQB and TTB concentrations; b) T = TTB significantly greater than QQB; c) nd = not detected at a statistically significant level; d) Q = QQB at significantly higher concentrations than TTB.

the results from the experiment described above using two Teflon filters in series, show that concentrations on the TTB filters were significantly higher than those on the QQB filters for the target n-alkanes but not for the target PAHs. Due to the limited number of data sets in which TTB concentrations were available and the apparent discrepancies between the concentrations of the target n-alkanes and PAHs, it is difficult to draw any conclusions from these experiments. For example, if the concentrations measured on the backup filters are affected by physical adsorption alone, then, due to the differences in surface area, the concentrations measured on the QBBs should be greater than those on the TTBs. However, these results indicate that what is being measured on the TTB is not controlled simply by physical adsorption. Clearly, further work is needed in this area in order to better understand gas phase adsorption to filters. Gas phase adsorption of many classes of trace organic compounds to QFFs and/or TMFs is currently being investigated in the laboratory by Bidleman et. al. (1989), and Pankow et. al. (1990), and in the field by Hart and Giger (1990).

4.2.2.3. Comparison of Particulate Concentrations from QFFs and TMFs

The extent to which gas phase adsorption to QFFs is important can be examined by looking at the ratios of the concentrations of the target compounds on the primary QFFs and TMFs. While McDow and Huntzicker (1989) have reported that gas adsorption to QFFs can be a significant artifact for organic carbon, Ligocki

(1986) reported that, on a compound by compound basis, gas adsorption was not of a problematic magnitude (i.e. ~10%) for most PAHs. The results of the comparison between the filters from this study indicate that gas adsorption can be a significant artifact and is compound class dependent.

The primary QFF/TMF ratios for the targeted n-alkanes and PAHs and the significance levels for the deviations of the ratios from 1.0 are summarized in Table 4.8. For the targeted n-alkanes, 13 of the 16 n-alkanes exhibited average ratios greater than 1.0. For the n-alkanes that exhibited appreciable concentrations in the gas phase (~C16 - C25), six out of the ten compounds exhibited ratios that were significantly ($P \leq 0.05$) greater than 1.0. For the targeted PAHs, 10 of the 11 had ratios greater than 1.0. For the compounds that had appreciable concentrations in the gas phase (phenanthrene to benzo(b+k)fluoranthene), two of the five exhibited ratios that were significantly greater than 1.0. Thus, greater than 50% of the target compounds experienced significant gas adsorption to the QFFs.

GFF/TMF ratios for PAHs have been found to range between 0.25 to 0.76 (Grosjean, 1983), 0.66 to 1.03 (Fitz et. al., 1984), and 0.61 to 1.16 (Ligocki, 1986). For the PAHs studied here, the ratio ranged from 0.83 to 1.13. As noted by Ligocki and Pankow (1989), however, there is no single correct value of the QFF/TMF ratio. That ratio will depend on the compound and sampling conditions.

As discussed by Ligocki and Pankow (1989), the potential artifact associated with chemical reactions of compounds collected on a filter can be examined by comparing the concentrations of compounds that have differing degrees of reactivity under typical atmospheric sampling conditions. PAHs are compounds that exhibit a wide range of reactivities and have been extensively studied in atmospheric particulate material.

Benzo(a)pyrene (BaP) is of particular interest in the above context. It was one of the first carcinogens identified in ambient particulate matter. Consequently, it is one of the most intensively studied PAHs. Numerous studies have been completed on the reactivity of BaP associated with atmospheric particulate matter when exposed to reactive gases or ambient urban air. Pitts et. al. (1978) found various oxygenated and nitrated reaction products of BaP when a filter was spiked with BaP and exposed to ambient air. Brorstorm et. al. (1983) found losses of up to 40% of BaP in ambient particulate samples when 1 ppm NO_2 was added to the airstream. However, under similar conditions, Grosjean et. al. (1983) found no loss of BaP. These researchers have hypothesized that, when degradation occurred, the reactions were catalyzed by the GFF or QFF themselves.

The extent to which reactivity is important for this study can be examined by comparing: 1) the concentrations of BAP on both QFFs and the less reactive surface of the TMFs; and 2) by comparing the ratios of the concentrations of BaP to the concentrations of benzo(e)pyrene (BeP, a much less reactive isomer) collected on both filter types (Ligocki, 1986).

There were no significant differences in the concentrations of BaP measured on QFFs and TMFs (Table 4.8). The ratios of BaP/BeP for both filter types are presented in Table 4.9. While it appears that the QFF ratios are lower than the

Table 4.8. Summary of Primary QFF/TMF Ratios for Particulate n-Alkanes and PAHs in Portland, OR in 1988.

Compound	n[a]	Average ± 1s	p[b]
n-Alkanes			
C16	12	1.61 ± 0.70	0.01
C17	12	1.00 ± 0.50	0.98
C18	12	1.48 ± 1.21	0.20
C19	12	1.51 ± 1.31	0.20
C20	12	1.52 ± 0.88	0.07
C21	12	1.64 ± 0.55	0.00
C22	12	1.74 ± 0.84	0.01
C23	12	1.43 ± 0.59	0.03
C24	12	1.37 ± 0.39	0.01
C25	12	1.10 ± 0.15	0.06
C26	12	1.15 ± 0.33	0.15
C27	12	0.93 ± 0.20	0.24
C28	12	1.01 ± 0.21	0.91
C29	12	0.95 ± 0.25	0.53
C30	12	1.02 ± 0.48	0.86
C31	12	0.93 ± 0.15	0.15

Table 4.8 (cont'd.). Summary of Primary QFF/TMF Ratios for Particulate n-Alkanes and PAHs in Portland, OR in 1988.

Compound	n[a]	Average ± 1s	p[b]
PAHs			
ACE		na[c]	
FLU		na	
PHE	4	1.13 ± 0.17	0.22
ANT		na	
FLA	11	1.35 ± 0.45	0.04
PYR	8	1.00 ± 0.16	0.95
BaA	10	1.07 ± 0.21	0.30
CHR	8	1.24 ± 0.19	0.01
BFL	8	1.10 ± 0.20	0.21
BeP	8	1.04 ± 0.23	0.66
BaP	8	0.83 ± 0.26	0.10

a) n = number of observations; b) $P < 0.05$ means a significant difference of the ratio from 1; c) na = not available.

Table 4.9. BaP/BeP Ratios Measured on Primary QFFs and TMFs in Portland, OR in 1988.

Date	QFF	TMF
7/20	0.36	0.53
7/26	0.20	0.24
11/17	1.04	1.97
11/23	0.60	1.29
11/29	1.11	1.26
Average ± 1s	0.66 ± 0.40	1.06 ± 0.69

TMF ratios, the differences were not significant ($P = 0.05$). However, with coefficients of variation for the average ratios at approximately 60%, it is difficult to make any conclusions regarding reactivity of BaP and BeP on the QFFs.

Two points can now be made concerning the concentrations of compounds associated with the particulate phase. Within the uncertainty of the sampling and analytical methods: 1) gas phase adsorption to the QFFs led to a significant positive artifact for some compounds studied, and 2) filter catalyzed degradation was probably not a significant problem for the compounds studied here.

4.2.3. Gas Phase Sampling Efficiency

4.3.2.1. Breakthrough of Target Compounds on PUFSs

Breakthrough of an analyte on an adsorbent is a function of the sample volume, the adsorbent volume or mass, and the affinity of the analyte for the sorbent at the temperature of interest (Section 2.2.1.). Breakthrough on an adsorbent can be monitored by using a sampling train that utilizes two sorbent beds in series. The backup sorbent bed provides an indication of sampling efficiency. Experimentally, a measure of breakthrough can be defined as

$$B = \frac{[\text{backup}]}{[\text{primary}] + [\text{backup}]} \text{ x } 100 \qquad 4.6$$

Table 4.10 provides B values, ambient temperature, and sample volumes for both the quartz and Teflon sampling trains for the most volatile target compounds. A theoretical study of adsorbent sampling efficiency as a function of the number of theoretical plates (N) of the sorbent and the ratio of sample volume to breakthrough volume has been provided by Senum (1981). Bidleman et. al. (1984a, 1984b) have examined PUF under typical sampling conditions and determined N to be ~1 plate per cm of foam for PAHs and organochlorines. For an overall sampling efficiency of 95% and using two PUFSs, the primary plug must retain 75% of the incoming material. Therefore, a B value of <25% indicates quantitative trapping for a two sheet PUF system.

The application of chromatographic theory to gas phase sampling with an adsorbent is only an approximation. Uncertainties still remain in being able to accurately predict: 1) breakthrough when N is low (as is the case in many adsorbent sampling trains); 2) sampling efficiency when the ratio of sampling volume to retention volume is very small; and 3) breakthrough under conditions of changing ambient concentrations. Thus, the expression developed by Senum (1981) should only be used as an approximation and, if possible, confirmed by a second sampling method.

Quantitative trapping on the two PUFSs configuration was achieved for the n-alkanes less volatile than C18. For the target PAHs, compounds less volatile than phenanthrene were trapped quantitatively. Although the PUF configuration used in this study (rectangular sheets) is different from the PUF plug approach used in

Table 4.10a. Percent Breakthrough[a] (B) of the Most Volatile Target Alkanes on PUFSs During Sampling in Portland, OR in 1988.

	Breakthrough, B (%)											
	Sampling Date, T (°C), Sampling Train, and Volume (m^3)											
	2/27		3/16		4/9		7/20		7/26		8/1	
	13		13		14		22		31		19	
	Q	T	Q	T	Q	T	Q	T	Q	T	Q	T
	737	684	752	661	777	669	624	683	686	593	634	615
n-Alkanes												
C16	51	44	34	30	19	26	61	61	56	59	47	51
C17	38	49	23	20	13	13	57	57	53	53	44	43
C18	20	31	12	7	0	0	51	55	47	45	31	30
C19	27	34	0	0	0	0	37	39	28	28	18	18
C20	11	11	0	0	0	0	23	26	17	18	0	0
C21	0	0	0	0	0	0	13	20	8	7	0	0

Table 4.10a (cont'd.). Percent Breakthrough[a] (B) of the Most Volatile Target Alkanes on PUFSs During Sampling in Portland, OR in 1988.

	Breakthrough, B (%)											
	Sampling Date, T (°C), Sampling Train, and Volume (m^3)											
	8/7		8/19		8/31		11/17		11/23		11/29	
	19		20		18		8		9		11	
	Q	T	Q	T	Q	T	Q	T	Q	T	Q	T
	544	505	564	543	356	522	524	507	532	514	527	501
n-Alkanes												
C16	55	56	52	57	49	51	54	54	43	47	42	38
C17	48	43	44	50	40	44	37	39	26	35	32	33
C18	30	27	32	35	28	32	21	25	12	16	26	19
C19	10	7	21	24	16	20	13	14	0	8	6	7
C20	0	0	13	15	0	10	22	27	0	66	8	6
C21	0	0	0	8	0	0	0	0	0	0	34	0

Table 4.10b. Percent Breakthrough[a] (B) of the Most Volatile Target PAHs on PUFSs During Sampling in Portland, OR in 1988.

	Breakthrough, B (%)											
	Sampling Date, T (°C), Sampling Train, and Volume (m^3)											
	2/27		3/16		4/9		7/20		7/26		8/1	
	13		13		14		22		31		19	
	Q	T	Q	T	Q	T	Q	T	Q	T	Q	T
	737	684	752	661	777	669	624	683	686	593	634	615
PAHs												
ACE	na	na	na	na	na	na	49	na	49	57	na	na
FLU	na	na	na	na	na	na	59	60	51	51	30	33
PHE	na	na	na	na	na	na	24	26	24	21	0	0
ANT	na	na	na	na	na	na	19	30	6	4	0	0
FLA	21	22	0	0	0	0	5	6	0	0	0	0
PYR	na	na	na	na	na	na	0	0	0	0	0	0

Table 4.10b (cont'd.). Percent Breakthrough[a] (B) of the Most Volatile Target Alkanes on PUFSs During Sampling in Portland, OR in 1988.

Breakthrough, B (%)												
	Sampling Date, T (°C), Sampling Train, and Volume (m^3)											
	8/7		8/19		8/31		11/17		11/23		11/29	
	19		20		18		8		9		11	
	Q	T	Q	T	Q	T	Q	T	Q	T	Q	T
	544	505	564	543	356	522	524	507	532	514	527	501
PAHs												
ACE	27	55	57	62	58	57	53	55	46	45	58	49
FLU	34	35	38	45	30	36	29	29	na	76	39	26
PHE	10	11	15	17	15	18	11	16	4	5	17	11
ANT	0	0	0	0	0	0	9	13	11	12	0	1
FLA	0	0	7	6	0	0	3	3	2	0	2	2
PYR	0	0	6	6	0	0	3	3	0	0	2	2

a) B = ([backup]/([primary]+[backup]))*100%; b) na = not analyzed.

other studies (e.g. Bidleman et. al., 1974; Ligocki and Pankow, 1986), good agreement between the results of this study and previous studies was obtained for breakthrough at similar temperatures and ratios of volume sampled to retention volume. For example, for C18, Ligocki and Pankow (1986) obtained B = 17% at ~10°C, while this study obtained B = 22% at 14°C.

For the five sampling events when Teanx-TA ADCs were connected in parallel with the PUFSs, virtually no breakthrough was measured for the ADCs for any of the target compounds. The low breakthrough on the ADCs was a result of the low volumes of air sampled (~216 L), the inherent high affinities of the target compounds for Tenax-TA, and low sampling temperatures (~10°C) . In instances where both PUFS and ADC data is available and when B exceeded 25% on PUFSs, only ADC data will be used in the subsequent data analysis. When B $\leq$ 25%, the compounds were estimated to be collected quantitatively (> 95%) (Senum, 1981) and the PUFS concentrations were used in the subsequent data analysis. A comparison of the concentrations of target compounds collected on both PUFSs and ADCs will be presented in Section 4.2.5.1.

4.2.4. Atmospheric Concentrations of Target Compounds

4.2.4.1. Sampling Parameters

Fourteen events were sampled for both the gas and particulate phases at a variety of temperatures throughout the year in 1988. For each sampling event both the quartz and Teflon sampling trains were used for a total of 28 sets of concentration data. Ambient temperature, average sample volume, TSP, and PM-10 are given for each event in Table 4.11.

The effect of temperature on the vapor pressure of a given SOC and partitioning between the gas and particulate phases can be large. For example, the vapor pressure of fluorene increases by a factor of 3.6 between 10° and 20°C (Sonnefeld et. al., 1983). Temperature fluctuations during sampling were minimized in this study by operating at a relatively high volumetric flow rate (1.4 m^3/min) and sampling for a short period of time. During a given sampling event, the temperature rarely deviated by more than 4°C from the mean and thus, for the majority of the events, the effects of temperature fluctuations on partitioning during sampling were probably small.

Table 4.11. Sampling Parameters for Portland, OR in 1988.

Date	Vs[a] (m^3)	Va[b] (L)	T (°C)	TSP ($\mu g/m^3$)	PM-10 ($\mu g/m^3$)
2/27	Q 737 ± 74	na[c]	13 ± 2	82 ± 7	54 ± 4
	T 684 ± 68	na			
3/16	Q 752 ± 75	na	13 ± 4	74 ± 6	28 ± 2
	T 661 ± 66	na			
4/9	Q 777 ± 78	na	14 ± 3	46 ± 4	15 ± 1
	T 668 ± 67	na			
7/20	Q 683 ± 68	na	22 ± 7	65 ± 5	40 ± 3
	T 624 ± 62	na			
7/26	Q 686 ± 69	na	31 ± 4	58 ± 5	30 ± 2
	T 593 ± 59	na			
8/1	Q 634 ± 63	na	19 ± 3	37 ± 3	20 ± 2
	T 615 ± 61	na			
8/7	Q 544 ± 54	na	19 ± 5	29 ± 2	15 ± 1
	T 505 ± 51	na			
8/19	Q 564 ± 56	na	20 ± 4	36 ± 3	17 ± 1
	T 543 ± 54	na			

Table 4.11 (cont'd.). Sampling Parameters for Portland, OR in 1988.

Date	Vs[a] (m^3)	Va[b] (L)	T (°C)	TSP (µg/m^3)	PM-10 (µg/m^3)
8/31	Q 356 ± 36 T 522 ± 52	na na	18 ± 5	55 ± 4	25 ± 2
11/17	Q 524 ± 52 T 506 ± 51	220 ± 22 211 ± 21	8 ± 3	34 ± 3	25 ± 2
11/23	Q 532 ± 53 T 514 ± 51	195 ± 20 217 ± 22	9 ± 3	15 ± 1	11 ± 1
11/29	Q 527 ± 53 T 501 ± 50	215 ± 22 192 ± 19	11 ± 3	81 ± 6	56 ± 4
12/5	Q 522 ± 52 T 471 ± 47	204 ± 20 220 ± 20	7 ± 2	60 ± 5	34 ± 3
12/11	Q 527 ± 53 T 452 ± 45	218 ± 22 215 ± 22	10 ± 1	43 ± 3	22 ± 2

a) Vs = volume of air sampled for QFFs, TMFs, and PUFS; b) Va = volume of air sampled for ADCs; c) na = not applicable.

4.2.4.2. Gas Phase Concentrations

Typical PUFS and ADC primary, backup, and blank chromatograms are given in Figures 4.7 - 4.9, respectively. The peaks for the surrogate and internal standards are labeled in each chromatogram; each of those peaks correspond to ~10 ng. For each event, a blank PUFS was analyzed to determine the blank corrected concentrations of the target compounds associated with the sampled PUFSs. A blank ADC was also run whenever ADC samples were analyzed. Mean blank values for the PUFSs and ADCs calculated for the 14 sampling events are presented in Table 4.12. For the target n-alkanes, the blank levels for the ADCs were generally much lower than the blank levels for the PUFSs. None of the target PAHs were detected at significant levels on the blank ADCs.

The concentrations for the target compounds associated with the primary and backup sorbents beds were calculated in the following manner: 1) the absolute mass of the target compound associated with the primary, backup, and blank sorbent beds was calculated (Section 4.1.6.4); 2) recoveries (ng) relative to the surrogate standard were calculated; 3) primary and backup sorbent sample mass amounts were considered nonzero only if they exceeded the blank mass amounts at the 95% confidence level; 4) if the significance test was passed, the mass on the blank was subtracted from the sample mass amounts on the primary (or backup bed); 5) atmospheric concentrations were calculated by dividing the blank-corrected sample mass amounts by the corresponding sample volumes. The blank levels were

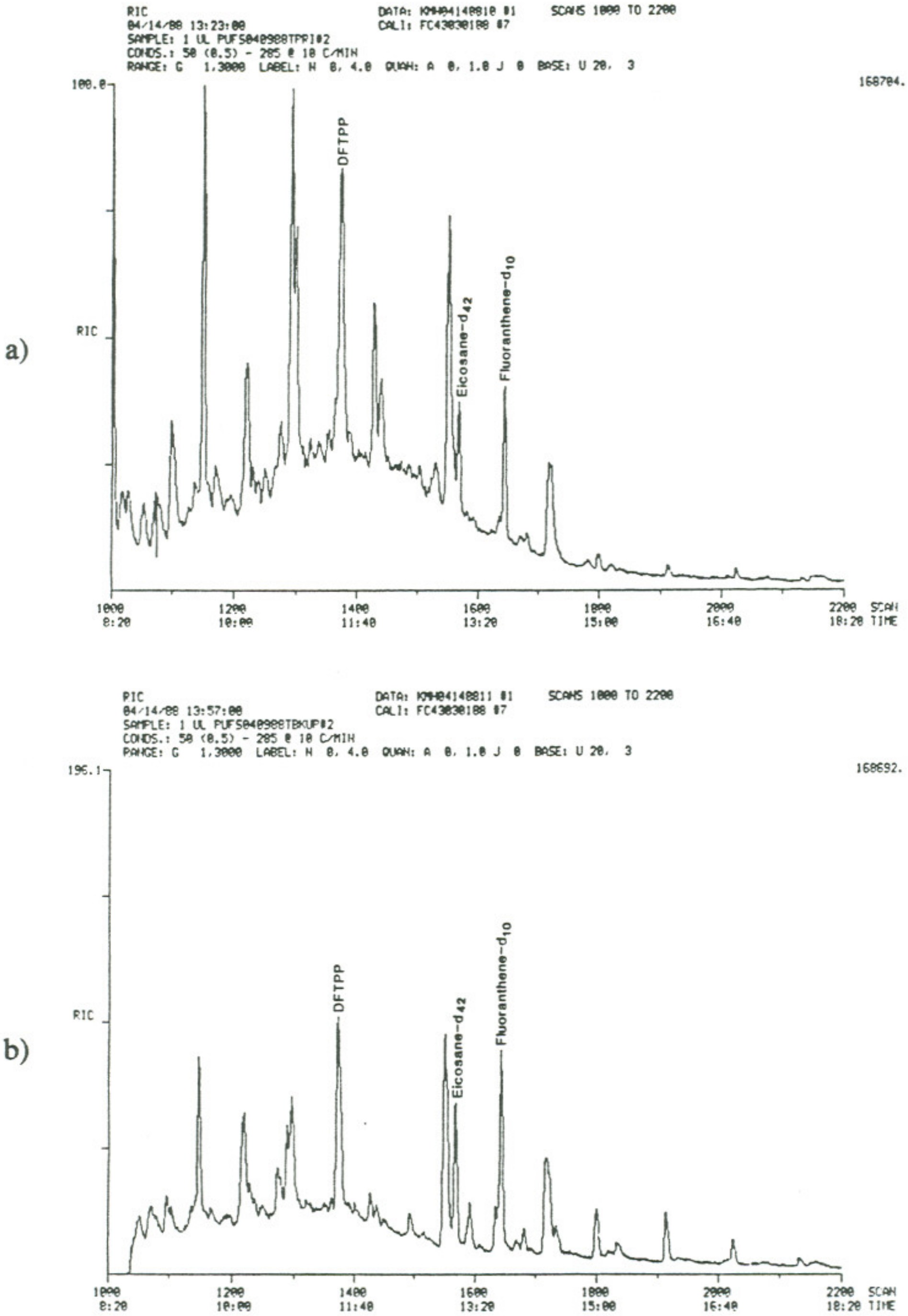


Figure 4.7. a) Typical chromatogram of a primary PUFS from Portland, OR in 1988. b) Typical chromatogram of a backup PUFS from Portland, OR in 1988.

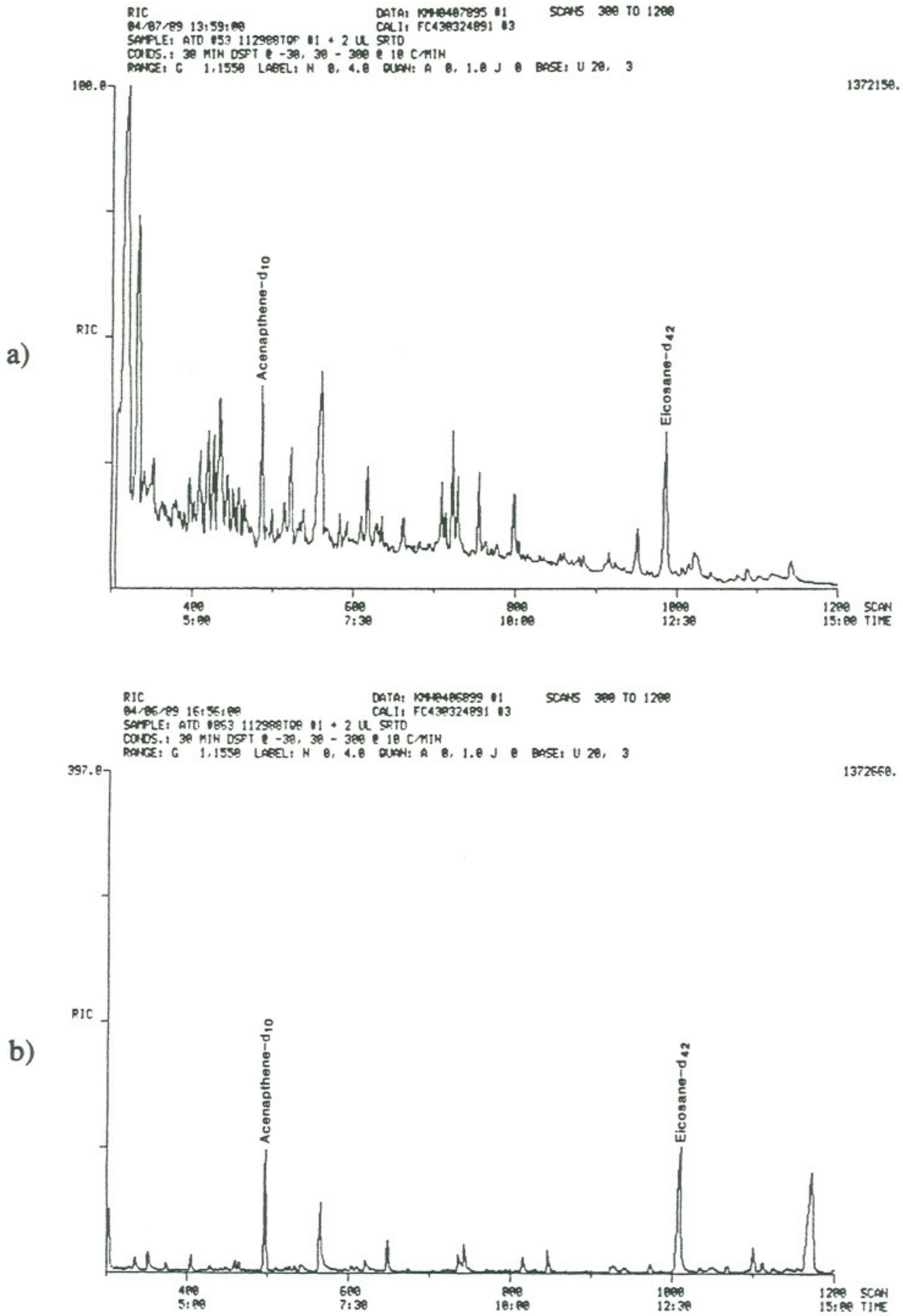


Figure 4.8. a) Typical chromatogram of a primary ADC from Portland, OR in 1988. b) Typical chromatogram of a backup ADC from Portland, OR in 1988.

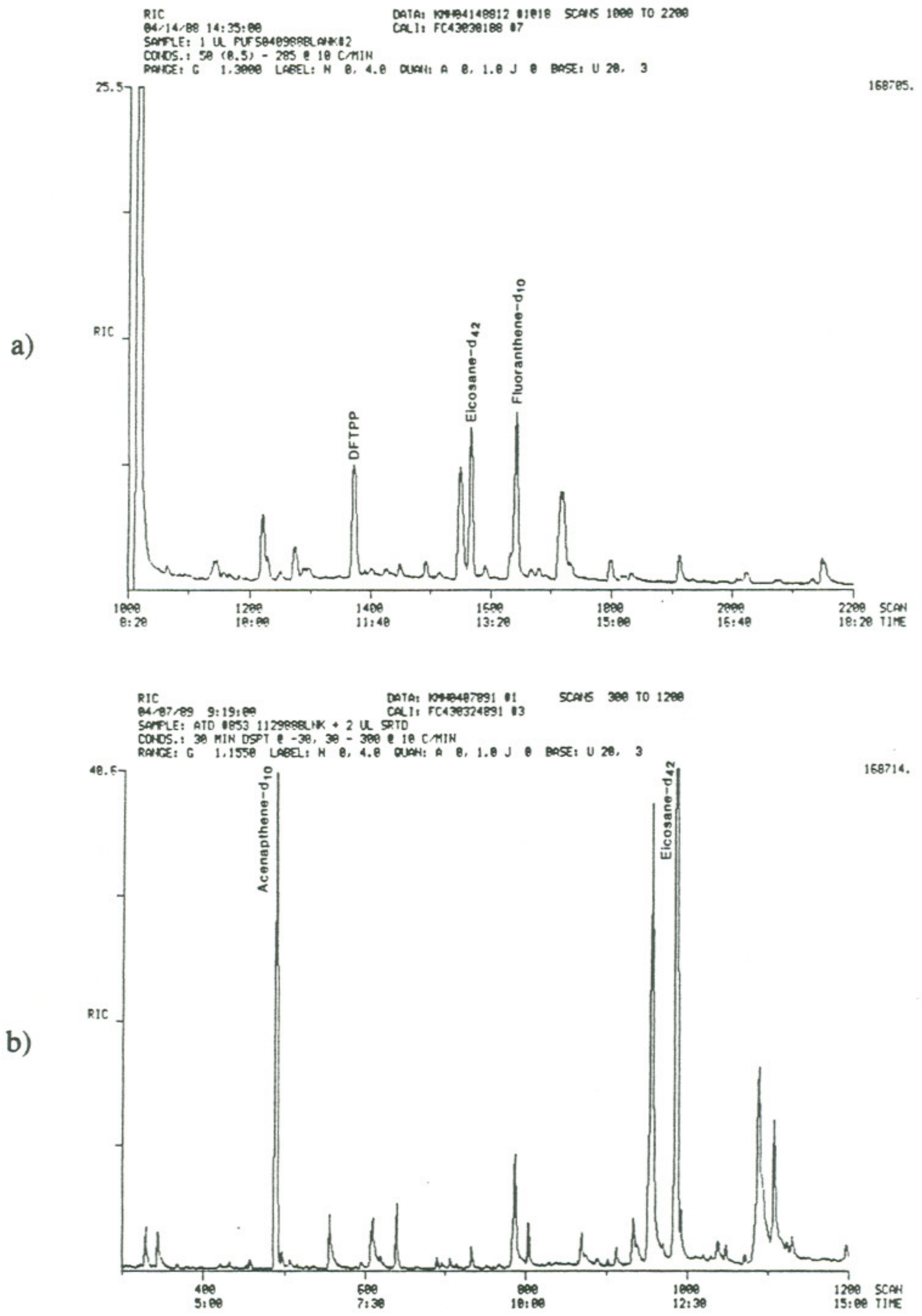


Figure 4.9. a) Typical chromatogram of a blank PUFS from Portland, OR in 1988. b) Typical chromatogram of a blank ADC from Portland, OR in 1988.

Table 4.12. Comparison of the Blank Levels on PUFS and ADC Sorbent Beds for the SOC Target Compounds for Samples Collected in Portland OR in 1988.

CPD	PUFS[a] (ng) (n = 14)	ADC[a] (ng) (n = 5)
n-Alkanes		
C16	926.6 ± 941.9	0.10 ± 0.06
C17	485.1 ± 481.9	0.08 ± 0.04
C18	280.9 ± 219.4	0.07 ± 0.04
C19	426.0 ± 315.9	0.09 ± 0.07
C20	188.6 ± 197.3	0.13 ± 0.12
C21	242.6 ± 288.8	0.11 ± 0.08
C22	237.7 ± 249.3	0.07 ± 0.04
C23	286.3 ± 533.2	0.05 ± 0.08
C24	132.6 ± 257.4	nd[b]
C25	3.14 ± 11.33	0.08 ± 0.15
PAHs		
ACE	20.00 ± 57.07	nd
FLU	38.57 ± 59.53	nd
PHE	228.0 ± 268.3	nd
ANT	143.1 ± 226.6	nd

Table 4.12 (cont'd.). Comparison of the Blank Levels on PUFS and ADC Sorbent Beds for the SOC Target Compounds for Samples Collected in Portland, OR in 1988.

CPD	PUFS[a] (ng) (n = 14)	ADC[a] (ng) (n = 5)
FLA	34.29 ± 35.48	nd
PYR	26.86 ± 27.07	nd
BaA	38.3 ± 124.3	nd
CHR	38.57 ± 75.10	nd

a) mean ± 1s; b) nd = not detected at a statistically significant level.

generally <5% of the sample levels for the ADCs and generally <10% for the PUFSs.

The blank-corrected atmospheric gas phase concentrations for all sampling events are given in Table A2. No n-alkanes less volatile than C27 or PAHs less volatile than BaA were detected at significant levels on the PUFSs or ADCs. The event to event variability in the concentrations of the target n-alkanes >C23 were within a factor of 2 - 3. However, an order of magnitude difference was seen between the concentrations from the highest and lowest loading events for C19 to C22. The highest loading events were obtained during November and December, where influences from residential heating may have been high.

Unlike the n-alkanes, the concentrations of the target PAHs in the gas phase were fairly constant from event to event. The highest concentrations for the PAHs in the gas phase were measured in November and December. It is possible that motor vehicles on a nearby road were the source of the relatively constant concentrations measured during the majority of the year. During the winter months, the additional contribution of PAHs from residential heating may have been responsible for the elevated levels during that season.

4.2.4.3. Particulate Phase Concentrations

Chromatograms for typical QFF and TMF extracts are presented in Figures 4.4 and 4.5 (Section 4.2.2). The blank levels associated with the filters are given in Table 4.13. The blank levels for the QFF extracts are similar to those presented by Ligocki and Pankow (1989). For all target compounds, the QFF extracts had significantly lower blank levels than the TMF extracts. These lower levels are undoubtedly due to the presampling clean up method of baking the QFFs at 600°C for four hours.

Using the same criteria as the gas phase data, an amount in the particulate phase was considered real if it was statistically significantly higher than that of the blanks, and was above the minimum quantitation limit of ~0.5 ng. Significant concentrations were found on both primary and backup QFFs and TMFs. The blank-corrected atmospheric particulate phase concentrations are presented in Table A2. For compounds in which a comparison could be made, the concentrations associated with the particulate phase for the target compounds were, in general, much lower than that in the gas phase. While particulate phase concentrations were rarely above 10 ng/m^3, it was not uncommon for gas phase concentrations of the same compounds in the winter to be 80 ng/m^3.

Table 4.13. Comparison of the Blank Levels on QFF and TMF Filters for the SOC Target Compounds for Samples Collected in Portland, OR in 1988.

CPD	QFF[a] (ng) (n = 14)	TMF[a] (ng) (n = 14)
n-Alkanes		
C16	7.71 ± 8.45	161.4 ± 114.2
C17	5.00 ± 5.79	179.7 ± 111.8
C18	3.29 ± 6.08	202.3 ± 118.3
C19	2.29 ± 5.39	142.0 ± 118.7
C20	6.86 ± 16.7	83.77 ± 72.83
C21	9.00 ± 17.7	93.43 ± 77.97
C22	8.43 ± 16.3	91.1 ± 149.0
C23	9.57 ± 12.9	54.29 ± 79.03
C24	3.29 ± 7.35	38.57 ± 51.35
C25	2.71 ± 6.47	39.43 ± 76.18
PAHs		
ACE	nd[a]	nd
FLU	nd	nd
PHE	nd	nd
ANT	nd	nd

Table 4.13 (cont'd.). Comparison of the Blank Levels on QFF and TMF Filters for the SOC Target Compounds for Samples Collected in Portland, OR in 1988.

CPD	QFF[a] (ng) (n = 14)	TMF[a] (ng) (n = 14)
FLA	nd	3.71 ± 9.38
PYR	2.86 ± 7.01	3.4 ± 12.4
BaA	5.9 ± 14.9	16.29 ± 34.12
CHR	nd	3.14 ± 8.03

a) mean ± 1s; b) nd = not detected at a statistically significant level

4.2.5. Reproducibility

4.2.5.1. Comparison of Concentrations Obtained with PUFSs and Tenax-TA ADCs

For the last five events sampled in 1988, an effort was made to obtain more accurate estimates of the gas phase concentrations of the target compounds by sampling with ADCs. As can be seen from Tables 4.14a and 4.14b, excellent agreement was obtained between the measurements from PUFSs and ADCs. The mean coefficients of variation (CV) between the two methods, over all of the events sampled, for the target n-alkanes ranged from 6 to 15% for C16 through C21. Similar results were obtained for the target PAHs, the mean CVs between the two methods ranged from 6 to 13% for acenapthene through pyrene. The CVs were calculated for each sampling train by dividing the mean concentration for the two methods by standard deviation of the mean. The results of a t-test show that there were no significant differences ($p = 0.05$) in the concentrations measured by the two methods. The results from this comparison are consistent with those obtained from the PUF breakthrough data. Thus, under the sampling conditions used in this study, the results of both methods are consistent with quantitative collection of the target compounds in the gas phase.

Table 4.14a. Atmospheric of Gas Phase Concentrations obtained in Portland, OR in 1988 with PUFSs and Tenax-TA ADCs and Mean Coefficient of Variation (CV) Between Methods.

		Concentration (ng/m³)					
		Sample Date and Sampling Train					
		11/17		11/23		11/29	
CPD	Method	Q	T	Q	T	Q	T
n-Alkanes							
C16	PUFS	29.09	39.16	18.51	16.62	59.48	57.99
	ADC	35.36	41.23	24.11	22.89	64.33	66.45
C17	PUFS	35.52	41.69	18.09	16.41	72.42	70.94
	ADC	39.87	44.56	22.22	19.57	79.56	78.67
C18	PUFS	25.74	26.50	11.34	9.87	40.18	50.05
	ADC	27.92	29.55	13.12	13.65	39.34	42.89
C19	PUFS	15.50	20.52	2.66	4.16	34.52	29.54
	ADC	16.03	19.56	2.89	3.72	35.56	31.33
C20	PUFS	1.52	7.93	0.25	1.19	11.06	13.42
	ADC	1.74	6.53	0.34	1.14	11.56	12.85
C21	PUFS	nd	0.64	nd	nd	nd	1.07
	ADC	nd	nd	nd	nd	nd	0.86

Table 4.14a (cont'd.). Atmospheric of Gas Phase Concentrations obtained in Portland, OR in 1988 with PUFSs and Tenax-TA ADCs and Mean Coefficient of Variation (CV) Between Methods.

		Concentration (ng/m^3)					
		Sample Date and Sampling Train					
		12/5		12/11			
CPD	Method	Q	T	Q	T	Mean	% CV
n-Alkanes							
C16	PUFS	85.93	64.65	29.86	24.58		
	ADC	94.34	72.48	35.37	28.95		11
C17	PUFS	58.31	50.79	25.14	23.53		
	ADC	66.53	55.37	27.98	27.03		9
C18	PUFS	31.57	34.84	18.43	15.12		
	ADC	30.55	35.92	20.61	16.47		9
C19	PUFS	38.36	32.24	12.06	10.61		
	ADC	39.74	34.35	13.76	9.34		6
C20	PUFS	10.76	13.67	4.53	3.14		
	ADC	11.98	12.98	4.77	3.96		9
C21	PUFS	0.45	2.25	0.29	0.53		
	ADC	0.63	2.47	0.25	0.67		15

Table 4.14b. Atmospheric of Gas Phase Concentrations obtained in Portland, OR in 1988 with PUFSs and Tenax-TA ADCs and Mean Coefficient of Variation (CV) Between Methods.

		Concentration (ng/m^3)					
		Sample Date and Sampling Train					
		11/17		11/23		11/29	
CPD	Method	Q	T	Q	T	Q	T
PAHs							
ACE	PUFS	5.09	5.04	2.34	2.25	9.35	9.66
	ADC	6.24	6.33	2.98	2.89	10.33	10.75
FLU	PUFS	24.33	20.17	0.53	3.33	39.30	54.68
	ADC	29.67	24.13	0.75	3.77	44.26	58.16
PHE	PUFS	35.45	32.09	20.93	19.26	38.99	66.07
	ADC	37.65	29.91	21.44	23.47	39.79	62.76
ANT	PUFS	11.85	7.88	5.93	8.07	14.81	21.38
	ADC	10.17	8.36	6.17	7.75	15.95	23.56
FLA	PUFS	18.16	16.50	8.73	7.41	31.62	40.95
	ADC	20.21	15.04	8.39	8.27	30.06	38.84
PYR	PUFS	13.24	12.13	5.79	6.15	20.61	24.76
	ADC	14.04	11.39	6.47	5.42	19.23	22.56

Table 4.14b (cont'd.). Atmospheric of Gas Phase Concentrations obtained in Portland, OR in 1988 with PUFSs and Tenax-TA ADCs and Mean Coefficient of Variation (CV) Between Methods.

		Concentration (ng/m^3)					
		Sample Date and Sampling Train					
		12/5		12/11			
CPD	Method	Q	T	Q	T	Mean	% CV
PAHs							
ACE	PUFS	1.70	2.94	9.79	11.03		
	ADC	2.34	3.25	10.69	12.94		13
FLU	PUFS	3.39	3.25	23.65	28.02		
	ADC	4.48	3.97	25.08	29.17		11
PHE	PUFS	145.9	164.2	96.31	121.5		
	ADC	124.5	146.4	90.57	98.77		9
ANT	PUFS	84.87	88.81	39.84	49.43		
	ADC	79.54	94.25	43.11	52.39		8
FLA	PUFS	38.63	50.63	17.29	24.72		
	ADC	41.06	48.39	16.02	23.45		6
PYR	PUFS	25.03	31.04	10.83	14.85		
	ADC	22.93	29.57	9.31	12.94		7

4.2.5.2. Mass Balance Comparison of Quartz and Teflon Sampling Trains

As described earlier, two samplers equipped with quartz and Teflon sampling trains were used for all 14 events. Since gas adsorption of some of the target compounds to QFFs can lead to significant sampling artifacts (Section 4.2.2), a comparison was made between the total concentration (gas and particulate phases) measured on each sampling train. The comparison was examined in a three step process. Firstly, for a given compound, the total concentration was calculated for both the quartz and Teflon sampling trains. Secondly, for a given compound, a CV (mean concentration from the two sampling trains divided by the standard deviation of the means and multiplied by 100%) was calculated from the total concentration data for each sampling event. Thirdly, the CVs from all of the sampling events were averaged.

A comparison of the average CVs (%) for the target compounds is presented in Table 4.15. For the n-alkanes C16 to C31, the average CVs ranged from 6 to 15%. The average CV for all of the target n-alkanes combined was 10%. The average CVs for the target PAHs were slightly higher, ranging from 8 to 35%, and averaging 16% for all of the PAHs combined. The sampling dates were also examined in a similar fashion to see if there were any differences between the concentrations collected for different events. Good agreement was found between concentrations collected on the quartz and Teflon sampling trains for all events and all compounds. Although not tabulated, the average CV for all target compounds

Table 4.15. Summary of the Average Coefficient of Variation[a] (%) Between the Total Concentration Collected on the Quartz Sampling Train and the Teflon Sampling Train for the Target Compounds Collected in Portland, OR in 1988.

Compound	% CV[b] (n = 14)
n-Alkanes	
C16	9
C17	5
C18	6
C19	11
C20	12
C21	8
C22	7
C23	15
C24	14
C25	9
C26	13
C27	11
C28	10
C29	9
C30	11
C31	10

Table 4.15 (cont'd.). Summary of the Average Coefficient of Variation[a] (%) Between the Total Concentration Collected on the Quartz Sampling Train and the Teflon Sampling Train for the Target Compounds collected in Portland, OR in 1988.

Compound	% CV (n = 14)
PAHs	
ACE	15
FLU	18
PHE	12
ANT	29
FLA	11
PYR	8
BaA	35
CHR	9
BFL	9
BeP	9
BaP	20

a) the average of the CVs between samplers for each sampling event, for a given compound; b) mean concentration from the two sampling trains divided by the standard deviation of the means and multiplied by 100%.

collected for a single event ranged from 8 to 19% and averaged 10%. This degree of uncertainty was comparable to the uncertainty of the sampling and analytical methods.

Chapter 5. Organic and Elemental Carbon Analyses

Since partitioning of a compound between the gas and particulate phases depends to a large extent on the physical and chemical characteristics of the particulate matter, a number of measurements were performed to better characterize the particulate matter collected in this study. In particular, measurements of TSP and PM-10 by ODEQ (Section 4.3.1.1) and elemental and organic carbon (EC and OC) concentrations of the particulate matter measured by this study, were examined. The amount of total particulate carbon (TPC) is calculated from the sum of the EC and OC concentrations.

Ligocki and Pankow (1989) have postulated that atmospheric trace organic compounds might associate more closely to the carbonaceous portion of atmospheric particulate matter and that the activity in the particulate phase might be better represented by F/TPC as opposed to F/TSP in the expression for K. The results from the comparisons between A/(F/TSP) and A/(F/TPC) will be presented in Section 6.1. This chapter will be devoted to further characterizing the particulate matter collected during the sampling events for carbon content and comparing these results with those of other researchers.

5.1. Experimental Procedures

After each sampling event, the intact filter holders were covered with muffle-furnace-baked aluminum foil and brought back to the laboratory. One 47 mm diameter punch was taken from each QQP, QQB, TQB, and blank QFF and placed in a separate aluminum foil lined petri dish and stored at 5 °C until analysis. Since the QFFs have collection efficiencies of >99% for atmospheric particulate matter (Section 2.1), and since elemental carbon (EC) is only present in the particulate phase, it has been assumed that any carbon found on any QQB and TQB filters was organic carbon (OC) sorbed from the gas phase.

The particulate material that was collected on the primary and backup QFFs was analyzed for EC and OC by a thermo-optical method developed by Johnson et. al. (1982) and Huntzicker et. al. (1982). Briefly, organic carbon is measured by rapidly heating a 1 cm^2 QFF punch in an oxygen free environment (100% He). The volatilized OC is oxidized to CO_2, then reduced to CH_4 and measured with a flame ionization detector. Following this step, elemental carbon is measured by reducing the oven temperature, adding O_2 to achieve a 2% O_2 and 98% He environment, and then ramping the temperature up to oxidize the EC to CO_2. The resulting CO_2 is then measured in the same fashion as the OC above. During the entire analysis, the reflectance of the filter is monitored using a He-Ne laser to help distinguish between the OC and EC fractions. In particular, the laser signal allows a correction for the portion of OC that is pyrolytically converted to EC during the

OC oxidation step. Without this correction, the EC concentration would be seriously overestimated. The OC and EC measurements were performed by Sunset Laboratories (Forest Grove, OR).

5.2. Elemental Carbon Concentrations

EC concentrations for all 14 sampling events on the QQP filter are presented in Table 5.1. EC concentrations (µg C/m^3) showed a seasonal variability with the highest levels being measured in the winter months. The concentrations ranged from 0.83 to 6.37 µg C/m^3 and averaged 2.31 µg C/m^3 over the ten month sampling period. The average concentration can be compared to the EC concentrations reported by Shah et. al. (1986) for over 1000 samples taken at 46 urban sites around the United States as part of the National Air Surveillance Network (NASN) project in 1975. From their study, Shah et. al. (1986) reported that EC concentrations ranged from 0.9 to 7.7 µg C/m^3. Thus, the EC concentrations measured in this study are consistent with those measured in other urban areas.

Table 5.1. Elemental and Organic Carbon Concentrations on QFFs for both Quartz and Teflon Sampling Trains in Portland, OR in 1988.

Date	FV[a] (cm/s)	Filter	EC[b]	OC[c]
			μg C/m^3	
2/27	66	QQP	3.13	18.52
		QQB		2.03
	61	TQB		3.30
3/16	67	QQP	1.53	11.52
		QQB		1.04
	59	TQB		2.86
4/9	70	QQP	0.83	6.60
		QQB		0.59
	60	TQB		1.49
7/20	62	QQP	2.67	16.30
		QQB		2.40
	56	TQB		4.69
7/26	62	QQP	1.11	9.57
		QQB		1.55
	54	TQB		4.45
8/1	57	QQP	1.23	4.75
		QQB		0.73
	56	TQB		1.67
8/7	49	QQP	1.24	6.07
		QQB		1.08
	46	TQB		2.72
8/19	51	QQP	1.59	7.72
		QQB		1.40
	49	TQB		3.17

Table 5.1 (cont'd.). Elemental and Organic Carbon Concentrations on QFFs for both Quartz and Teflon Sampling Trains in Portland, OR in 1988.

Date	FV[a]	Filter	EC[b]	OC[c]
	(cm/s)		μg C/m³	
8/31	49	QQP	3.26	8.99
		QQB		1.62
	47	TQB		2.79
11/17	48	QQP	2.39	8.53
		QQB		0.85
	46	TQB		2.47
11/23	49	QQP	1.30	5.20
		QQB		1.03
	47	TQB		1.79
11/29	48	QQP	6.37	22.27
		QQB		2.58
	46	TQB		4.59
12/5	48	QQP	4.65	31.38
		QQB		3.15
	na[d]	na		na
12/11	48	QQP	1.06	12.74
		QQB		1.32
	na	na		na

a) FV = face velocity; b) EC = elemental carbon; c) OC = organic carbon; d) na = not available.

5.3. Organic Carbon Concentrations

5.3.1. QQP Filter

The OC concentrations measured on the primary QFFs were always significantly ($P = 0.05$) higher than the corresponding EC concentrations (Table 5.1). OC concentrations also showed seasonal variability with the highest concentrations being measured during the winter months. The OC concentrations on the primary QFFs ranged from 4.75 to 31.4 µg C/m^3 and averaged 10.5 µg C/m^3 over the ten months sampled. This is also within the range reported by Shah et.al. (1986) of 2.7 to 13.4 µg C/m^3 from the 1975 NASN study.

5.3.2. QFF / QFF Backup Filter

McDow and Huntzicker (1989) examined the amount of OC on the backup QFF as a function of sampler face velocity (volumetric flow rate/superficial surface area of the filter). They reported that the measured concentration of OC decreased with increasing face velocity and attributed the trend to gas phase adsorption to the QFF. They concluded that gas phase adsorption to the filter could be greatly reduced by operating at a face velocity > 40 cm/s. Even though the samples collected in this study were obtained at face velocities > 40 cm/s, significant concentrations of OC were found on the QQB for all events sampled. An average of 1.53 µg C/m^3 was found on the QQB filters for the 14 events sampled.

The extent of gas adsorption to a QFF can also be examined by looking at the fraction of OC on the QQB to that on the QQP (Table 5.2). The range of the OC fraction (QQB/QQP) was quite narrow (9 to 20%), with an average and standard deviation (1s) of 14 ± 4% for the 14 events sampled. These results agree quite well with those obtained by McDow (1986) of 21 ± 8% for the OC fraction at approximately the same face velocity collected in Portland, OR during 1986. Thus, there were no significant differences between the results of this study and those of McDow at the 95% confidence level for OC measured on QQB filters.

5.3.3. TMF / QFF Backup Filter

The results from the measurement of OC concentration on the backup QFF behind a primary TMF (i.e. TQB) for the events sampled are presented in Table 5.2. The average OC concentration on the TQB was always significantly ($P = 0.05$) higher than that measured on the QQB for the same event. The range of OC measured on the TQB filter was 1.46 to 4.69 µg C/m^3, and averaged 3.00 µg C/m^3.

The OC fraction of TQB/QQP can also be examined and compared to the results obtained for the QQB/QQP fraction in Section 5.3.2. The average TQB/QQB fraction of OC for all of the sampling events was significantly ($P = 0.05$) higher than the average QQB/QQP fraction of OC. The TQB/QQP fractions for OC ranged from 21 to 46%, and averaged 31 ± 9% in this study and are

Table 5.2. Fraction of Organic Carbon Found on Quartz and Teflon Backup Filters vs. Quartz Primary and Ratio of Organic Carbon on Backup Filters in Portland, OR in 1988.

	OC (%)		
Date	QQB/QQP	TQB/QQP	TQB/QQB
2/27	11	18	1.64
3/16	9	25	2.78
4/9	9	22	2.44
7/20	15	29	1.93
7/26	16	46	2.88
8/1	15	35	2.33
8/7	18	45	2.50
8/19	18	41	2.28
8/31	18	31	1.72
11/17	10	29	2.90
11/23	20	34	1.70
11/29	12	21	1.75
12/5	10	na[d]	na
12/11	10	na	na
AVE ± 1s	14 ± 4%	31 ± 9%	2.24 ± 0.48

consistent with the results obtained by McDow (1986) who reported 44 ± 23% for the same fraction with samples collected in Portland, OR 1986.

The ratio of the OC concentration on the TQB filters to that on the QQB filters can also be used to estimate the relative importance of gas adsorption of OC between the two sampling trains. The range of the OC concentration ratio TQB/QQB was 1.64 to 2.90, averaged 2.24 ± 0.48, and was significantly greater than 1.0 using a one-sided t-test at the 95% confidence level. There was no significant difference between the results of this study and those of McDow (1986), who obtained 2.05 ± 0.64 for the same ratio under similar sampling conditions. An important result in this study is that, on the average, the OC concentration measured on the TQB filter was more than twice the OC concentration measured on the QQB filter.

5.4. Comparison of Organic Carbon Concentrations Found on the Backup Filters and the Target Compounds

Since n-alkanes and PAHs constitute a significant fraction of all of the OC found in the atmosphere, and since the target compounds were chosen to be representative of a portion of the atmospheric n-alkanes and PAHs, a comparison between the sum of the gas phase concentrations of target compounds and the OC concentrations on the backup filters is of interest. The TQB/QQB ratios for the sums of the gas phase concentrations of all of the target compounds and OC concentrations measured for each sampling date are presented in Table 5.3. Those TQB/QBB ratios ranged from 0.67 to 2.27 and averaged 1.26 ± 0.37 (1s). The average TQB/QQB ratio was significantly ($P = 0.05$) lower than the ratio obtained for OC (TQB/QBB = 2.24 ± 0.48). Therefore, the target compound ratios found in this study did not mimic the trends of the TQB/QQB ratios measured for OC. Thus, it appears that organic compounds other than the target compounds might be responsible for the higher concentrations of OC measured on the TQB filters.

An effort was made to identify some of the non-target compounds on the backup QFF filters. This was accomplished by examining the major peaks in the chromatograms of the QFF extracts to see if any classes of compounds or characteristic ions of non-target compounds, that are thought to be at high concentrations in the atmosphere, were present in the filter extracts. For example, $m/z = 73$ amu ($-CH_2CH_2COOH$) was monitored as it is a characteristic ion of long chain fatty acids. However, monitoring characteristic ions of non-target compounds during a chromatographic run provided very little qualitative information. The extracts from the filters produced rather complex chromatograms and mass spectra and no particular classes of compounds or characteristic ions could be distinguished from the relatively high baseline levels of all ions in the mass spectra. However, the column cleanup step (Section 4.1.6.2) that was used to remove the highly polar compounds may have removed some compounds that might be responsible for the relatively high TQB/QQB OC ratio. The hypothesis that polar compounds might be responsible for higher concentrations of OC on TQB filters as opposed to QBB

Table 5.3. Ratios of Organic Carbon Concentrations and Total Gas Phase Concentration of Target Compounds on the Quartz and Teflon Sampling Trains from Portland, OR in 1988.

Date	OC TQB/QQB	TC[a] TQB/QQB
2/27	1.64	1.41
3/16	2.78	1.11
4/9	2.44	1.24
7/20	1.93	1.13
7/26	2.88	1.28
8/1	2.33	1.22
8/7	2.50	1.43
8/19	2.28	1.23
8/31	1.72	1.08
11/17	2.90	2.27
11/23	1.70	0.67
11/29	1.75	1.09
AVE ± 1s	2.24 ± 0.48	1.26 ± 0.37

a) TC = sum of all of the target compounds gas phase concentrations.

filters is being investigated in the laboratory by Bidleman et. al. (1989) and in field sampling by Hart and Giger (1990).

5.5. Comparison of TSP, PM-10, and TPC Concentrations

The results of the TSP, PM-10, and TPC measurements for each sampling event are presented in Table 5.4. Since PM-10 and TPC concentrations are components of atmospheric particulate matter, it is not surprising that they follow the same trends as the TSP data. For example, when the highest value of TSP was measured (81 µg/m^3), the highest values of PM-10 and TPC were also recorded (56 and 28.64 µg/m^3, respectively).

The relationship between TPC, TSP, and PM-10 can be examined by looking at the correlation of TSP and PM-10 with TPC. While a relatively low correlation coefficient ($r^2 = 0.66$) was obtained by comparing the concentrations of TPC and TSP, a much higher correlation ($r^2 = 0.88$) was obtained by comparing TPC and PM-10. The linear least squares regression equations for the comparisons are TPC = 0.26(TSP) - 0.39 and TPC = 0.43(PM-10) + 0.69.

The correlations between TSP, TPC, and PM-10 can be can be thought of in terms of a typical atmospheric particle distribution. Atmospheric particulate matter is typically in the form of a bimodal distribution. The two modes are the fine and coarse particulate modes. The fine particulates typically have aerodynamic diameters <2 µm. Most of these particles are emitted directly into the atmosphere

Table 5.4. TSP, PM-10, and TPC Concentrations Measured During the Sampling Events in Portland, OR in 1988.

	$\mu g/m^3$					
Date	TSP	PM-10	TPC	TSP/ TPC	PM-10/ TPC	PM-10/ TSP
2/27	82	54	22	4.0	2.5	0.7
3/16	74	28	13	5.7	2.2	0.4
4/9	46	15	7.4	6.2	2.0	0.3
7/20	65	40	19	3.4	2.1	0.6
7/26	58	30	11	5.4	2.8	0.5
8/1	37	20	6.0	6.2	3.3	0.5
8/7	29	15	7.3	4.0	2.1	0.5
8/19	36	17	9.3	3.9	1.8	0.5
8/31	55	25	12	4.5	2.0	0.5
11/17	34	25	11	3.1	2.3	0.7
11/23	15	11	6.5	2.3	1.7	0.7
11/29	81	56	29	2.8	2.0	0.7
12/5	60	34	13	3.4	2.7	0.6
12/11	43	22	14	3.1	1.6	0.5
AVERAGE				4.2	2.2	0.6

from combustion processes or are the result of gas to particle conversion reactions (Whitby, 1975). The coarse particles generally have aerodynamic diameters > 2 µm and are mechanically derived (e.g. dust and sea spray).

High volume samplers used for TSP measurements typically collect particulate material that has an aerodynamic diameter <25 µm (ODEQ, 1989). PM-10 samplers use a specially configured head to limit sampling of atmospheric particulate matter to particles <10 µm in diameter. Since carbonaceous particulate matter is normally associated with the fine particulate mode (< 2 µm), it makes sense that a higher correlation is obtained between TPC and PM-10 than between TPC and TSP.

5.6. Reproducibility of Carbon Measurements

5.6.1. Replicate Analyses

The precision of the thermo-optical carbon analyzer was estimated by running four samples in duplicate and one in triplicate (Table 5.5). As mentioned in Section 5.1, QQP filters, rather than backup QFFs, were used in these experiments so that both EC and OC could be determined from a single run. Excellent precision was obtained for both EC and OC measurements. The average CV for all five analyses was 9% for EC and 3% for OC. These precision estimates are similar to those obtained by McDow (1986) and Turpin (1989).

Table 5.5. Comparison of the Concentrations of Organic Carbon and Elemental Carbon Obtained for Replicate Measurements in Portland, OR in 1988.

Date	Filter		EC	OC
			µg C/m³	
7/20	QQP		2.67	16.30
	QQP		2.19	16.40
	QQP		2.80	15.70
		AVE	2.55	16.13
		CV (%)	13	2
11/17	QQP		2.39	8.53
	QQP		2.08	8.93
		AVE	2.24	8.73
		CV (%)	10	3
11/23	QQP		1.30	5.20
	QQP		1.60	4.79
		AVE	1.45	5.00
		CV (%)	15	6
11/29	QQP		6.37	22.27
	QQP		5.70	23.68
		AVE	6.04	22.98
		CV (%)	8	4
12/11	QQP		1.06	11.68
	QQP		1.05	11.54
		AVE	1.06	11.61
		CV (%)	1	1
AVERAGE CV (%)			9	3

Therefore, within the uncertainty of the thermo-optical technique, the results from the EC and OC measurements made in this study are consistent with the results obtained by previous researchers.

Chapter 6. Atmospheric Partitioning of Target Compounds

6.1. Equilibrium Distribution Constants

As described in Section 3.1, assuming artifact-free sampling, for a given compound and sampling event, an equilibrium distribution constant (K) can be defined

$$K = \frac{A}{F/(TSP)} \qquad 6.1$$

where A and F are the adsorbent bed and filter retained concentrations (ng/m^3), respectively, and TSP is the total suspended particulate concentration (µg/m^3). As described in Section 3.3, within a class of compounds, K has been found to depend on vapor pressure (p°_L) according to

$$\log K = \log \frac{A}{F/(TSP)} = p^\circ_L + \log C \qquad 6.2$$

Figure 6.1 graphically represents the above relationship for n-alkanes C16 - C23 using experimental data from this study for samples collected in Portland, OR in 1988. Results from a least squares linear regression on the data show that the

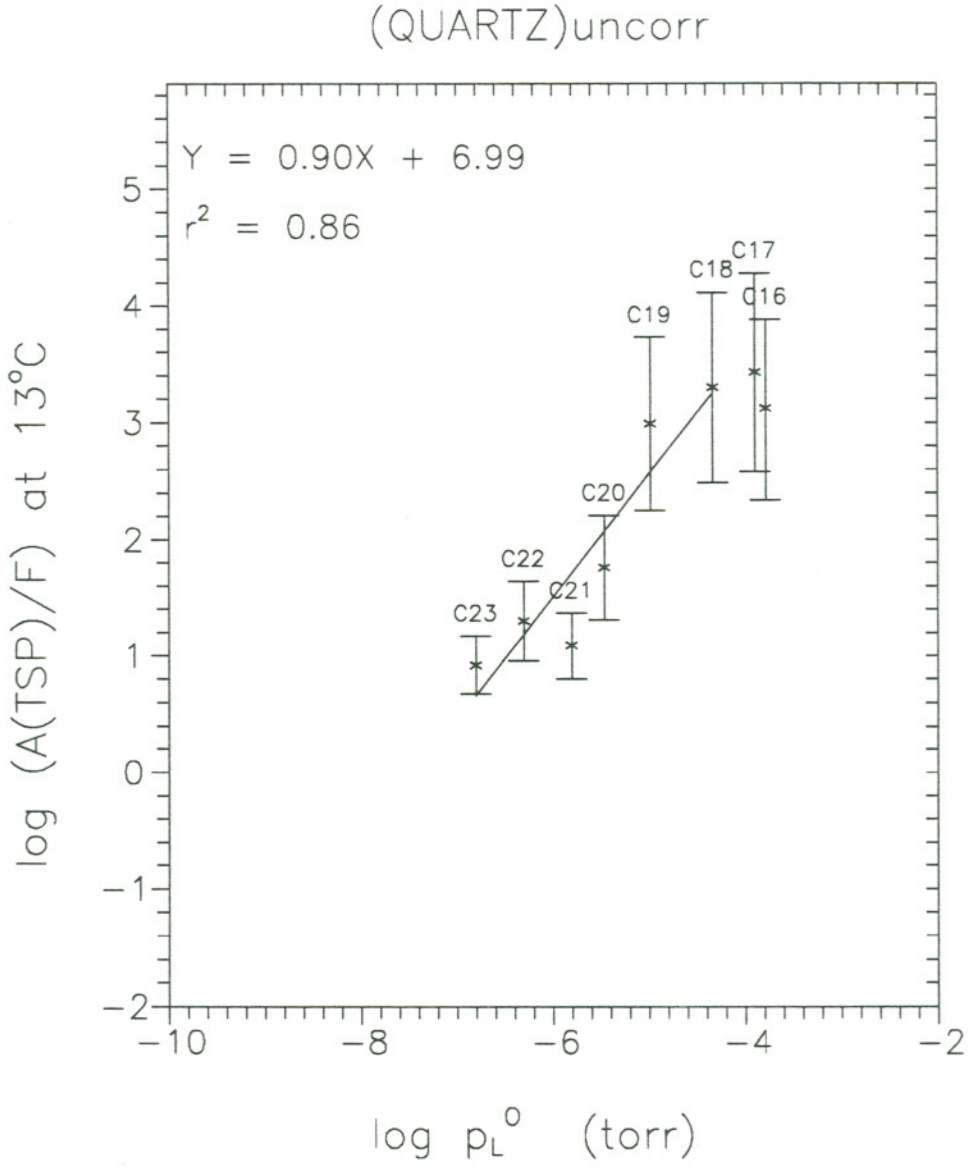


Figure 6.1. Log A(TSP)/F vs. log p°_L for the target n-alkanes from samples collected in Portland, OR on 2/27/88.

slope is close to +1 (0.90) and the y-intercept (6.99) is close to a value of 7.43 that is predicted from equilibrium adsorption theory (eq 3.2). Plots of log A(TSP)/F vs. log p°_L and their corresponding regression equations for the target SOCs for all of the sampling events will be discussed in Section 6.1.2.

6.1.1. Calculation of Equilibrium Distribution Constants Using Values of A and F Corrected for Gas Adsorption to QFFs

As described in Section 4.2.2, gas adsorption to quartz fiber filters (QFFs) was found to be a significant positive sampling artifact for the particulate phase for all of the target n-alkanes with vapor pressures in the 10^{-3} - 10^{-5} torr range and some PAHs in a similar volatility range. It was concluded that the concentrations of gas phase components measured on a Teflon-quartz backup filter (TQB) (rather than a quartz-quartz backup filter (QQB)) provide the best estimates of the extent of gas adsorption on QFFs since: 1) there were no significant differences in the concentrations of the target compounds between the QQB and TQB filters for the most volatile compounds; and 2) the TQB filters had a significantly higher concentration of intermediate volatility target compounds. The determination of the gas and particulate phase concentrations is presented in Figure 6.2 for the quartz and Teflon sampling trains in both an uncorrected and corrected for gas adsorption form.

Figure 6.2. Schematic of the quartz and Teflon sampling trains along with equations to calculate the uncorrected and corrected, for gas adsorption to a quartz fiber filter, concentrations.

Quartz Sampling Train		**Teflon Sampling Train**	
QFF ———	F_1 = QQP	TMF ———	F_3 = TQP
QFF ———	F_2 = QQB	QFF ———	F_4 = TQB
PUFS ═══	A_1	PUFS ═══	A_3
PUFS ═══	A_2	PUFS ═══	A_4

Uncorrected Concentrations in the Gas and Particulate Phases

$F_{QU} = F_1$

$F_{TU} = F_3$

$A_{QU} = A_1 + A_2$

$A_{TU} = A_3 + A_4$

Corrected Concentrations in the Gas and Particulate Phases

$F_{QC} = F_1 - F_4$

$F_{TC} = F_3$

$A_{QC} = A_1 + A_2 + F_2 + F_4$

$A_{TC} = A_3 + A_4 + F_4$

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where F = measured particulate phase concentration; A = measured gas phase concentration; QFF = quartz fiber filter; TMF = Teflon membrane filter; PUFS = polyurethane foam sheet.

6.1.2. Equilibrium Distribution Constants for the Target n-Alkanes

Plots of log A(TSP)/F vs. log p°_{L} for the target n-alkanes are given in Figures 6.3 - 6.14. Four plots are presented for each sampling event, both uncorrected and corrected values of log A(TSP)/F for the quartz and Teflon sampling trains. For the plots which are "uncorrected" for gas adsorption to the QFFs, the error bar associated with each log A(TSP)/F value corresponds to a propagated error of ± 24%. For the "corrected" plots, the error bar associated with each log A(TSP)/F value corresponds to a propagated error of ± 34%.

The parameters from a least squares linear regression are presented in Table 6.1. Since estimates of the uncertainty were available for the values of log A(TSP)/F, a weighted regression was also completed for each of the plots (Table 6.1). Each of the log A(TSP)/F values were weighted by the inverse of the variance associated with that value (Davies and Goldsmith, 1984; Minitab, 1985). Since this approach takes the uncertainty of each log A(TSP)/F value into account, a better estimate of the relationship is available with the weighted parameters.

The parameters from a least squares linear regression are given in the top left hand corner of each plot and the regression line in the plots only extends over the range of data points which were used for the regression. In several of the plots, some of the data points for the more volatile compounds were excluded. The data points that were excluded from the regression equation will be examined in Section 6.2. The equations for the best fit line from a least squares and weighted

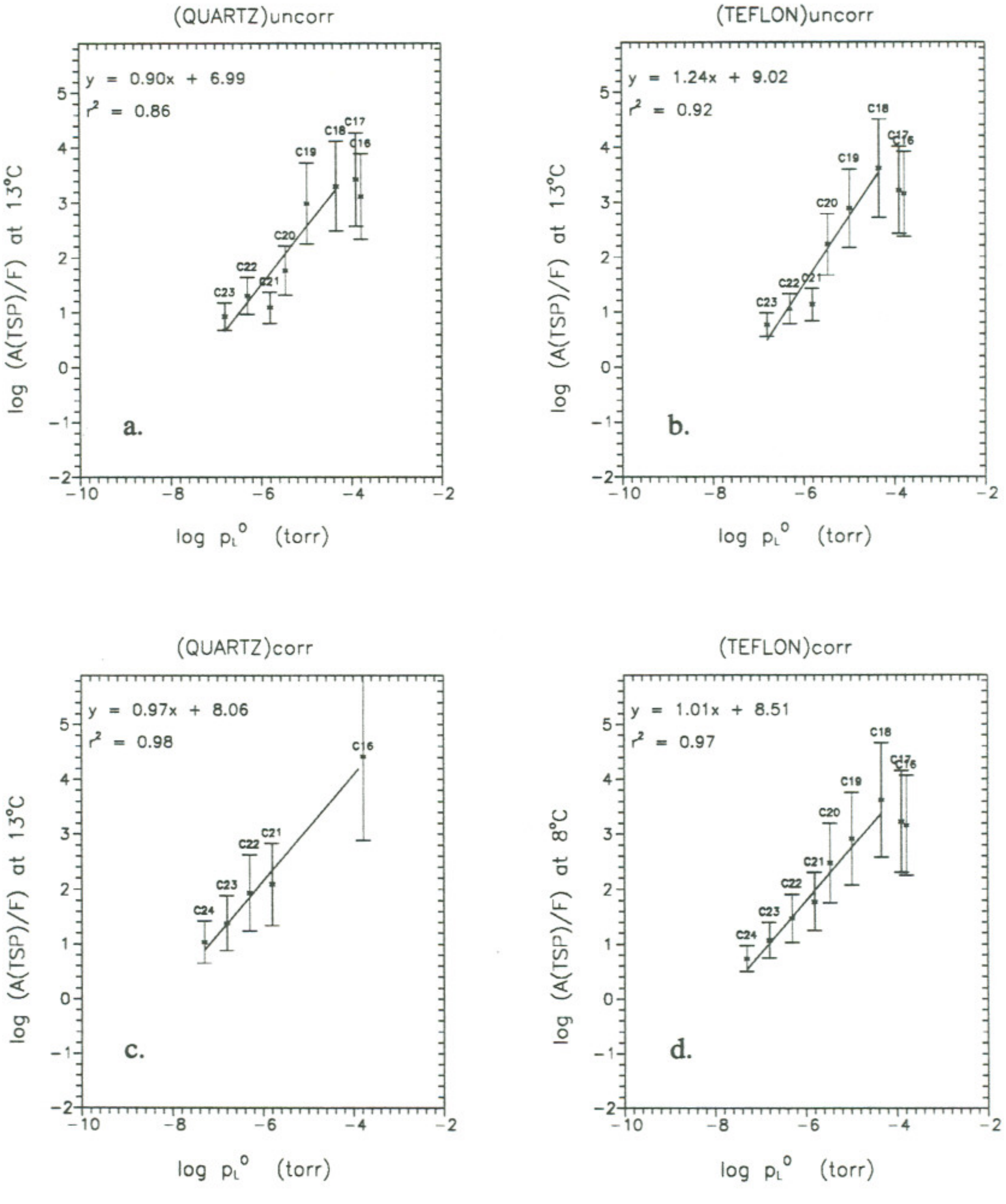

Figure 6.3. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 2/27/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

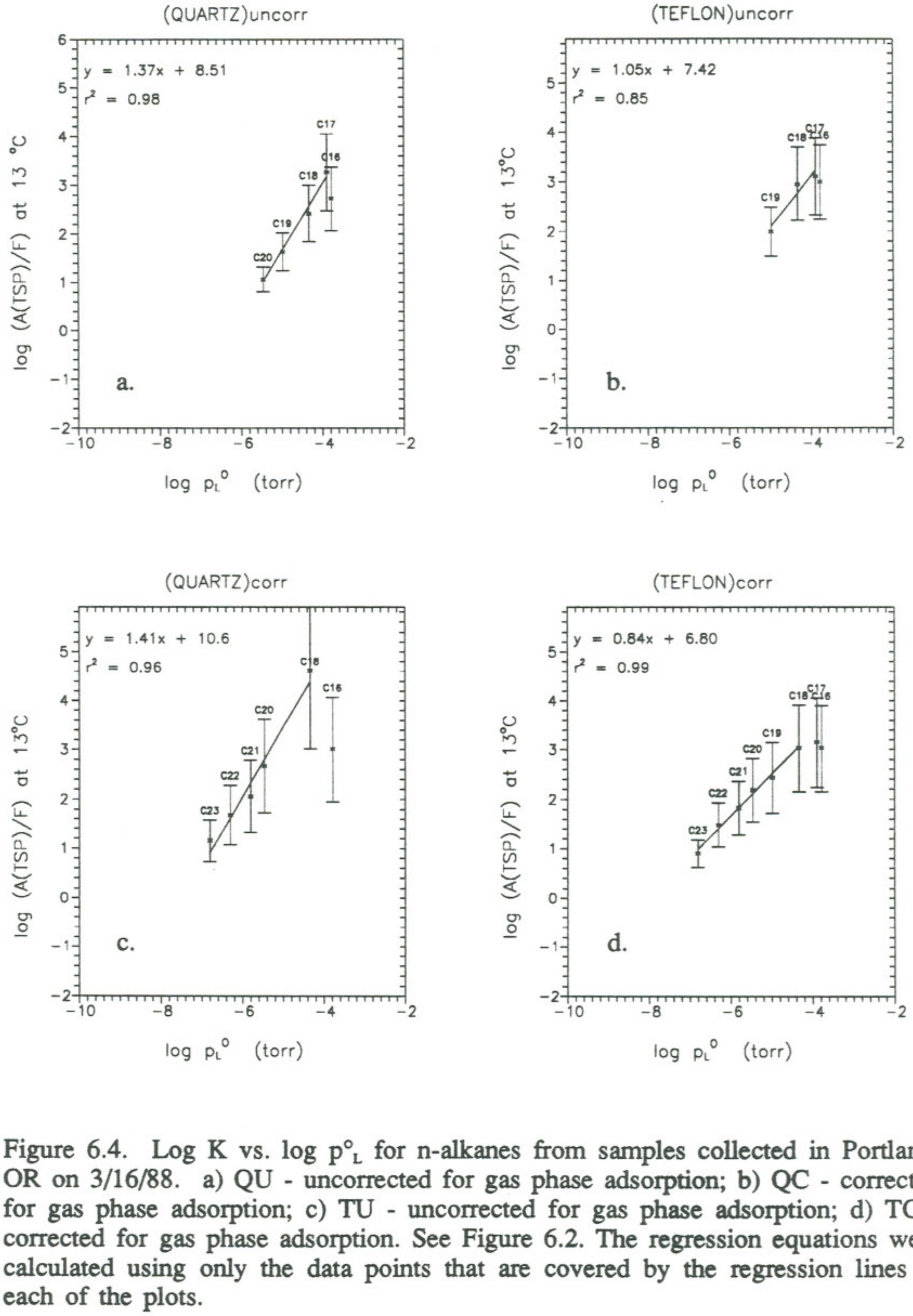

Figure 6.4. Log K vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 3/16/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

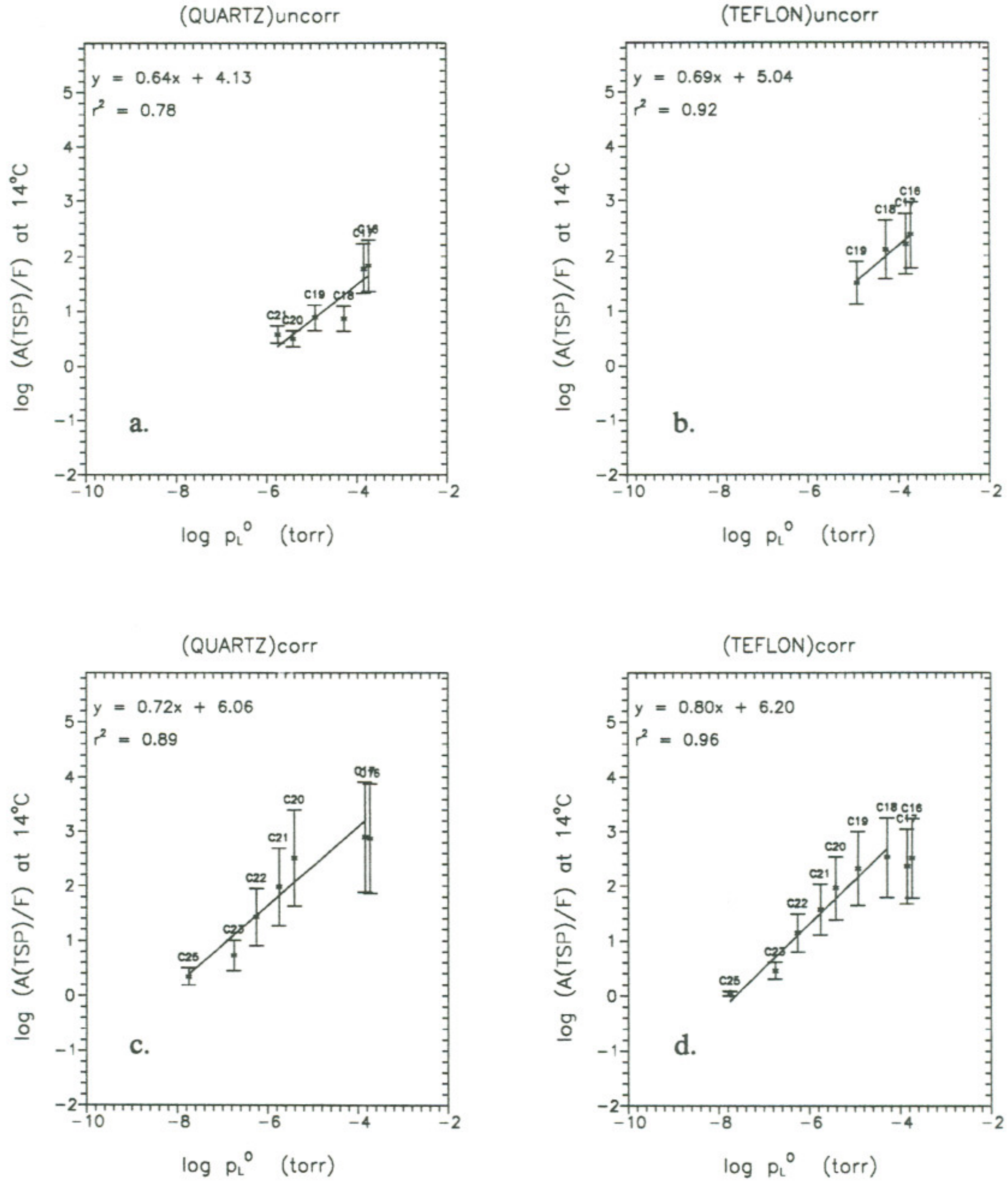

Figure 6.5. Log K vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 4/9/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

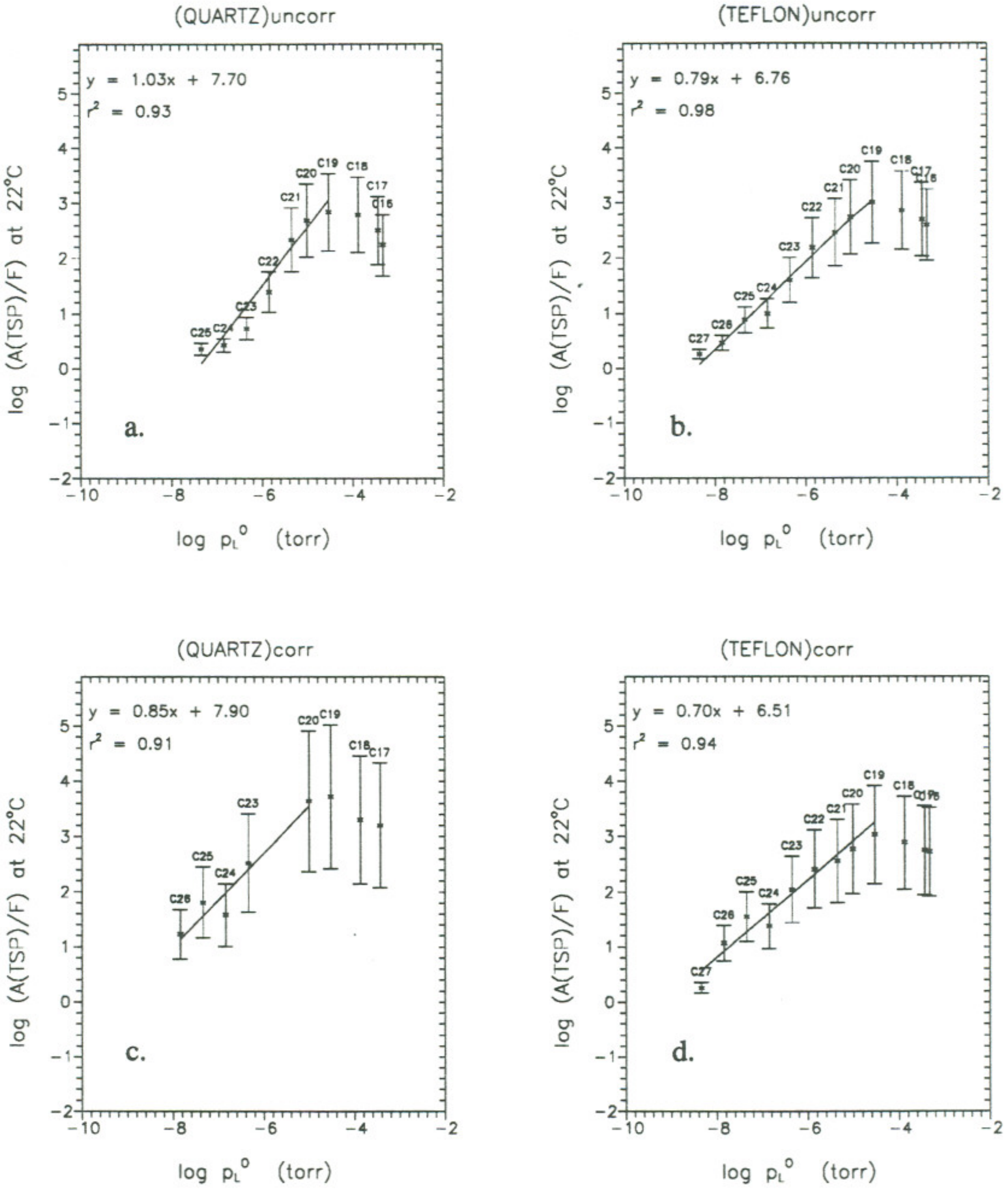

Figure 6.6. Log K vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 7/20/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

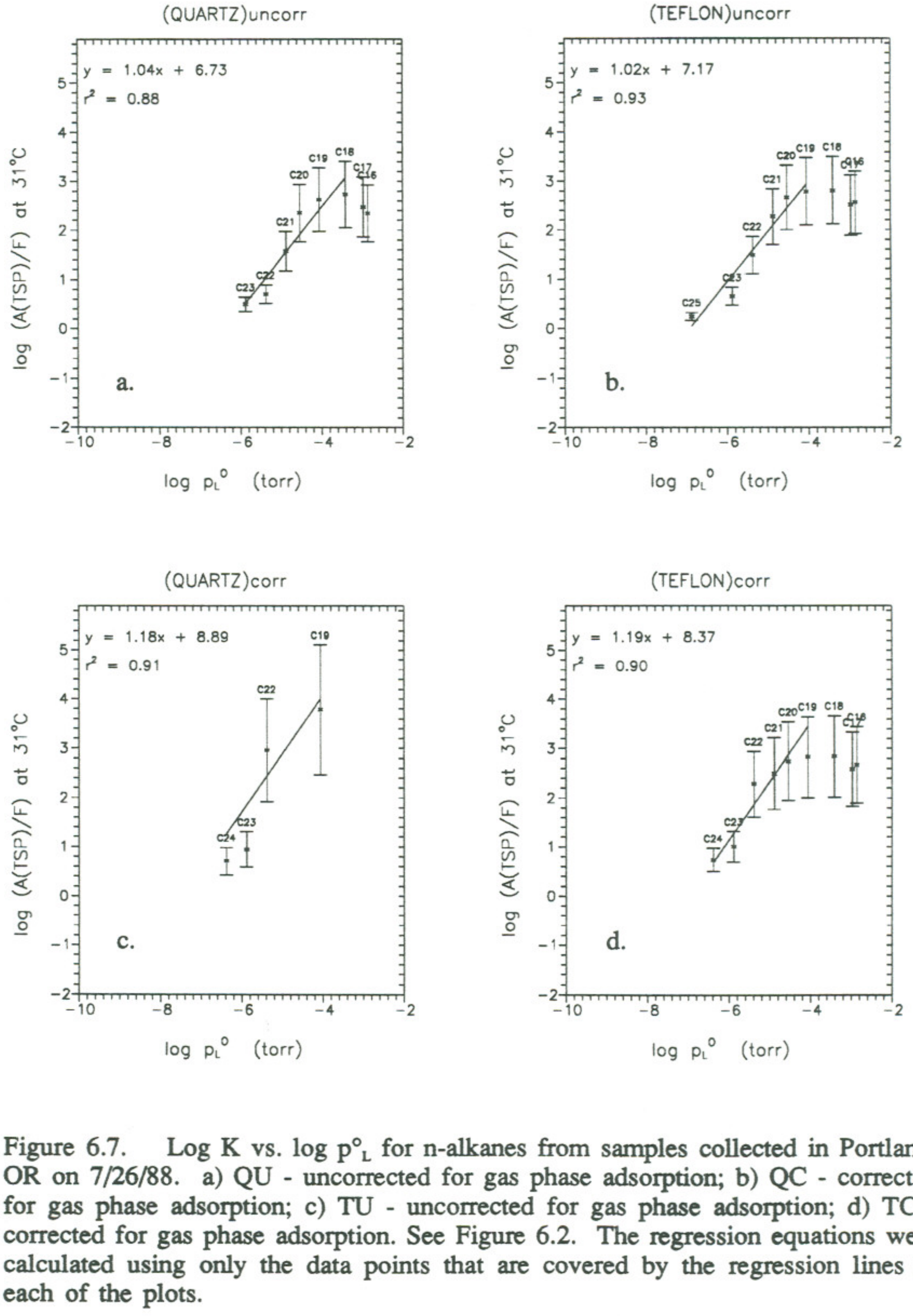

Figure 6.7. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 7/26/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

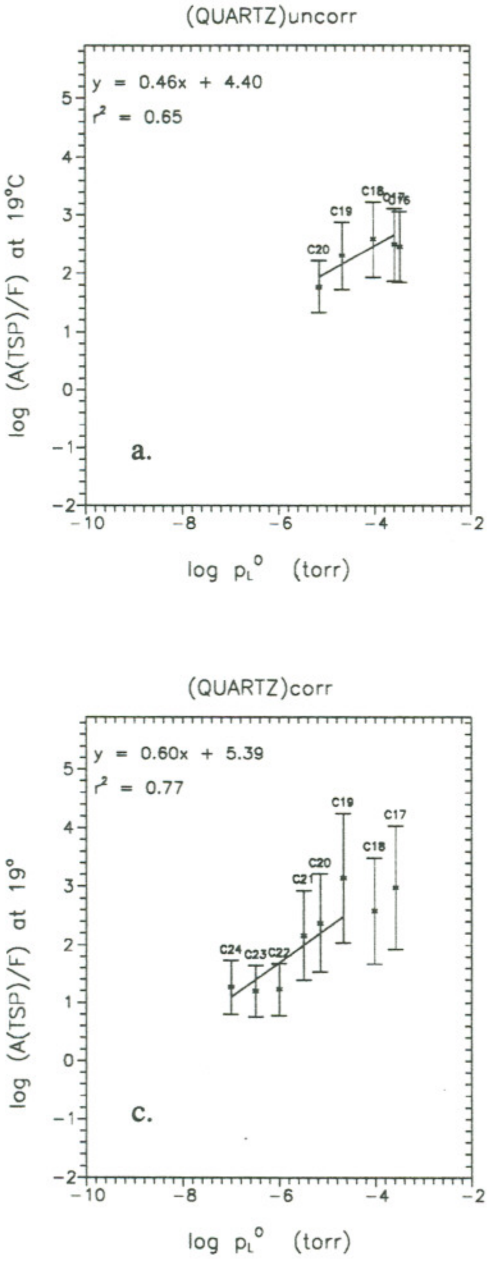

Figure 6.8. Log K vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 8/1/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2 The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

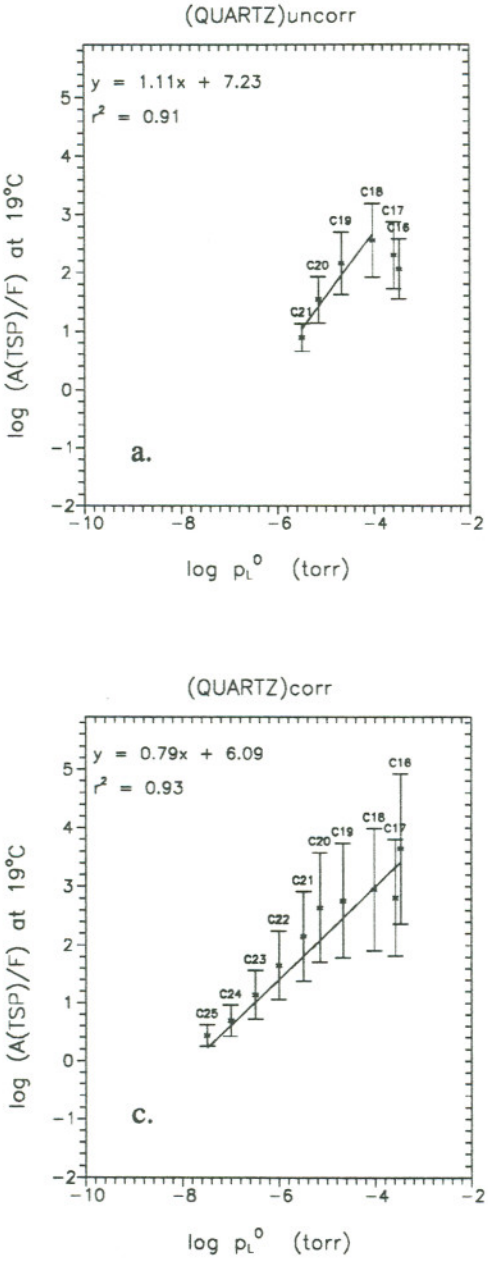

Figure 6.9. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 8/7/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

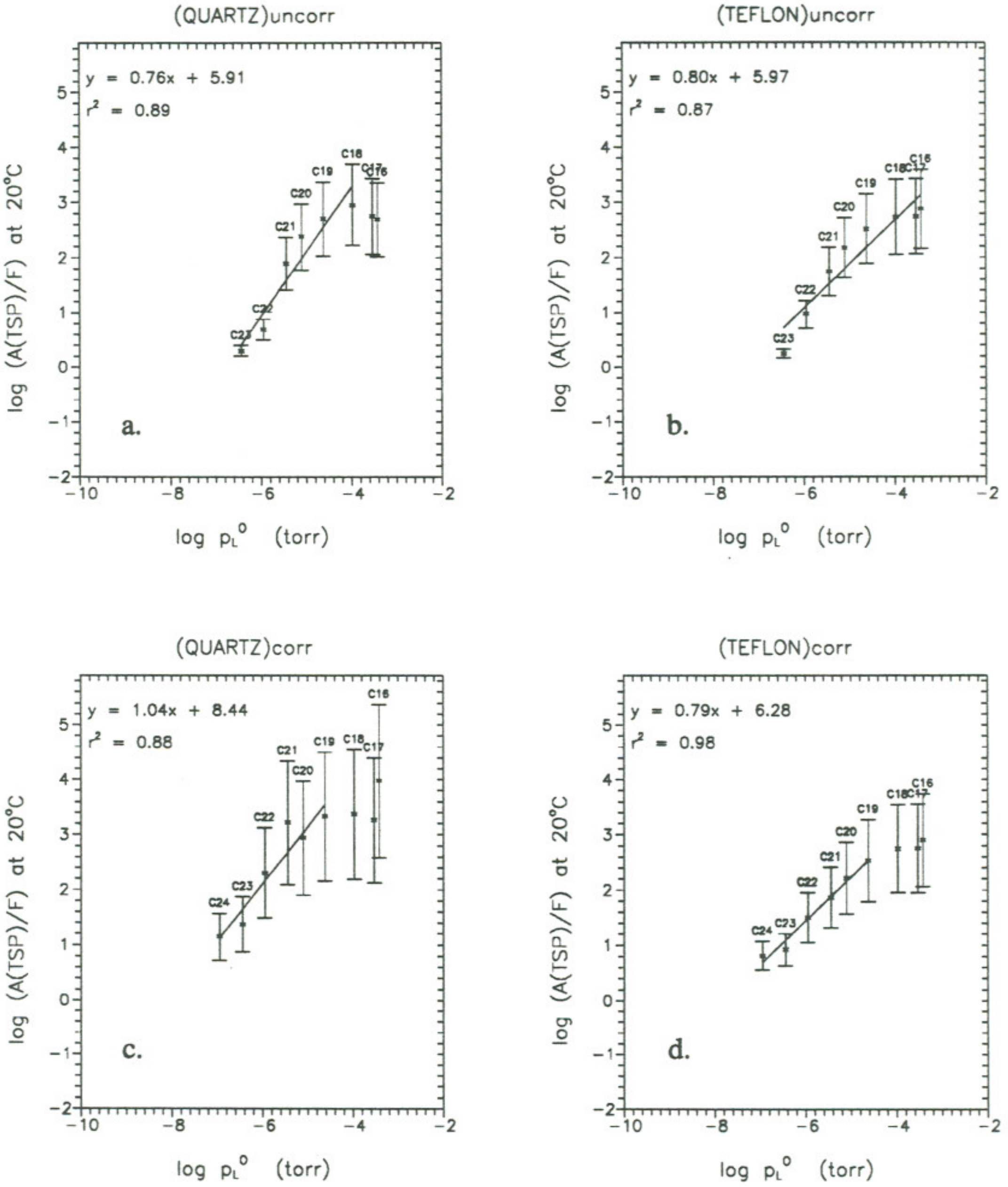

Figure 6.10. Log K vs. log p°_{L} for n-alkanes from samples collected in Portland, OR on 8/19/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

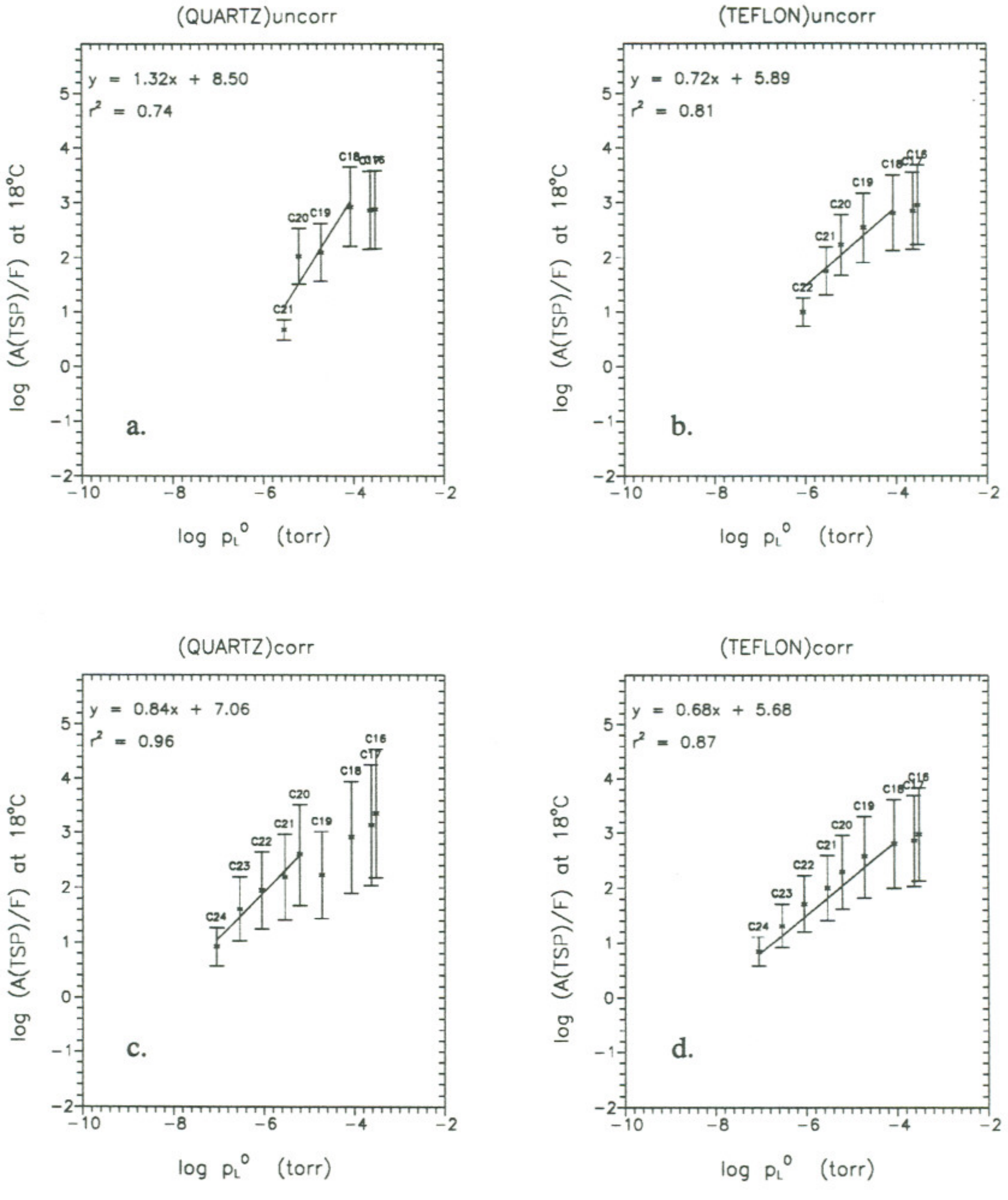

Figure 6.11. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 8/31/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

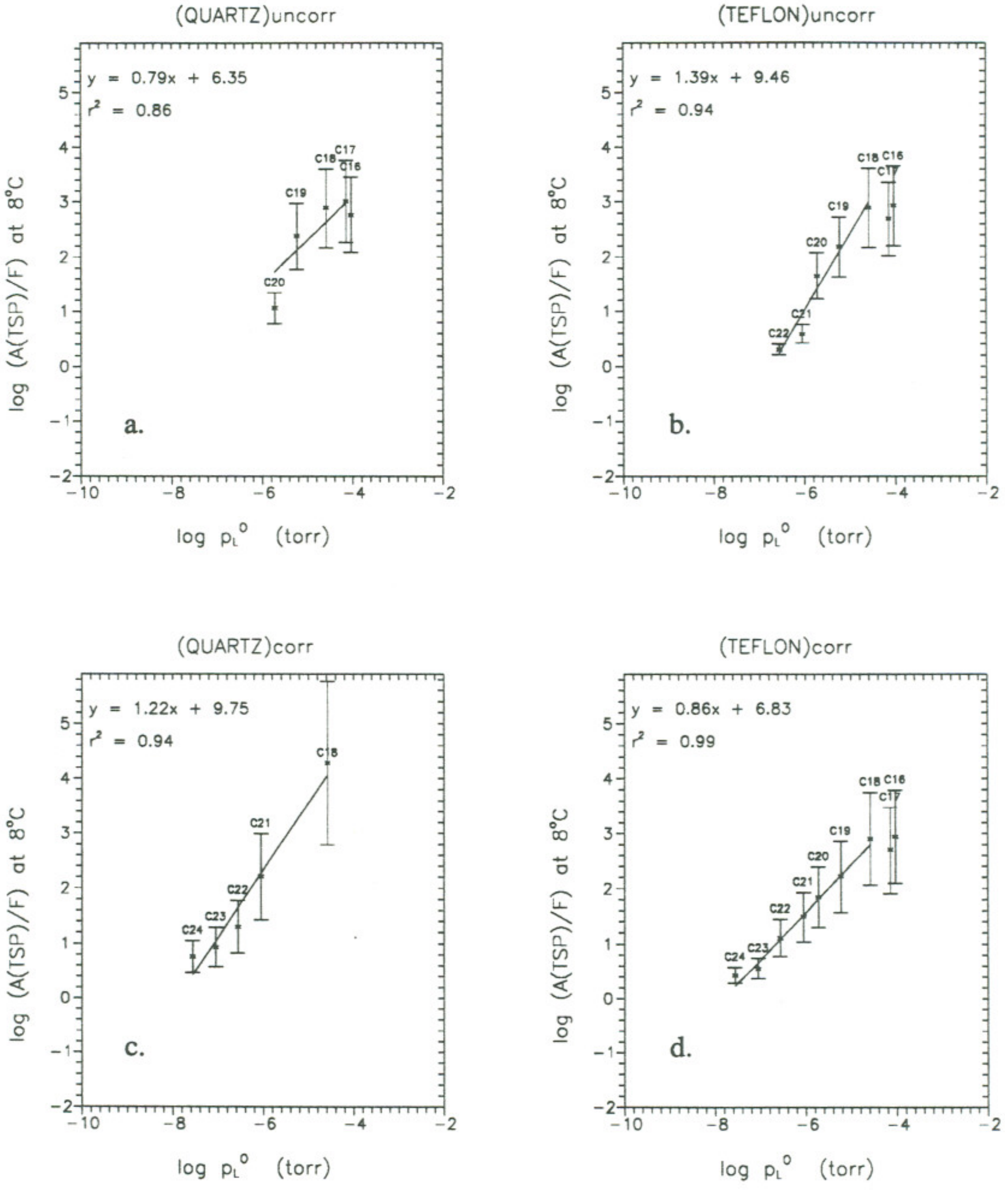

Figure 6.12. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 11/17/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

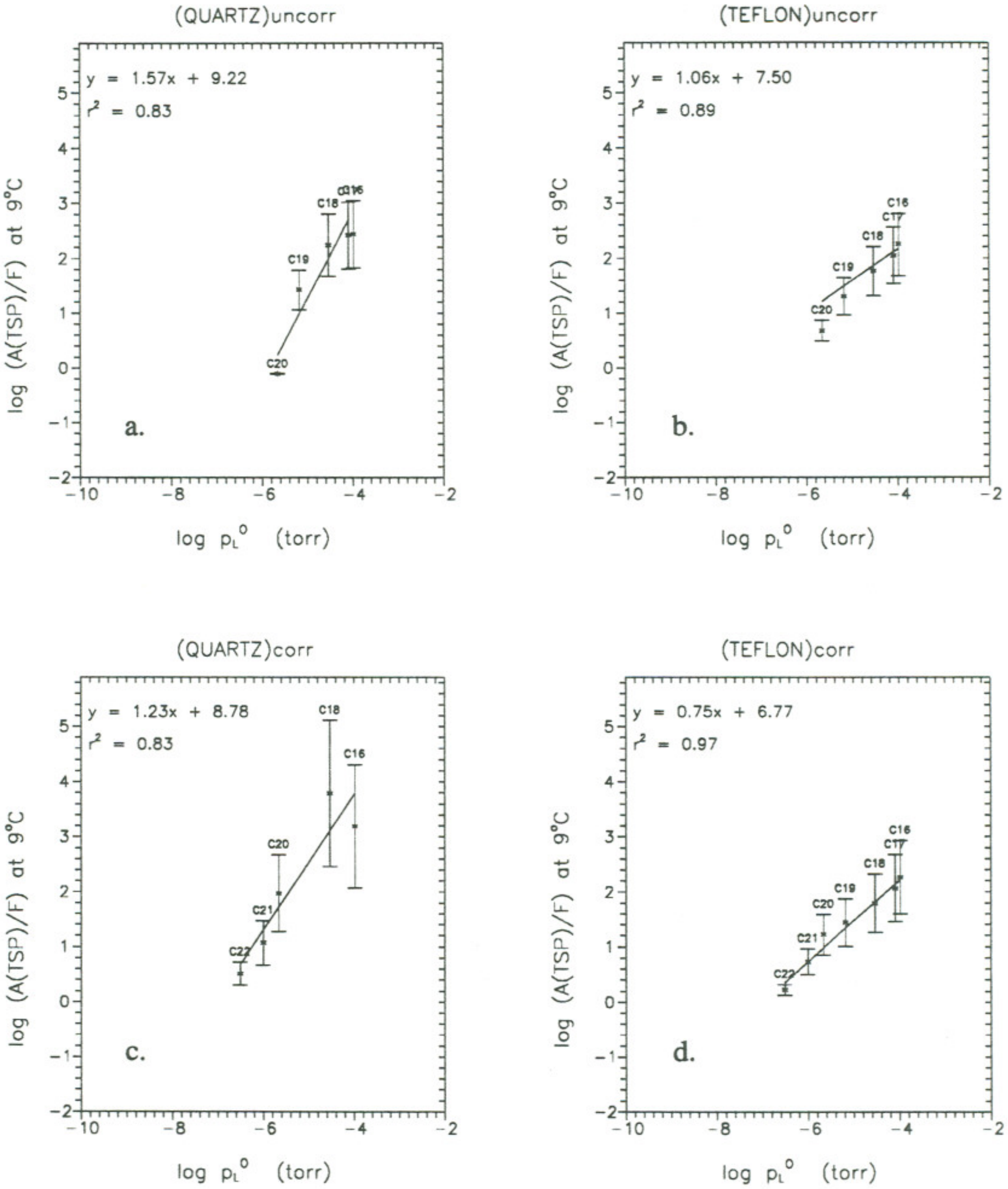

Figure 6.13. Log K vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 11/23/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

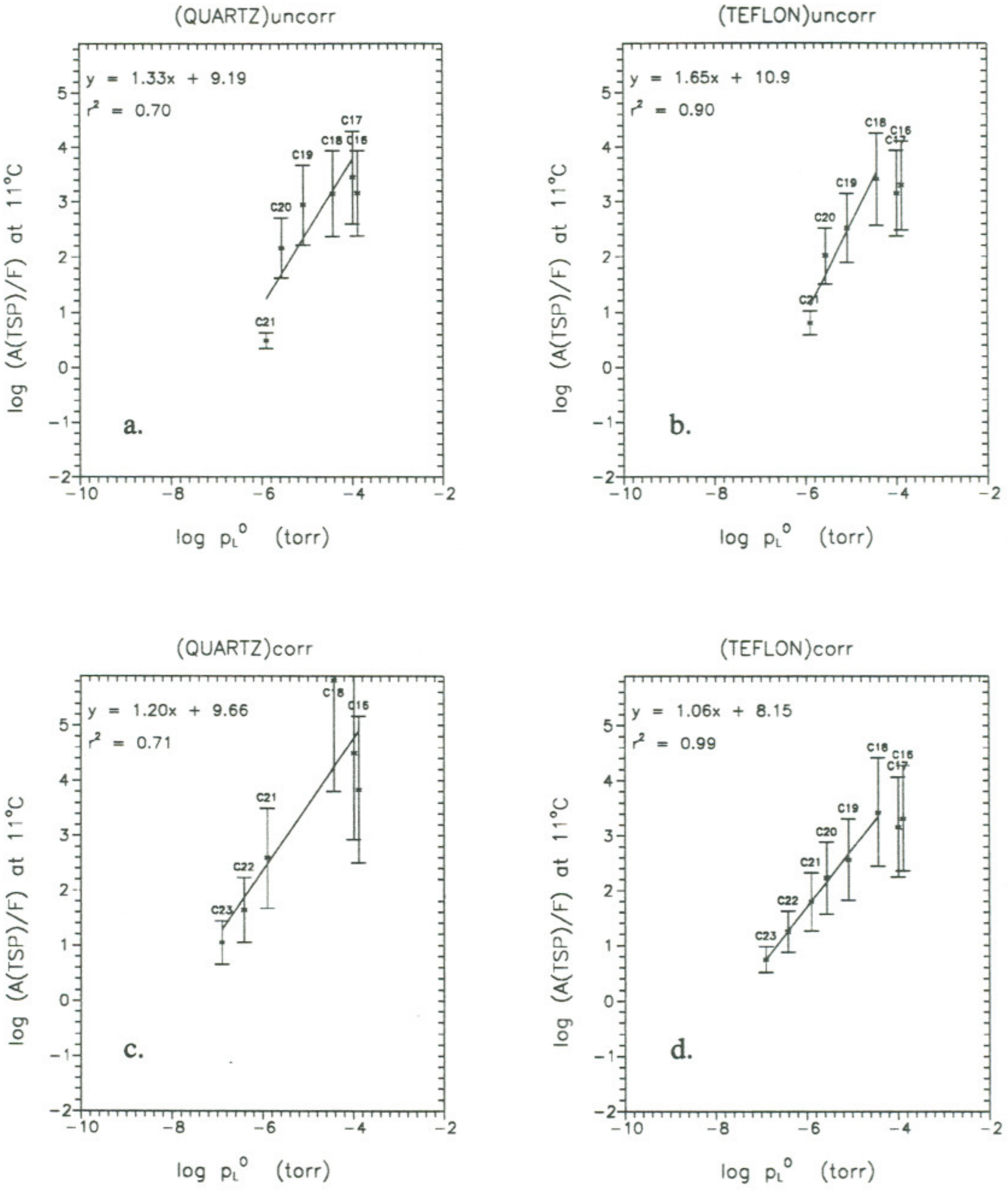

Figure 6.14. Log K vs. log p°_L for n-alkanes from samples collected in Portland, OR on 11/29/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

Table 6.1. Regression Equations for the n-Alkanes for log A(TSP)/F vs. log p°_L Plots (Figures 6.2 - 6.13) for the Full Data Set Collected in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

			Weighted	
Date/plot	m	b	m	b
2/27				
QU	0.90 ± 0.14	6.99 ± 0.72	0.79 ± 0.16	6.27 ± 0.95
QC	0.97 ± 0.07	8.06 ± 0.41	0.87 ± 0.08	7.47 ± 0.56
TU	0.94 ± 0.15	7.23 ± 0.77	0.89 ± 0.13	6.83 ± 0.83
TC	0.68 ± 0.11	6.31 ± 0.64	0.73 ± 0.08	6.53 ± 0.48
3/16				
QU	1.17 ± 0.19	7.49 ± 0.86	1.16 ± 0.12	7.41 ± 0.61
QC	0.88 ± 0.29	7.37 ± 1.60	0.82 ± 0.19	6.90 ± 1.15
TU	0.87 ± 0.25	6.59 ± 1.08	0.93 ± 0.21	6.81 ± 0.95
TC	0.72 ± 0.05	6.09 ± 0.27	0.79 ± 0.05	6.42 ± 0.29
4/9				
QU	0.64 ± 0.15	4.13 ± 0.70	0.47 ± 0.15	3.23 ± 0.78
QC	0.67 ± 0.09	5.68 ± 0.53	0.67 ± 0.08	5.62 ± 0.59
TU	0.69 ± 0.12	5.04 ± 0.49	0.71 ± 0.10	5.13 ± 0.49
TC	0.65 ± 0.07	5.29 ± 0.40	0.64 ± 0.05	5.13 ± 0.41
7/20				
QU	0.61 ± 0.13	5.12 ± 0.68	0.63 ± 0.09	5.02 ± 0.62
QC	0.52 ± 0.11	5.68 ± 0.65	0.56 ± 0.09	5.77 ± 0.64
TU	0.55 ± 0.07	5.11 ± 0.40	0.59 ± 0.04	5.28 ± 0.33
TC	0.47 ± 0.07	4.86 ± 0.40	0.64 ± 0.07	5.80 ± 0.52

Table 6.1 (cont'd.). Regression Equations for the n-Alkanes for log A(TSP)/F vs. log p°_L Plots (Figures 6.2 - 6.13) for the Full Data Set Collected in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

			Weighted	
Date/plot	m	b	m	b
7/26				
QU	0.68 ± 0.17	4.88 ± 0.73	0.80 ± 0.12	5.25 ± 0.70
QC	1.18 ± 0.21	8.89 ± 1.22	1.12 ± 0.27	8.43 ± 1.81
TU	0.62 ± 0.13	4.93 ± 0.61	0.69 ± 0.08	5.04 ± 0.53
TC	0.61 ± 0.12	5.00 ± 0.60	0.77 ± 0.08	5.67 ± 0.54
8/1				
QU	0.38 ± 0.14	4.01 ± 0.60	0.42 ± 0.13	4.17 ± 0.59
QC	0.57 ± 0.13	5.29 ± 0.69	0.62 ± 0.10	5.51 ± 0.58
TU	0.48 ± 0.16	4.20 ± 0.71	0.59 ± 0.16	4.68 ± 0.76
TC	0.50 ± 0.06	4.14 ± 0.31	0.54 ± 0.05	4.61 ± 0.28
8/7				
QU	0.58 ± 0.22	4.56 ± 0.96	0.71 ± 0.19	5.04 ± 0.93
QC	0.86 ± 0.07	6.49 ± 0.40	0.83 ± 0.06	6.31 ± 0.36
TU	0.43 ± 0.14	4.20 ± 0.62	0.49 ± 0.13	4.45 ± 0.63
TC	0.61 ± 0.07	5.08 ± 0.38	0.76 ± 0.05	5.86 ± 0.39
8/19				
QU	0.81 ± 0.17	6.03 ± 0.82	1.00 ± 0.12	6.82 ± 0.76
QC	0.69 ± 0.12	6.36 ± 0.62	0.80 ± 0.10	6.80 ± 0.62
TU	0.80 ± 0.12	5.97 ± 0.57	1.04 ± 0.10	7.09 ± 0.64
TC	0.62 ± 0.05	5.23 ± 0.27	0.66 ± 0.05	5.42 ± 0.31

Table 6.1 (cont'd.). Regression Equations for the n-Alkanes for log A(TSP)/F vs. log p°_{L} Plots (Figures 6.2 - 6.13) for the Full Data Set Collected in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

			Weighted	
Date/plot	m	b	m	b
8/31				
QU	0.93 ± 0.23	6.47 ± 1.05	1.24 ± 0.24	7.77 ± 1.28
QC	0.69 ± 0.07	5.88 ± 0.36	0.79 ± 0.07	6.35 ± 0.42
TU	0.62 ± 0.09	5.31 ± 0.46	0.68 ± 0.14	5.52 ± 0.76
TC	0.68 ± 0.09	5.68 ± 0.48	0.98 ± 0.11	7.18 ± 0.76
11/17				
QU	0.76 ± 0.10	6.15 ± 0.56	0.57 ± 0.10	4.76 ± 0.77
QC	1.22 ± 0.16	9.75 ± 1.01	0.87 ± 0.25	7.37 ± 1.38
TU	1.06 ± 0.15	7.50 ± 0.79	1.09 ± 0.15	7.53 ± 0.96
TC	0.75 ± 0.05	6.77 ± 0.28	0.74 ± 0.06	6.02 ± 0.91
11/23				
QU	1.42 ± 0.30	8.42 ± 1.41	1.81 ± 0.27	10.2 ± 1.55
QC	1.23 ± 0.27	8.77 ± 1.46	1.28 ± 0.19	8.96 ± 1.18
TU	0.57 ± 0.04	4.54 ± 0.23	0.59 ± 0.04	4.60 ± 0.23
TC	0.74 ± 0.06	5.27 ± 0.29	0.84 ± 0.06	5.78 ± 0.35
11/29				
QU	1.13 ± 0.34	8.10 ± 1.65	1.65 ± 0.34	10.4 ± 1.96
QC	1.20 ± 0.33	9.66 ± 1.79	1.18 ± 0.19	9.34 ± 1.25
TU	1.10 ± 0.24	7.89 ± 1.17	1.39 ± 0.25	9.21 ± 1.37
TC	0.86 ± 0.08	6.95 ± 0.41	0.93 ± 0.06	7.33 ± 0.35

least squares approach for each sampling event when some of the more volatile data points were excluded are given in Table 6.2. The specific compounds that were excluded in the above regression equations are also included in Table 6.2.

In many cases, for compounds in the C16 - C20 range (10^{-3} - 10^{-5} torr), the particulate phase concentration that was measured on the primary QFF was actually gas adsorbed onto the filter. As a result of the gas adsorption correction on the QFFS, the QU plots typically had more data points in the C16 - C20 range than the QC plots. Conversely, the QC plots generally had one or two more compounds in the C22 - C24 range (10^{-6} - 10^{-8} torr), due to the addition of the gaseous phase compounds adsorbed onto the backup quartz filter to the compounds collected on the PUFSs. However, even with the addition of one or two compounds in the C22 - C24 range, the QU plots typically had more total data points than the QC plots.

In contrast to the situation observed with the quartz data, the TU plots always had fewer data points than the TC plots. As with the QC plots, this difference was a result of the addition of the gaseous phase compounds adsorbed onto the TQB filter to the compounds collected on the PUFSs.

The number of data points available for each plot was also a function of temperature. For example, at 19°C (8/7/88) the least volatile compound found on any of the plots was C25, while at 9°C (11/23/88) the least volatile compound found was C22. As the temperature decreases, a compound's vapor pressure and subsequent concentration in the gas phase also decreases. This causes a

Table 6.2. Regression Equations for the n-Alkanes for log A(TSP)/F vs. log p°_{L} Plots (Figures 6.2 - 6.13) with Data Points Excluded Collected in Portland OR, 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

Date/ Plot	Compounds Excluded[a]	m	b	Weighted m	Weighted b
2/27					
QU	16,17	1.05 ± 0.21	7.50 ± 1.20	0.75 ± 0.25	5.97 ± 1.58
QC		na	na	na	na
TU	16,17	1.24 ± 0.17	9.02 ± 0.94	0.94 ± 0.23	7.15 ± 1.42
TC	16,17	1.01 ± 0.08	8.51 ± 0.49	0.88 ± 0.07	7.64 ± 0.49
3/16					
QU	16	1.37 ± 0.10	8.51 ± 0.51	1.31 ± 0.08	8.19 ± 0.43
QC	16	1.41 ± 0.16	10.6 ± 0.80	1.20 ± 0.14	9.34 ± 0.91
TU	16	1.05 ± 0.15	7.42 ± 1.33	1.10 ± 0.26	7.62 ± 1.20
TC	16,17	0.84 ± 0.05	6.80 ± 0.20	0.88 ± 0.04	7.03 ± 0.26
4/9					
QU		na	na	na	na
QC	16	0.72 ± 0.11	6.06 ± 1.69	0.68 ± 0.10	5.71 ± 0.75
TU		na	na	na	na
TC	16,17	0.80 ± 0.06	6.20 ± 0.38	0.66 ± 0.08	5.28 ± 0.58
7/20					
QU	16,17,18	1.03 ± 0.11	7.70 ± 0.67	0.74 ± 0.16	5.77 ± 1.10
QC	17,18,19	0.85 ± 0.13	7.90 ± 0.89	0.76 ± 0.18	7.24 ± 1.34
TU	16,17,18	0.79 ± 0.05	6.76 ± 0.32	0.66 ± 0.06	5.86 ± 0.45
TC	16,17,18	0.70 ± 0.06	6.51 ± 0.46	0.84 ± 0.08	7.38 ± 0.65

Table 6.2 (cont'd.). Regression Equations for the n-Alkanes for log A(TSP)/F vs. log p°_{L} Plots (Figures 6.2 - 6.13) with Data Points Excluded Collected in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

Date/ Plot	Compounds Excluded[a]	m	b	Weighted m	Weighted b
7/26					
QU	16,17	1.04 ± 0.17	6.73 ± 0.83	1.03 ± 0.17	6.56 ± 0.93
QC		na	na	na	na
TU	16,17,18	1.02 ± 0.13	7.17 ± 0.67	0.78 ± 0.14	5.63 ± 0.94
TC	16,17,18	1.15 ± 0.13	8.16 ± 0.74	1.03 ± 0.11	7.42 ± 0.72
8/1					
QU	16	0.46 ± 0.18	4.40 ± 0.79	0.51 ± 0.17	4.57 ± 0.78
QC	17,18	0.98 ± 0.09	7.69 ± 0.51	0.93 ± 0.07	7.36 ± 0.43
TU	16,17	0.77 ± 0.27	5.74 ± 1.32	0.91 ± 0.28	6.39 ± 1.41
TC	16,17	0.76 ± 0.07	5.96 ± 0.41	0.76 ± 0.10	5.72 ± 0.57
8/7					
QU	16,17	1.11 ± 0.20	7.23 ± 0.96	1.25 ± 0.20	7.92 ± 1.07
QC		na	na	na	na
TU	16,17	0.76 ± 0.16	5.91 ± 0.74	0.84 ± 0.17	6.25 ± 0.84
TC	16,17	0.77 ± 0.05	6.05 ± 0.30	0.86 ± 0.04	6.61 ± 0.31
8/19					
QU	16,17	1.17 ± 0.18	8.05 ± 0.94	1.23 ± 0.15	8.27 ± 1.10
QC	16,17,18	1.04 ± 0.17	8.44 ± 0.99	1.05 ± 0.15	8.48 ± 1.34
TU		na	na	na	na
TC	16,17,18	0.79 ± 0.06	6.28 ± 0.33	0.75 ± 0.09	6.01 ± 0.56

Table 6.2 (cont'd.). Regression Equations for the n-Alkanes for log A(TSP)/F vs. $\log p^\circ_L$ Plots (Figures 6.2 - 6.13) with Data Points Excluded Collected in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

Date/ Plot	Compounds Excluded[a]	m	b	Weighted m	Weighted b
8/31					
QU	16,17	1.32 ± 0.17	8.50 ± 2.12	1.68 ± 0.46	10.2 ± 2.48
QC		na	na	na	na
TU	16,17,18	0.72 ± 0.13	5.89 ± 0.82	0.74 ± 0.24	5.89 ± 0.38
TC		na	na	na	na
11/17					
QU	16	0.79 ± 0.15	6.35 ± 0.98	0.51 ± 0.14	4.27 ± 1.06
QC		na	na	na	na
TU	16,17	1.39 ± 0.18	9.46 ± 1.00	1.16 ± 0.28	7.98 ± 1.73
TC	16,17	0.86 ± 0.04	6.83 ± 0.27	0.76 ± 0.10	6.17 ± 0.61
11/29					
QU	16	1.33 ± 0.41	9.19 ± 2.08	1.89 ± 0.44	11.8 ± 2.56
QC	16	1.98 ± 0.14	14.6 ± 0.83	1.72 ± 0.22	12.9 ± 1.43
TU	16,17	1.65 ± 0.31	10.9 ± 1.61	1.96 ± 0.37	12.5 ± 2.12
TC	16,17	1.06 ± 0.05	8.15 ± 0.22	1.06 ± 0.03	8.16 ± 0.20

a) n-ALkanes excluded from the regression equation. C16 = 16, C17 = 17, and C18 = 18.

fundamental change in the gas/particle distribution. For a given compound, as the temperature decreases, the ratio of the concentrations in the gas and particulate phases will decrease. Thus, for C25, going from 18 down to 9°C was enough to lower the gas phase concentration below the method quantitation limit.

In looking more closely at the results from the regression analyses, a number of points can now be made. Firstly, without excluding any data values, the average of r^2 for all of the sampling events increased from 0.74 to 0.84 for QU to QC and 0.82 to 0.90 for TU to TC. Thus, not only were there more compounds in each of the TC plots, but the log A(TSP)/F values were much better predicted by the regression equations in the TC data than in the other three plots.

A similar trend was also found in the case when a few of the more volatile compounds were excluded from the data set. Upon the removal of these one or two outlying points from each plot, the average values of r^2 were much higher, 0.84 and 0.97 for QU and TC, respectively. The values of r^2 were not only consistently higher, but they were also much more consistent within each filter group. For example, the coefficient of variation (CV) for the average values of r^2 decreased from ~17% to ~11% for the QU plots and from ~9% to ~2% for the TC plots, going from the complete data set to the data set in which the some of the points were excluded, respectively. Thus, not only did the correlateability increase when the points were excluded, but the precision associated with the average fit for all events also increased.

As mentioned in the previous section, if the quantity $N_s e^{(Q1 - Qv)/RT}$ is constant from compound to compound, a slope of +1 is expected from a log A(TSP)/F vs. log p°_L plot at a given temperature . The average slopes (± 1s), for all of the events sampled without excluding any data points were 0.83 ± 0.29, 0.89 ± 0.27, 0.82 ± 0.07, and 0.75 ± 0.13, for the QU, QC, TU, and TC plots, respectively. When examining the QU, QC, and TU plots for individual sampling events, the results from both regression analyses (unweighted and weighted) indicate that in ~50% of the events sampled, the slope was not significantly different from +1 at the 95% confidence level. In ~25% of the events, the slope associated with TC plots was not significantly different than +1. A factor in the lower number of slopes that were not significantly different from +1 in the TC plots, relative to the other three, was the much higher precision associated with the slopes.

The y-intercept (log C) was also compared to what would be expected from the equilibrium adsorption theory discussed in Section 3.2. The value of log C is strongly dependent on the quantity $N_s e^{(Q_1 - Q_v)/RT}$. Since N_s may be expected to be relatively constant from compound to compound (Pankow, 1988), and $(Q_1 - Q_v)$ is ~3 kcal/mol (Bidleman et. al., 1986; Pankow, 1988; Ligocki and Pankow, 1989) for the target n-alkanes and PAHs, estimates of the value of log C can be predicted as a function of sampling temperature. The predicted values of log C averaged 7.46 and ranged from 7.43 - 7.51 for the events sampled. The average values obtained from the log A(TSP)/F vs log p°_L plots for all of the data points were 5.67 ± 1.78 and 7.93 ± 1.56 for the QC and TC plots, respectively. When the predicted values of log C were compared to those obtained on specific sampling dates, no significant difference (P = 0.05) was observed in any of the cases.

Analyses of the slopes of the data sets when some of the data points were excluded show much closer fits to the predicted value of +1. The average slopes for the data sets with excluded certain data points were 1.17 ± 0.32, 1.20 ± 0.37, 1.01 ± 0.39, and 0.87 ± 0.13 for the QU, QC, TU, and TC plots, respectively. For the QU, QC, and TU plots, the slopes were not significantly different from +1 in >90% of the sampling events at the 95% confidence level. The typically lower level of precision associated with QU slopes was a major factor in the QU slopes not being significantly different from +1. For the TC plots, in ~60% of the sampling events the slope was not significantly different from +1.

The number of events in which there were no significant differences between the predicted and observed slopes was somewhat lower for the TC plots than for the other three types of plots. Therefore, some gas adsorption to TMFs cannot be ruled out. If there was a small amount of gas adsorption for compounds in the ~C16 - C20 range to the TMFs, the concentrations measured with TMFs and PUFSs would be higher and lower, respectively, than what is actually present in the atmosphere. This would result in artificially low values of log A(TSP)/F. This would also cause the slope to be artificially low.

The y-intercepts (log C) for the data in which a few of the data points were excluded were compared to the values predicted from equilibrium adsorption theory. As was the case when all of the data was examined, there were no significant (P = 0.05) differences in the values of log C obtained from experimental data for all of the events for the n-alkanes and those predicted from equilibrium adsorption theory.

6.1.3. Equilibrium Distribution Constants for the Target PAHs

Plots of log A(TSP)/F vs. log p°_L for the target PAHs are given in Figures 6.15 - 6.22. The format of the plots is the same as in Section 6.1.2. However, in contrast to the n-alkanes, no data points were excluded in the regression equations for any of the plots. The concentrations measured for the target PAHs were much lower than the n-alkanes. For most of the PAHs, both gas and particulate phase concentrations were often not available as the concentration in one of the phases was below the method quantitation limit. Since there were rarely more than four data points per graph, it was usually difficult to determine what the actual slope from the data was, let alone if one data point differed from that of another.

Since the extent of gas adsorption to backup QFFs was very small for the target PAHs, when observed at all, there was very little difference between the four types of plots. The average value of r^2 was >93% in all four types of plots and was very consistent within each type of plot over the range of events sampled. For example, the highest CV associated with the average value of the correlation coefficient was only ~7% for the QC plots.

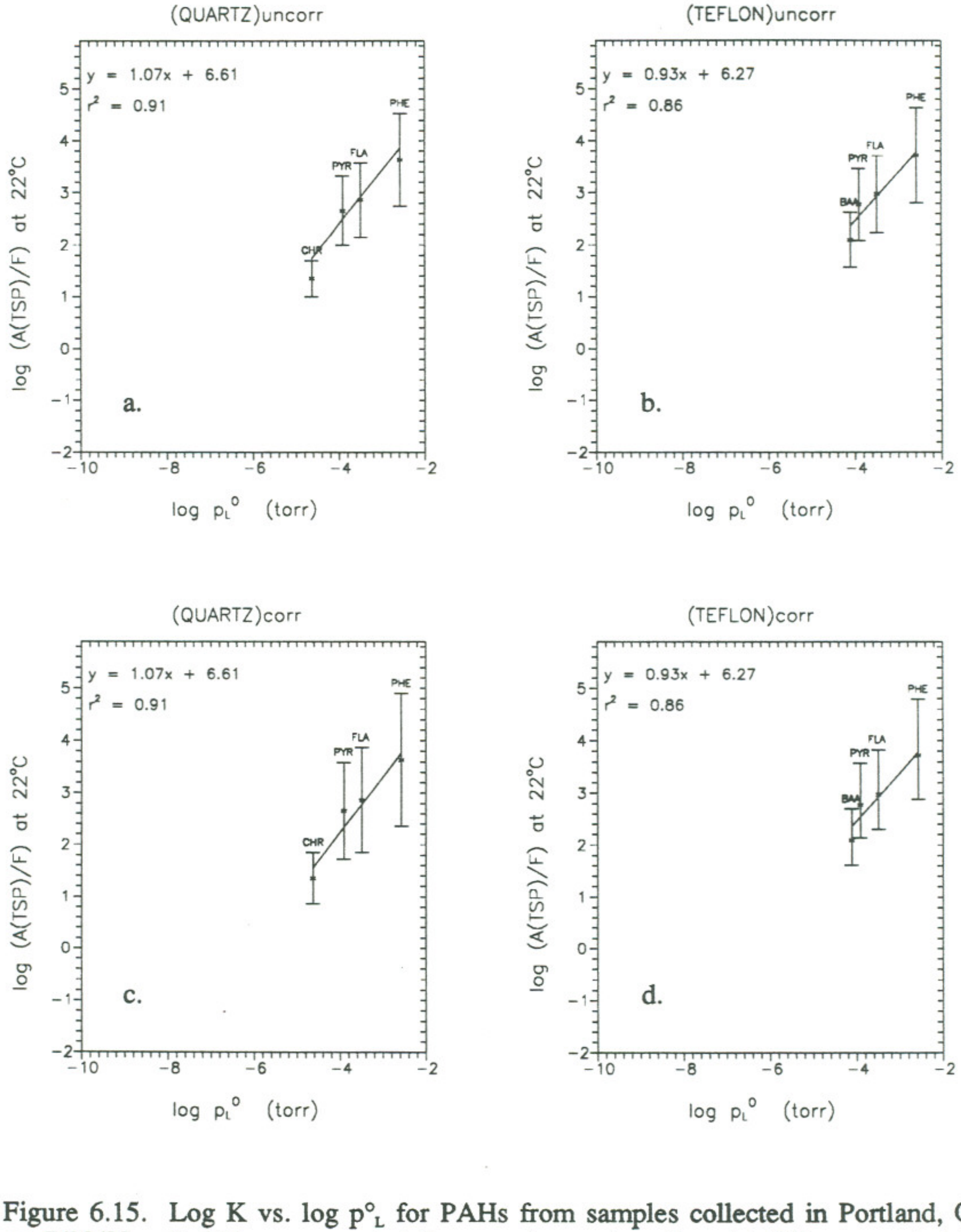

Figure 6.15. Log K vs. log p°_{L} for PAHs from samples collected in Portland, OR on 7/20/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

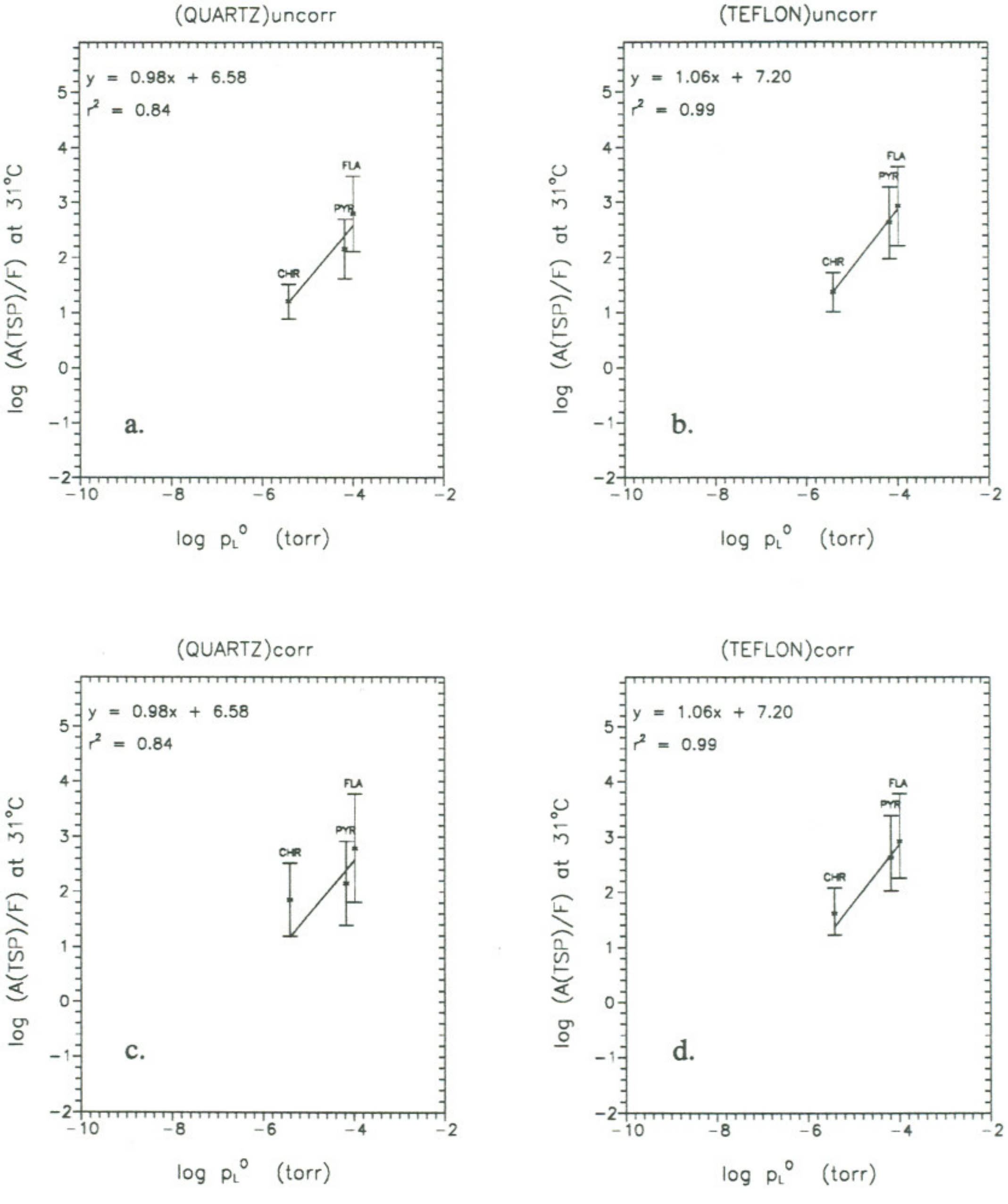

Figure 6.16. Log K vs. log p°_L for PAHs from samples collected in Portland, OR on 7/26/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

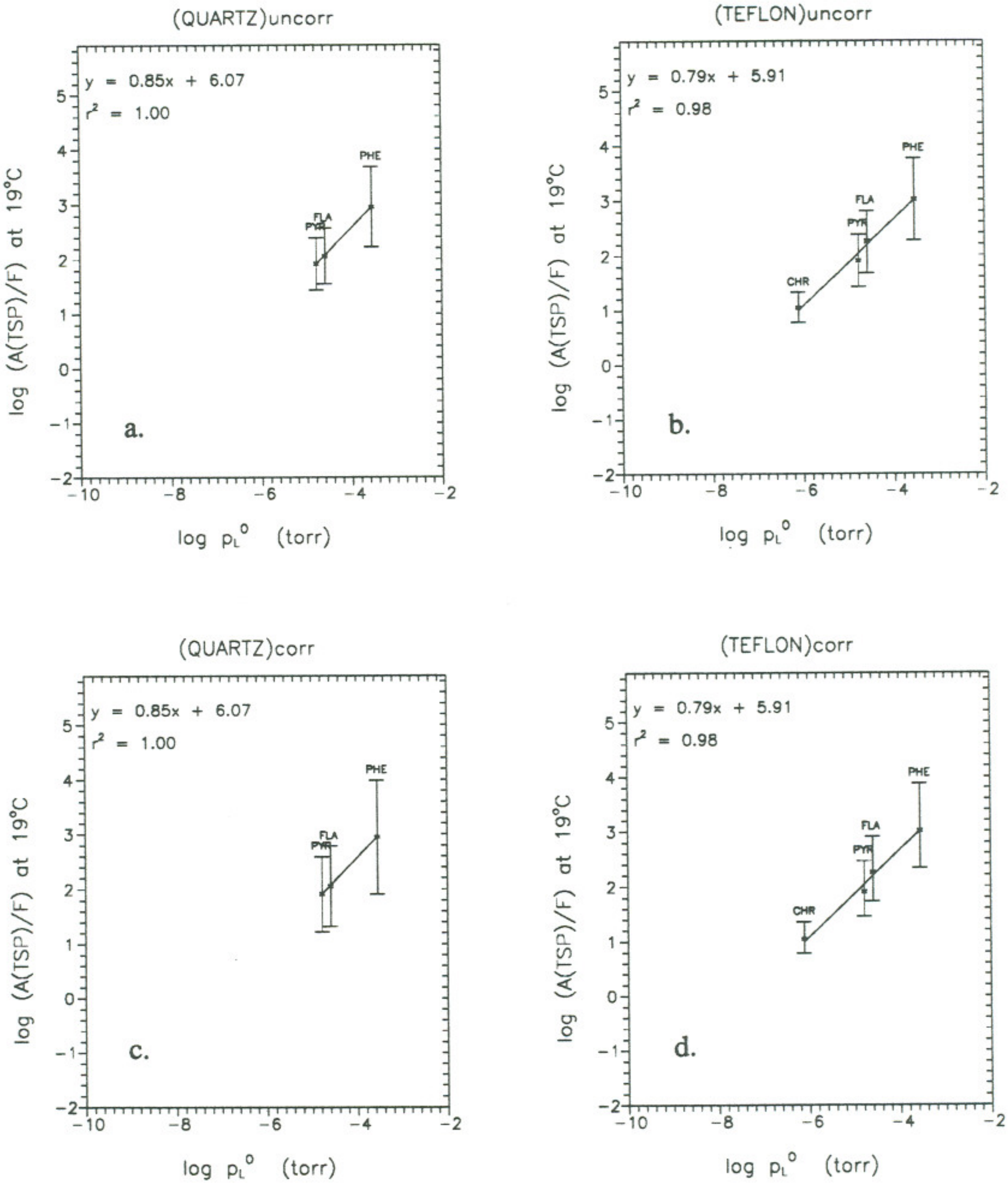

Figure 6.17. Log K vs. log p°_{L} for PAHs from samples collected in Portland, OR on 8/7/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

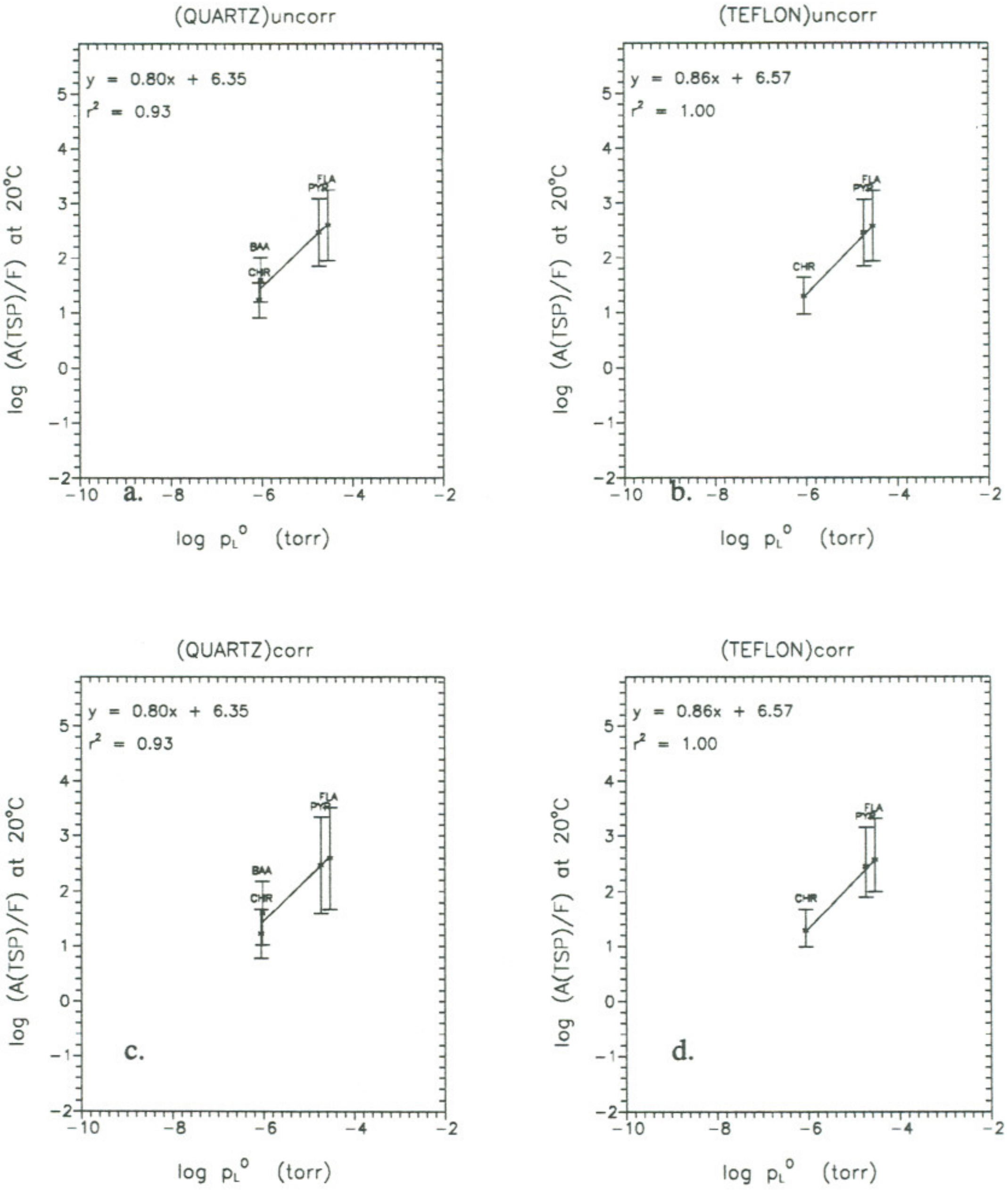

Figure 6.18. Log K vs. log p°_L for PAHs from samples collected in Portland, OR on 8/19/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

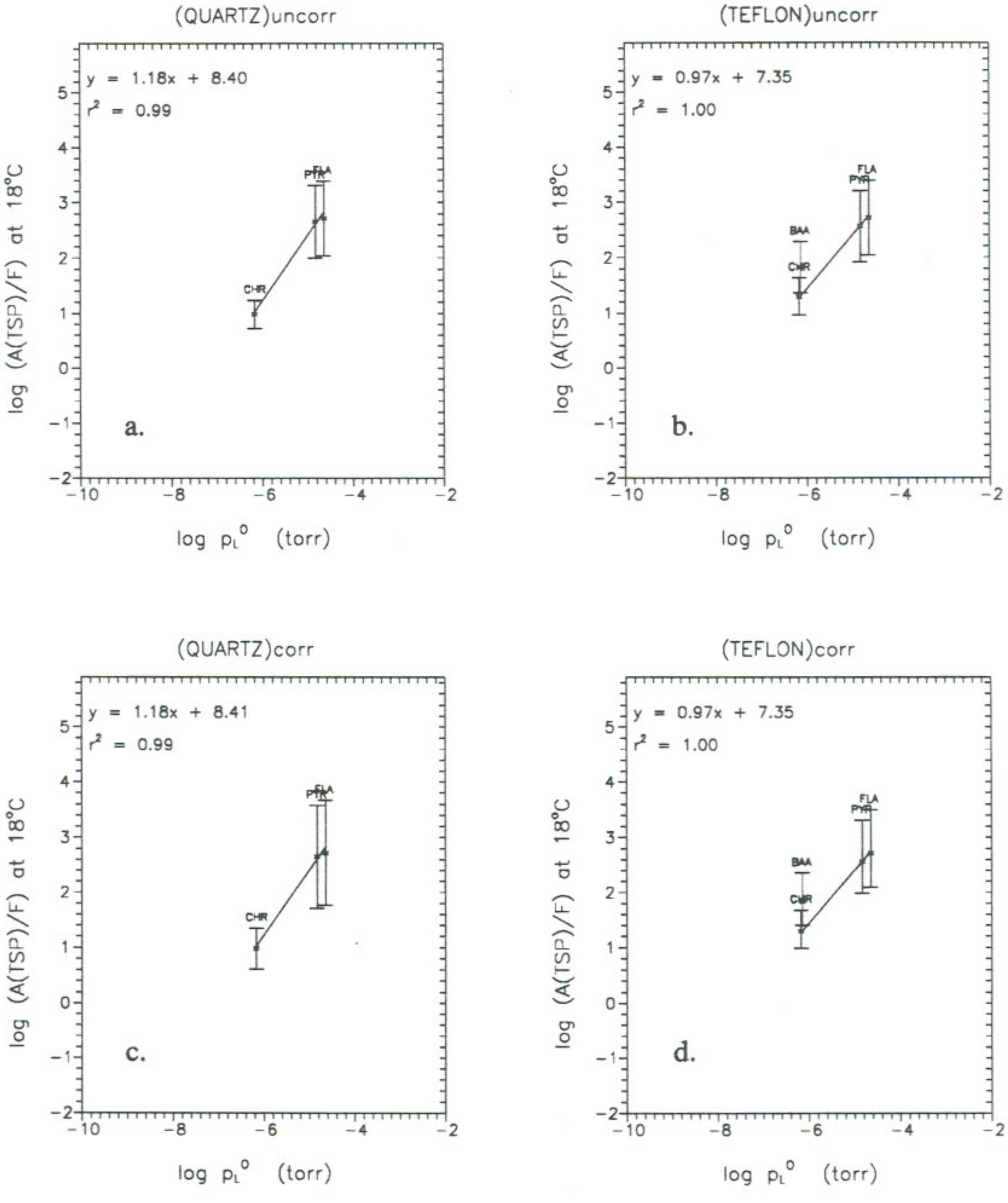

Figure 6.19. Log K vs. log p°$_L$ for PAHs from samples collected in Portland, OR on 8/31/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

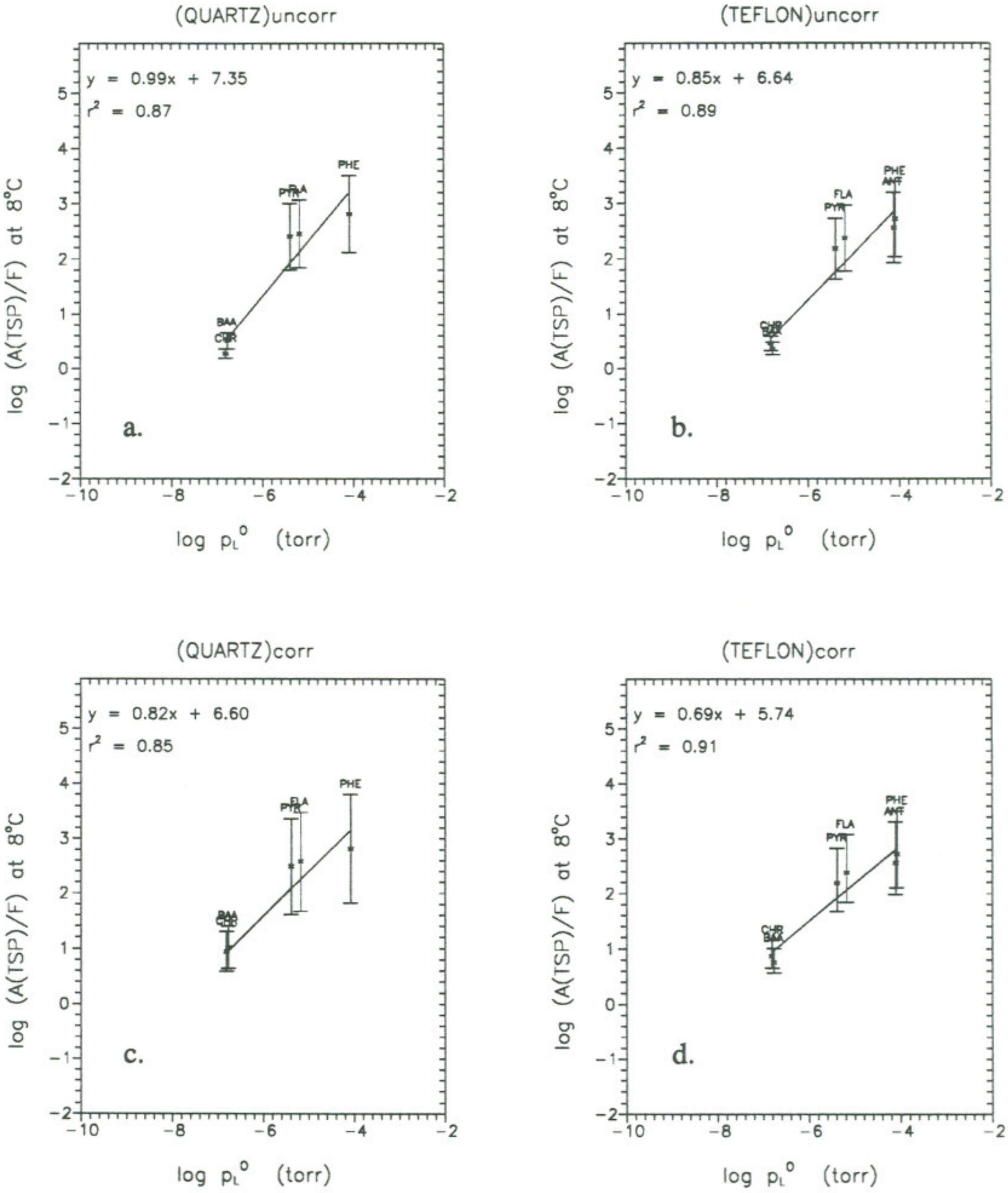

Figure 6.20. Log K vs. log p°_{L} for PAHs from samples collected in Portland, OR on 11/17/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

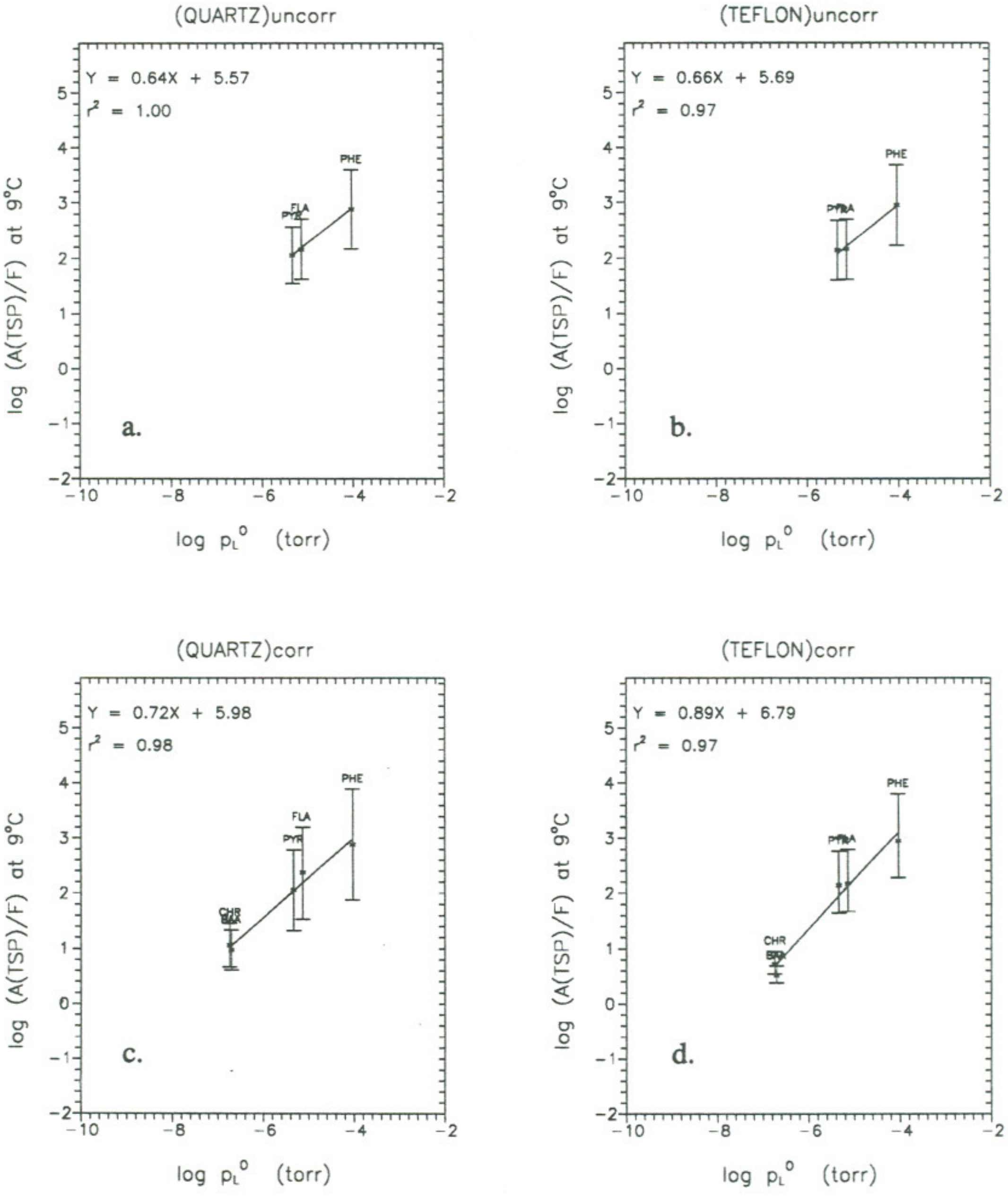

Figure 6.21. Log K vs. log p°_L for PAHs from samples collected in Portland, OR on 11/23/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

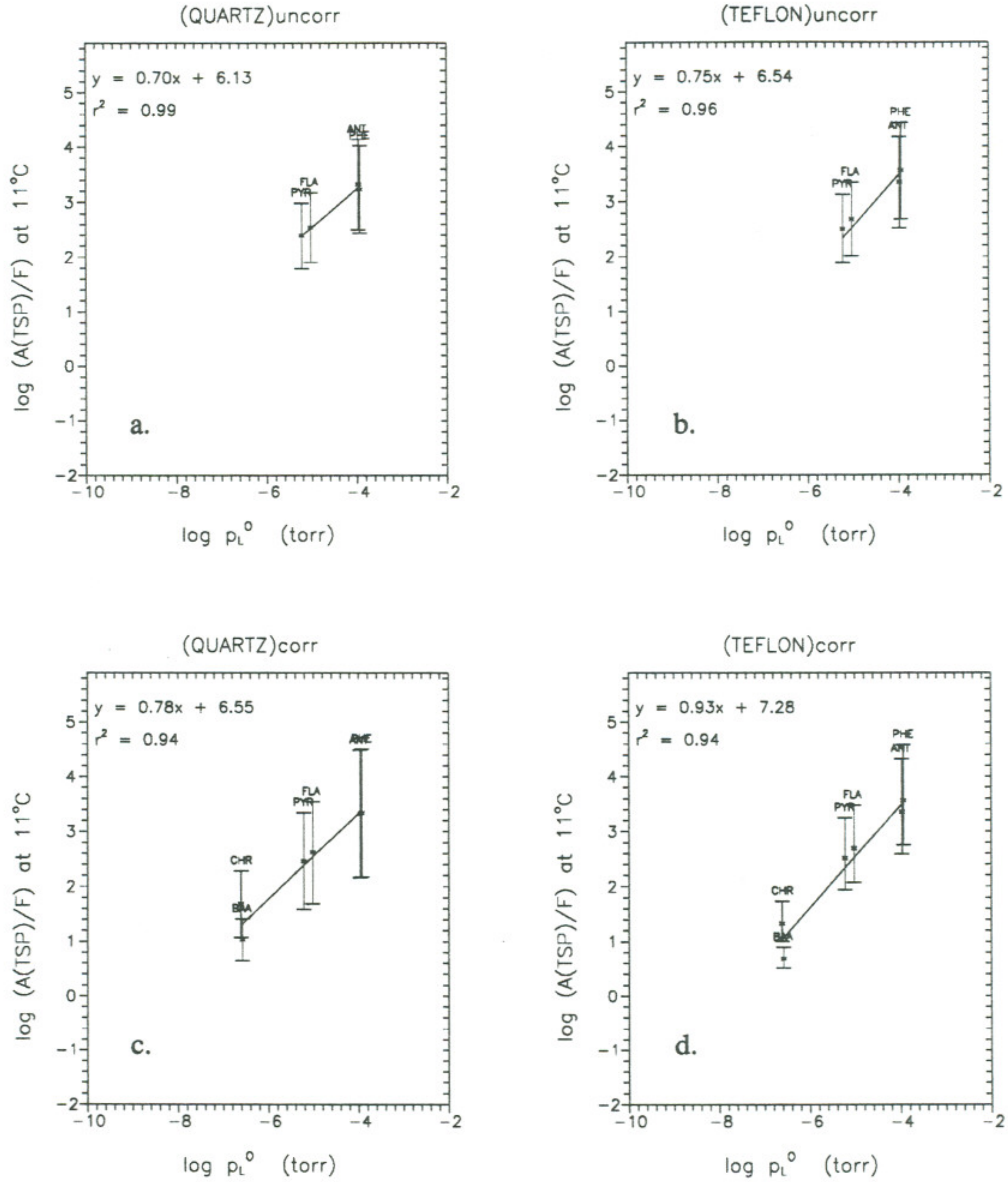

Figure 6.22. Log K vs. log p°_L for PAHs from samples collected in Portland, OR on 11/29/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. The regression equations were calculated using only the data points that are covered by the regression lines in each of the plots.

The slopes and y-intercepts obtained from least squares and weighted least squares linear regression analyses for the target PAHs are given in Table 6.3. Excellent agreement was obtained in all four types between the predicted slope of +1 and the slopes observed. The average slope for each type of plot was ~0.9 and there were no significant differences between the slopes from the regression analyses and the predicted value of +1 in ~90% of the events sampled for the four types of plots examined. One result of the high degree of correlation in all of the plots was that there were very little differences between the slopes obtained from the least squares and weighted least squares regression analyses. The y-intercepts were compared to the values predicted from equilibrium adsorption theory in a similar manner to that presented in Section 6.1.2. When the slope is assumed to be +1 and $(Q_1 - Q_v)$ ~3 kcal/mol (Bidleman et. al., 1986; Pankow, 1988; Ligocki and Pankow, 1989), there were no significant $(P = 0.05)$ differences in the experimental and predicted values of log C in any of the cases. Therefore, general agreement was obtained between experimental values of the slope and y-intercept from log A(TSP)/F vs. log p°_{L} plots and those predicted from equilibrium adsorption theory.

Table 6.3. Regression Equations of log A(TSP)/F vs. log p°_{L} Plots for the Target PAHs (Figures 6.15 - 6.22) in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F Values.

			Weighted	
Date/Plot	m	b	m	b
<u>7/20</u>				
QU	1.07 ± 0.20	6.61 ± 0.73	1.21 ± 0.19	7.12 ± 0.81
QC	1.07 ± 0.20	6.61 ± 0.73	1.21 ± 0.19	7.12 ± 0.81
TU	0.93 ± 0.21	6.27 ± 0.76	1.02 ± 0.27	6.56 ± 1.00
TC	0.93 ± 0.21	6.27 ± 0.76	1.02 ± 0.27	6.56 ± 1.00
<u>7/26</u>				
QU	0.98 ± 0.29	6.58 ± 1.34	0.92 ± 0.21	6.28 ± 1.07
QC	0.98 ± 0.29	6.58 ± 1.34	0.92 ± 0.21	6.28 ± 1.07
TU	1.06 ± 0.07	7.20 ± 0.32	1.05 ± 0.05	7.16 ± 0.25
TC	1.06 ± 0.07	7.20 ± 0.32	1.05 ± 0.05	7.16 ± 0.25
<u>8/7</u>				
QU	0.85 ± 0.02	6.07 ± 0.07	0.85 ± 0.02	6.06 ± 0.10
QC	0.85 ± 0.02	6.07 ± 0.07	0.85 ± 0.02	6.06 ± 0.10
TU	0.79 ± 0.06	5.91 ± 0.31	0.76 ± 0.06	5.74 ± 0.32
TC	0.79 ± 0.06	5.91 ± 0.31	0.76 ± 0.06	5.74 ± 0.32
<u>8/19</u>				
QU	0.80 ± 0.12	6.35 ± 0.66	0.84 ± 0.17	6.51 ± 0.99
QC	0.80 ± 0.12	6.35 ± 0.66	0.84 ± 0.17	6.51 ± 0.99
TU	0.86 ± 0.03	6.57 ± 0.16	0.86 ± 0.02	6.58 ± 0.13
TC	0.86 ± 0.03	6.57 ± 0.16	0.86 ± 0.02	6.58 ± 0.13

Table 6.3 (cont'd.). Regression Equations for log A(TSP)/F vs. log p°_{L} Plots for the Target PAHs (Figures 6.15 - 6.22) in Portland, OR in 1988. The Weighting Factors for the Weighted Regressions was the Inverse of the Variance of the log A(TSP)/F values.

			Weighted	
Date/Plot	m	b	m	b
8/31				
QU	1.18 ± 0.09	8.40 ± 0.49	1.19 ± 0.06	8.43 ± 0.37
QC	1.18 ± 0.09	8.40 ± 0.49	1.19 ± 0.06	8.43 ± 0.37
TU	0.97 ± 0.01	7.35 ± 0.05	0.97 ± 0.01	7.35 ± 0.05
TC	0.97 ± 0.01	7.35 ± 0.05	0.97 ± 0.01	7.35 ± 0.05
11/17				
QU	0.99 ± 0.19	7.35 ± 1.10	1.14 ± 0.20	8.16 ± 1.36
QC	0.82 ± 0.17	6.60 ± 0.95	0.91 ± 0.17	7.09 ± 1.10
TU	0.85 ± 0.13	6.44 ± 0.73	0.95 ± 0.12	6.93 ± 0.77
TC	0.69 ± 0.10	5.74 ± 0.54	0.77 ± 0.09	6.07 ± 0.55
11/23				
QU	0.64 ± 0.01	5.57 ± 0.07	0.64 ± 0.02	5.57 ± 0.08
QC	0.72 ± 0.06	5.98 ± 0.32	0.76 ± 0.07	6.12 ± 0.36
TU	0.66 ± 0.09	5.69 ± 0.43	0.65 ± 0.10	5.66 ± 0.54
TC	0.89 ± 0.08	6.79 ± 0.46	0.95 ± 0.12	7.13 ± 0.76
11/29				
QU	0.70 ± 0.05	6.13 ± 0.22	0.70 ± 0.04	6.12 ± 0.20
QC	0.78 ± 0.06	6.55 ± 0.35	0.83 ± 0.10	6.79 ± 0.63
TU	0.75 ± 0.07	6.54 ± 0.31	0.75 ± 0.06	6.53 ± 0.29
TC	0.93 ± 0.12	7.28 ± 0.62	1.03 ± 0.22	7.70 ± 1.41

6.1.4. Comparison of Equilibrium Distribution Constants for Target n-Alkanes and PAHs at Similar Vapor Pressures

According to partitioning theory (Section 3.1), when the atmospheric conditions and the quantity $N_s e^{(Q_1 - Q_v)/RT}$ for each compound are similar, two compounds that have similar vapor pressures will tend to partition between the gas and particulate phases to similar extents. Since N_s is not very compound dependent (Pankow, 1988) and the difference in enthalpies of desorption and vaporization (Q_1 - Q_v) is ~3 kcal/mol for many PAHs and n-alkanes (Bidleman et. al., 1986; Pankow, 1988; Ligocki and Pankow, 1989), the values of K should be similar for compounds that have similar vapor pressures.

For the events in which comparisons were possible, values of log A(TSP)/F for compounds with similar vapor pressures are given in Table 6.4. Since the best estimates of log A(TSP)/F are the gas phase adsorption corrected values, only the QC and TC values have been tabulated. With the coefficient of variation associated with each log A(TSP)/F value being ~34% and ~28% for the QC and TC values, respectively, there were no significant differences in the values of log A(TSP)/F between the n-alkanes and PAHs at similar vapor pressures for the same sampling event. In some instances, there was a larger difference in the values of log A(TSP)/F between the QC and TC values for the same compound than there was for the PAHs and alkanes, at similar vapor pressures. Therefore, for the conditions encountered in this study, the n-alkanes and PAHs were found to behave similarly.

Table 6.4. Comparison of Equilibrium Distribution Coefficients (K) for the Target n-Alkanes and PAHs at Similar Vapor Pressures in Portland, OR in 1988.

	PAHs			**n-Alkanes**		
Date	log p°_L (torr)	K QC	TC	log p°_L (torr)	K QC	TC
7/20	-3.44 (ANT)	2.96	3.07	-3.43 (C17)	3.30	2.85
7/26	-3.98 (FLA)	na[a]	3.03	-4.06 (C19)	3.89	na
	-5.41 (CHR)	na	1.71	-5.38 (C22)	na	2.38
8/7	-3.55 (PHE)	3.05	3.11	-3.58 (C17)	2.91	2.53
	-4.59 (FLA)	2.15	2.35	-4.67 (C19)	2.86	2.48
	-6.11 (CHR)	na	1.14	-6.00 (C22)	na	1.61

Table 6.4 (cont'd.). Comparison of Equilibrium Distribution Coefficients (K) for the Target n-Alkanes and PAHs at Similar Vapor Pressures in Portland, OR in 1988.

	PAHs			**n-Alkanes**		
		K			K	
Date	log p°_{L} (torr)	QC	TC	log p°_{L} (torr)	QC	TC
8/19	-4.53 (FLA)	2.70	2.68	-4.62 (C19)	3.43	2.85
	-6.02 (BaA)	1.89	1.39	-5.95 (C22)	2.40	1.60
8/31	-3.59 (PHE)	na	2.84	-3.52 (C16)	na	3.08
	-4.83 (PYR)	2.75	1.39	-4.72 (C19)	2.33	2.67
	-6.17 (CHR)	1.08	na	-6.05 (C22)	1.71	na

Table 6.4 (cont'd.). Comparison of Equilibrium Distribution Coefficients (K) for the Target n-Alkanes and PAHs at Similar Vapor Pressures in Portland, OR in 1988.

	PAHs			n-Alkanes		
Date	log p°_{L} (torr)	K QC	K TC	log p°_{L} (torr)	K QC	K TC
11/17	-4.08 (PHE)	na	2.82	-4.03 (C16)	na	3.04
	-4.11 (ANT)	na	2.67	-4.14 (C17)	na	2.80
	-5.18 (FLA)	na	2.48	-5.23 (C19)	na	2.32
11/23	-4.03 (PHE)	2.98	3.05	-3.98 (C16)	3.29	2.36
11/29	-3.96 (ANT)	3.42	3.45	-3.99 (C17)	4.59	3.28
	-5.02 (FLA)	na	2.79	-5.08 (C19)	na	2.66

6.1.5. Comparison of TSP, PM-10, and TPC in Equation 6.2

The data set from Figure 6.1 was used as an example to demonstrate the relationship between TSP, PM-10, and TPC in a K type expression. This was accomplished by substituting PM-10 and TPC for TSP into equation 6.2 and regressing these new types of K vs. log $p°_L$. The regression lines for the three cases are given in Figure 6.23. Since for a single event, the three K values are related by a multiplicative factor, the slopes for the three cases were the same (.90). The y-intercepts log A(PM-10)/F and log A(TPC)/F plots were decreased by amounts equal to log TSP/PM-10 and log TSP/TPC, respectively. The correlation coefficient (r^2) for each plot was 0.86.

While the previous paragraph compared different types of K (i.e. K_{TSP}, K_{PM-10}, and K_{TPC}) for a single sampling event, it is more useful to make a similar comparison for different sampling events at the same temperature (T). The different events might have different TSPs, PM-10s, and TPCs, and there may be a better correlation between log K and log $p°_L$ using PM-10 or TPC in K rather than TSP.

The values of log K from 11 of the 12 sampling events were separated into three temperature ranges; 9°C (3 events), 13°C (3 events), and 19°C (5 events). The data from 7/26 (31°C) was not included in any of the above ranges as the temperature was much higher than the highest range. The results of regression analyses of log K_{TSP}, K_{PM-10}, and K_{TPC} vs. log $p°_L$ at 9, 13, and 19°C for QC data

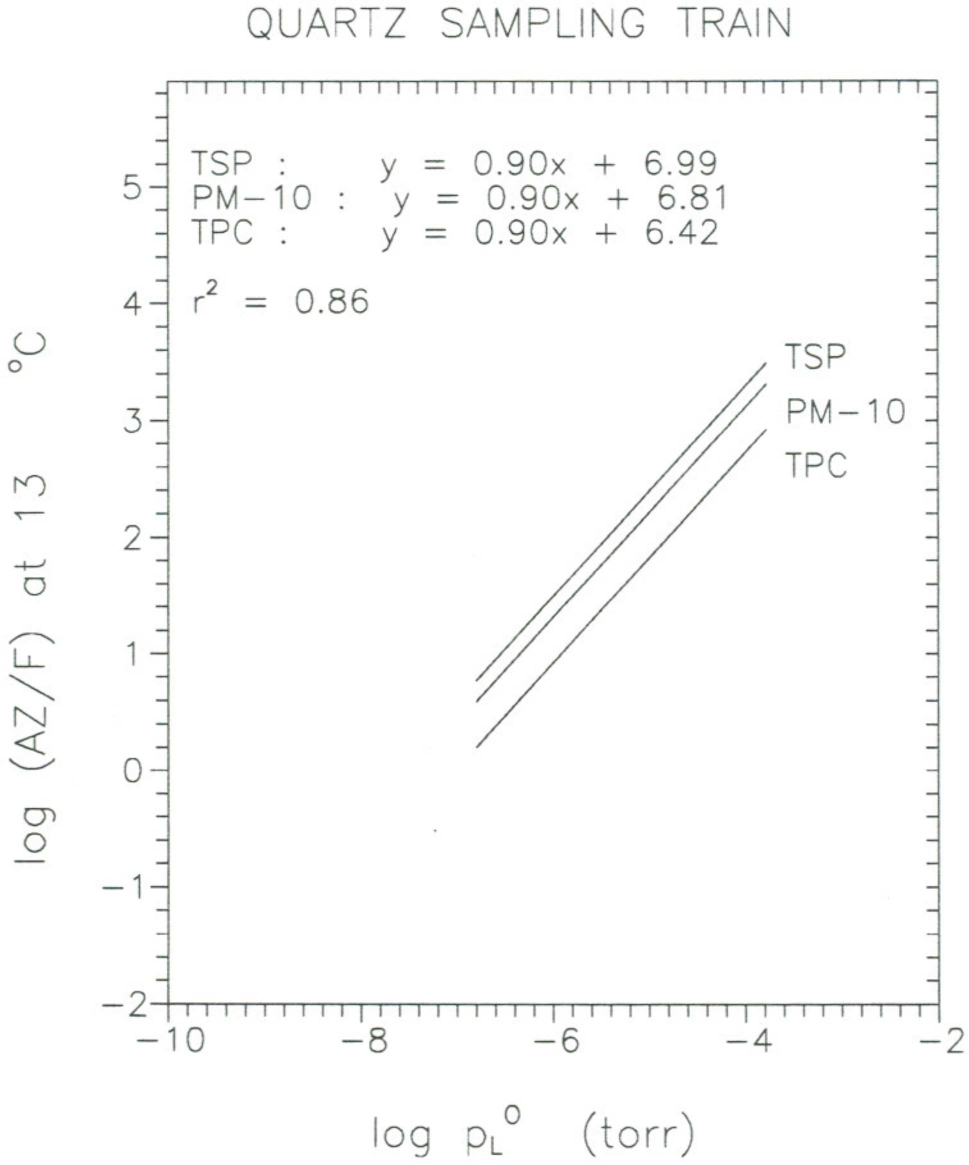

Figure 6.23. Log AZ/F vs. log p°_{L}, where Z = TSP, PM-10, or TPC; for the quartz sampling train for samples collected in Portland, OR on 2/27/88.

indicated that there was very little difference between the correlation coefficients from the three measures of K over the three temperature ranges. For example, at 13°C, r^2 was 0.92, 0.89, and 0.90 for regressions with K_{TSP}, $K_{PM\text{-}10}$, and K_{TPC}, respectively. Ligocki and Pankow (1989) obtained similar results for PAHs using TPC in a log K_{TPC} vs. log p°_{L} correlation. Thus, log K_{TSP}, log $K_{PM\text{-}10}$, and log K_{TPC} are highly correlated, and it does not appear that PM-10 or TPC play a preferential role in sorption in the urban atmosphere.

6.1.6. Equilibrium Distribution Constants as a Function of Temperature

Yamasaki et. al. (1982) applied linear Langmuir isotherm theory to examine the dependence of gas/particle distributions of PAHs in Tokyo on T and TSP (Section 3.1). In essence, they suggested that θ might be proportional to TSP and developed the expression

$$\log \frac{A(TSP)}{F} = \frac{m}{T} + b \qquad 6.3$$

Regression equations using QC and TC (Section 6.1.2) values of log A(TSP)/F vs. 1 / T for the target n-alkanes C16 to C23 and PAHs phenanthrene, fluoranthene, and benz(a)anthracene are presented in Table 6.5. Also presented in Table 6.5 are estimates of the regression parameters found by other researchers for these

Table 6.5. Regression Parameters and Literature Values for log A(TSP)/F vs. 1/T Plots for the Target n-Alkanes and PAHs.

Compound/Plot	m (± 1s)	b (± 1s)	m_w^a (± 1s)	b_w^b (± 1s)
C16				
QC	-2146 ± 4344	11.1 ± 15.1	-2727 ± 4151	13.0 ± 14.0
TC	1323 ± 1769	-1.63 ± 6.12	528 ± 1598	1.01 ± 5.52
C17				
QC	8298 ± 4026	-25.2 ± 13.9	5721 ± 4220	-16.4 ± 14.5
TC	1442 ± 2736	-2.07 ± 9.55	-80 ± 1988	3.00 ± 6.87
C18				
QC	7746 ± 4136	-23.2 ± 14.3	6702 ± 3917	-19.7 ± 13.5
TC	-94 ± 1825	3.18 ± 6.30	-2034 ± 1985	9.74 ± 6.87
Foreman (1986)	-1637	9.03		
C19				
QC	-7790 ± 3743	29.7 ± 12.7	-9554 ± 4451	35.6 ± 15.2
TC	-2687 ± 1876	11.9 ± 6.48	-4368 ± 1839	17.6 ± 6.39
Foreman (1986)	-1431	7.86		

Table 6.5 (cont'd.). Regression Parameters and Literature Values for log A(TSP)/F vs. 1/T Plots for the Target n-Alkanes and PAHs.

Compound/Plot	m (± 1s)	b (± 1s)	m_w^a (± 1s)	b_w^b (± 1s)
C20				
QC	-1015 ± 3506	37.6 ± 12.1	-8886 ± 2934	33.1 ± 8.03
TC	-4163 ± 1215	16.4 ± 4.20	-5240 ± 1398	20.3 ± 4.86
C21				
QC	-7255 ± 3660	27.3 ± 12.7	-9194 ± 3299	33.8 ± 11.6
TC	-5576 ± 1233	21.2 ± 4.26	-7398 ± 1509	27.4 ± 5.38
Foreman (1986)	-3836	15.76		
C22				
QC	-7126 ± 1825	26.2 ± 6.32	-9988 ± 2353	36.3 ± 8.29
TC	-5690 ± 1421	21.3 ± 4.91	-9049 ± 2018	32.7 ± 7.09
Foreman (1986)	-6563	25.1		

Table 6.5 (cont'd.). Regression Parameters and Literature Values for log A(TSP)/F vs. 1/T Plots for the Target n-Alkanes and PAHs.

Compound/Plot	m (± 1s)	b (± 1s)	$m_w{}^a$ (± 1s)	$b_w{}^b$ (± 1s)
<u>C23</u>				
QC	-4022 ± 2142	15.2 ± 7.39	-2630 ± 1539	10.2 ± 5.34
TC	-6734 ± 1617	24.3 ± 5.64	-9945 ± 2532	37.5 ± 8.90
Foreman (1986)	-6010	22.7		
<u>Phenanthrene</u>				
QC	-3178 ± 1490	14.4 ± 5.17	-3141 ± 1428	14.2 ± 4.97
TC	-3562 ± 1173	15.9 ± 4.08	-3770 ± 1691	16.6 ± 4.15
Foreman (1986)	-2033	11.0		
Yamasaki (1982)	-4122	18.5		
McVeety (1986)	-3500	14.3		

Table 6.5 (cont'd.). Regression Parameters and Literature Values for log A(TSP)/F vs. 1/T Plots for the Target n-Alkanes and PAHs.

Compound/Plot	m (± 1s)	b (± 1s)	m_w^a (± 1s)	b_w^b (± 1s)
Fluoranthene				
QC	-435 ± 1026	4.13 ± 3.54	-332 ± 1102	3.73 ± 3.81
TC	-1845 ± 1485	9.03 ± 5.13	-1785 ± 1759	8.72 ± 6.09
Foreman (1986)	-2580	12.1		
Yamasaki (1982)	-4420	18.5		
McVeety (1986)	-3670	14.1		

Table 6.5 (cont'd.). Regression Parameters and Literature Values for log A(TSP)/F vs. 1/T Plots for the Target n-Alkanes and PAHs.

Compound/Plot	m (± 1s)	b (± 1s)	m_w[a] (± 1s)	b_w[b] (± 1s)
<u>Pyrene</u>				
QC	119 ± 1210	2.06 ± 4.17	165 ± 1229	1.84 ± 4.23
TC	-1644 ± 1181	8.16 ± 4.07	-1479 ± 1221	7.54 ± 4.22
Foreman (1986)	-3720	16.2		
Yamasaki (1982)	-4180	17.6		
McVeety (1986)	-3820	14.5		

a) slope from a weighted linear regression, weighting factor was the inverse of the variance of log A(TSP)/F values; b) y-intercept from a weighted linear regression.

compound classes.

The trends in the log A(TSP)/F vs. 1 / T plots follow the expected trend: as 1 / T decreases, log A(TSP)/F increases. However, all the plots show a large degree of scatter ($r^2 < 0.65$), which makes a statistical comparison to other work difficult. For example, for a given compound there were order of magnitude differences of the regression parameters obtained from the quartz and Teflon corrected plots, but the standard deviations on the regression parameters were so large that there were no significant differences between the parameters obtained from the quartz and Teflon corrected plots. In all of the cases (QC and TC), for the n-alkanes, there were no significant differences between the regression parameters obtained in this study and those reported by Foreman (1986) in Columbia, SC for C18 to C23. However, it should be kept in mind that although no differences were found at the 95% confidence level, the CVs associated with the regression parameters were typically >50% in this study. Although Foreman (1986) gave no CVs for his regression parameters, three of his six cases had $r^2 < 0.40$. With such values of r^2, the CVs for his regression parameters were likely to be quite high.

The results of the regression analyses of log A(TSP)/F vs. 1 / T for the target PAHs were similar to those of the n-alkanes. Although the general trends of eq 6.3 were followed, there was a tremendous amount of scatter in the data. The average value of r^2 was ~0.30 for the five PAHs examined. Even with the CVs of the regression parameters averaging >50%, there were still significant differences in the slopes and y-intercepts obtained in this study and those reported in the literature in ~30% of the plots.

Since the results from the regression analysis of log A(TSP)/F vs. 1 / T were rather poor, a multiple regression was examined using relative humidity (RH) as a second factor (Table 6.6). RH was chosen as a second factor because a number of researchers have postulated that RH can effect the dynamics of gas/particle partitioning by coating the particles with water (Huntzicker, 1989; Thibodeaux, 1990; Pankow and Storey, 1990).

The inclusion of RH in the regression equation had a minimal effect on further increasing the correlatability of the TC n-alkanes data. However, there was a noticeable improvement in the QC data. For example, the correlateability, as measured by r^2, increased an average of 0.20 for each for the plots of the n-alkanes from C16 to C21. The difference in r^2 between the two plots also increased with increasing vapor pressure. For example, for C23 and C16 the difference in r^2 between the two regressions, was 0.03 and 0.50, respectively.

The target PAHs also showed an increase in correlateability when RH was factored into the regression for both the QC and TC plots. However, the magnitudes of the differences between r^2 (~0.10) were much less than for the n-alkanes. Thus, from the results of this study, it appears that RH may play at least a small role in gas/particle partitioning, and that RH should be considered when designing new laboratory and field experiments.

Table 6.6. Regression Equations for the Target n-Alkanes and PAHs of log A(TSP)/F vs. 1/T (Predictor m_1) and Relative Humidity (predictor m_2) Plots from Samples Collected in Portland, OR in 1988.

Compound/Plot	m_1 (± 1s)[a]	b (± 1s)	m_2 (± 1s)[b]	r^2
C16				
QC	-5974 ± 3682	21.6 ± 12.3	0.03 ± 0.01	0.54
TC	-1157 ± 2787	5.74 ± 8.83	0.02 ± 0.02	0.17
C17				
QC	4085 ± 4857	-11.9 ± 16.0	0.02 ± 0.02	0.63
TC	-890 ± 4494	4.87 ± 14.6	0.02 ± 0.02	0.07
C18				
QC	13043 ± 4243	-38.5 ± 14.1	-0.04 ± 0.02	0.69
TC	-1409 ± 2989	7.09 ± 9.48	0.02 ± 0.02	0.04
C19				
QC	-2105 ± 5982	12.6 ± 18.9	-0.04 ± 0.03	0.67
TC	-3274 ± 3148	13.6 ± 9.98	0.00 ± 0.02	0.18
C20				
QC	-7787 ± 3902	31.0 ± 12.9	-0.02 ± 0.02	0.67
TC	-4158 ± 2044	16.6 ± 6.49	0.00 ± 0.01	0.54

Table 6.6 (cont'd.). Regression Equations for the Target n-Alkanes and PAHs of log A(TSP)/F vs. 1/T (Predictor m_1) and Relative Humidity (Predictor m_2) Plots from Samples Collected in Portland, OR in 1988.

Compound/Plot	m_1 (± 1s)[a]	b (± 1s)	m_2 (± 1s)[b]	r^2
C21				
QC	-8874 ± 4754	31.2 ± 15.6	0.01 ± 0.02	0.36
TC	-5238 ± 2070	20.1 ± 6.57	0.00 ± 0.01	0.67
C22				
QC	-7475 ± 2977	27.2 ± 9.42	0.00 ± 0.01	0.63
TC	-3991 ± 2712	16.0 ± 8.49	-0.01 ± 0.02	0.67
C23				
QC	-3870 ± 3440	14.7 ± 11.0	-0.01 ± 0.02	0.28
TC	-7073 ± 2718	25.3 ± 8.64	0.00 ± 0.02	0.64
Phenanthrene				
QC	-5854 ± 3837	22.7 ± 11.2	0.01 ± 0.02	0.56
TC	-7035 ± 2684	26.7 ± 8.51	0.02 ± 0.01	0.82

Table 6.6 (cont'd.). Regression Equations for the Target n-Alkanes and PAHs of log A(TSP)/F vs. 1/T (Predictor m_1) and Relative Humidity (Predictor m_2) Plots from Samples Collected in Portland, OR in 1988.

Compound/Plot	m_1 (± 1s)[a]	b (± 1s)	m_2 (± 1s)[b]	r^2
Fluoranthene				
QC	-545 ± 956	3.94 ± 3.30	0.01 ± 0.01	0.24
TC	-3596 ± 2384	14.4 ± 7.57	0.01 ± 0.01	0.21
Pyrene				
QC	1027 ± 2997	-0.09 ± 9.27	0.00 ± 0.02	0.17
TC	-10138 ± 68471	34.4 ± 18.1	0.02 ± 0.76	0.50

a) 1 / T predictor variable; b) RH predictor variable.

6.2. Deviation From Theoretical Predictions at High Values of p°_L on the Equilibrium Distribution Constant for the Target n-Alkanes

As shown in Figures 6.3 - 6.14 and Table 6.1, there appears to be a significant deviation (~0.5 log units) between the log A(TSP)/F values for the higher volatility n-alkanes ($p^\circ_L \sim 10^{-3}$ to 10^{-4} torr) in the C16 to C17 range and what would be expected from a best fit regression equation for the lower volatility ($p^\circ_L < 10^{-4}$ torr) compounds in the C18 to C24 range. Lower than expected values of log A(TSP)/F for some of the more volatile compounds have also been observed in other studies of partitioning (Bidleman et. al., 1986; Ligocki and Pankow, 1989; McVeety, 1986). For example, Ligocki and Pankow (1989) observed acenaphthylene and fluorene to have lower values of log A(TPC)/F, where TPC is the total particulate carbon concentration, when compared to what would be expected from the best fit line from less volatile PAHs. This non-linearity may be caused by a fraction of a compound in the particulate phase being bound and nonexchangeable with the gas phase (Section 3.3); Pankow (1988) derived a expression to predict the magnitude of this effect.

The magnitude of the nonexchangeable fraction (x %) can be calculated by rearranging eq 3.14 and using estimates of log C from the nonexchangeable regression equation assuming a slope of +1. The values of x for the n-alkanes of interest and the four types of plots, described in Section 6.1.1, are presented in Table 6.7. Due to the lower number of log A(TSP)/F values available for the

Table 6.7. Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
2/27 QU	C16	3.55	3.32
	C17	0.83	0.53
TU	C16	3.35	2.95
	C17	2.49	1.97
TC	C16	3.35	2.95
	C17	2.44	3.50
3/16 QU	C16	5.45	2.49
	C18	0.99	na[c]
QC	C16	5.21	5.10
	C18	0.98	na
TU	C16	2.77	2.64
	C17	0.73	0.56
TC	C16	4.34	4.48
	C17	2.87	3.06

Table 6.7 (cont'd.). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
<u>4/9</u> QC	C16	4.67	4.67
TC	C16	9.26	9.77
	C17	12.7	13.3
	C18	6.58	8.39
<u>7/20</u> QC	C16	22.6	22.6
	C17	13.3	13.3
	C18	6.38	6.44
	C19	0.90	1.17
QC	C16	2.87	2.89
	C17	1.74	1.78
TU	C16	11.4	11.4
	C17	9.23	9.29
	C18	6.34	6.51
	C19	3.39	4.17

Table 6.7 (cont'd.). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
7/20 TC	C16	8.92	8.93
	C17	8.36	8.37
TC	C18	6.09	6.14
	C19	3.90	4.18
7/26 QU	C16	16.4	16.8
	C17	12.1	12.6
TU	C16	10.9	11.0
	C17	12.0	12.1
	C18	5.57	5.75
TC	C16	8.79	8.73
	C17	10.6	10.5
	C18	5.60	5.38
	C19	3.53	2.54

Table 6.7 (cont'd.). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
8/1			
QU	C16	7.64	7.88
QC	C16	2.91	2.89
	C17	6.97	6.92
	C18	1.19	0.89
TU	C16	11.0	10.9
	C17	10.8	10.8
TC	C16	10.6	10.7
	C17	11.5	11.6
	C18	9.38	9.67
	C19	4.55	5.86
8/7			
QU	C16	15.4	14.4
	C17	8.47	7.69
TU	C16	6.39	6.43
	C17	7.50	7.56

Table 6.7 (cont'd.). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
8/7			
TC	C16	5.78	5.91
	C17	7.49	7.66
8/19			
QU	C16	4.91	4.28
	C17	4.05	3.24
QC	C16	0.07	na
	C17	1.25	0.77
TU	C16	3.18	3.27
	C17	4.46	4.56
	C18	3.91	4.23
8/31			
QU	C16	3.33	0.12
	C17	2.97	na
TU	C16	3.98	3.98
	C17	5.06	5.06

Table 6.7 (cont'd.). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
11/17			
QU	C16	3.72	4.21
	C17	1.57	2.22
TC	C17	4.25	4.53
	C18	0.86	1.64
TU	C16	1.09	na
	C17	2.72	0.12
TC	C16	2.32	2.54

Table 6.7 (cont'd). Nonexchangeable Fraction (x) Calculated from the Best Fit Non-Weighted and Weighted Regression Equations (Assuming a Slope of +1) of the Target n-Alkanes for QU, QC, TU, and TC Measured in Portland, OR in 1988.

Date/Plot	CPD	x (%) nw[a]	x (%) w[b]
11/29			
QU	C16	2.52	na
QC	C16	0.84	0.54
	C17	0.08	na
TU	C16	1.33	na
	C17	2.07	na
TC	C16	2.15	2.07
	C17	2.93	2.82

a) result from a non-weighted linear regression; b) result from a weighted regression; c) na = not available.

target PAHs, no estimates of x were calculated for the PAHs.

The trends in x as a function of the plot type (i.e. QU,QC,TU, and TC) can be demonstrated by looking at the x values for C16. For the QU plots, x averaged 8.55% and ranged from 3.33 to 22.6%. The QC plots gave much smaller values, they averaged 2.76% and ranged from 0.07 to 5.21%. The explanation for the average values of x for the QU plots being ~3 times that of the QC plots is gas adsorption to the QFFs. Gas adsorption to the QFFs would cause the log A(TSP)/F values to be artificially low, thus predicting an artificially high value of x. The TU and TC plots had very similar values of x, with the averages for C16 being 5.80 and 5.87% with ranges of 1.09 to 11.42 and 2.15 to 10.6%, respectively.

While the values of x for the QU plots appear to overestimate the magnitude of the nonexchangeable effect, it is not clear that any one of the other values of x from the QC, TU, and TC fits is more correct than the others. However, for each case the true value of x is likely to be within the range provided by the three values.

The QC values of x represent the lower end, and the values of x from the TU and TC plots represent the upper end. It is possible that the values of x calculated from the TU and TC plots could be artificially high from some gas adsorption to TMFs. For typical sampling conditions experienced in Portland, the average nonexchangeable fraction for C16 was found to be between 2.76 and 5.87%.

While the above discussion implies that there is only one factor responsible for the nonlinearity in the log A(TSP)/F vs. log p°_L plot, in actuality, there could by many contributing factors. One factor could be the presence of highly sorptive sites on the particulate matter. The possibility of non-uniform sorptive surfaces on the particulate matter is very real. However, as noted by Pankow (1988), if there were some highly sorptive sites available on the particulate surface, the more volatile compounds would tend to be displaced from those sites by the more strongly sorbing, less volatile compounds. Thus, the most likely explanation for the nonlinearity of the plots is a small percentage of a compound bound in the particulate matter and nonexchangeable with the surrounding gas phase.

6.3. Fraction Associated with the Particulate Phase

As described in Section 3.2, Junge (1977) was the first to develop an expression to predict the partitioning of a compound between the gas and particulate phases. Based on a linear Langmuir isotherm, Junge derived

$$\phi = \frac{c_J\theta}{p^\circ + c_J\theta} \qquad 6.4$$

where c_J is a constant, θ is aerosol surface area concentration (cm^2/cm^3), p° is the vapor pressure of the pure compound (torr). The value of ϕ can be determined experimentally by

$$\phi = \frac{c_p}{c_g + c_p} \qquad 6.5$$

where c_p and c_g are the gas- and particulate-phase associated atmospheric concentrations (ng/m^3), respectively. Using linear Langmuirian adsorption theory (Section 3.1), Pankow (1987) derived an expression for c_J as

$$c_J = 760RTN_s e^{(Q1\text{-}Qv)/RT} \qquad 6.6$$

If $N_s e^{(Q1\text{-}Qv)/RT}$ is relatively constant from compound to compound and for given sample of particulate matter, c_J will likewise be constant. For PAHs, c_J has been estimated to be ~1.3 at 20°C (Pankow, 1987). Thus, if a compound's vapor pressure is known, the extent that the compound will partition to the particulate phase can be estimated by eq. 6.4 if θ is known.

Values of θ have been estimated to range from 10^{-7} to 10^{-5} cm^2/cm^3 for background and urban air particulate matter (Junge, 1977). Junge's values of θ are very similar to those reported by Whitby (1978) for the Los Angeles air basin assuming non-porous particles. Whitby (1978) estimated θ to be 4.2×10^{-7} and 1.1×10^{-5} cm^2/cm^3 for background and urban air, respectively. While Whitby's (1978) values of θ provide estimates of the aerosol surface area concentration for Los

Angeles, accurate values of θ are needed from the particular atmospheric conditions of interest in order to provide an estimate of the partitioning for a given compound under those conditions.

One can expect there will be much variation in θ, not only between different locations, but also at the same location as a function of time. For example, Whitby (1978) estimated that, in a particular location, daily variations in θ can exceed an order of magnitude. This variation will be the result either of the movement of different air parcels over the site of interest, or changes in the chemical and physical characteristics of the air parcel (e.g. gas to particle conversion reactions).

The ability to use eq. 6.4 to estimate the extent to which a compound will partition to the particulate phase for particular atmospheric conditions requires an accurate estimate of θ. While this study did not measure the particle size distributions for the sampling events, an estimate of the quantity $c_J\theta$ can be obtained by noting that

$$\log \frac{A}{F} = \log p^{\circ}_{L} + \frac{1}{c_J\theta} \qquad 6.7$$

Therefore, assuming a constant $N_s e^{(Q1-Qv)/RT}$, a plot of log A/F vs. log p°_{L} will have a slope of +1 and a y-intercept of log $1/c_J\theta$. With the quantity $c_J\theta$ available for each sample event, θ can be estimated by using an estimate of c_J from eq. 6.6. It should be kept in mind that θ obtained from this method will be both sampling site and event specific.

6.3.1. Fraction in the Particulate Phase for n-Alkanes

Since plots of log A/F vs. log p°_{L} are very similar to Figures 6.3 - 6.14, except that all of the points are shifted down by an amount equal to log TSP, they will not be given here. Table 6.8 lists $c_J\theta$ from log A/F vs. log p°_{L} plots (eq. 6.7) when a slope of +1 is assumed. The data points for the compounds which are thought to have been affected by nonexchangeable effects (Section 6.2) were excluded when determining the values of $c_J\theta$.

The values of $c_J\theta$ for the four different types of plots (Section 6.1.2) were quite different within each sampling event. The highest values were typically associated with the QU plots. This is most likely due to gas adsorption onto the QFFs. The best estimates of the ratio A/F, corrected for sampling artifacts, are probably given by either the QC or the TC data. Since there can be only one value of $c_J\theta$ for a given compound, an average of $c_J\theta$ was determined from the QC and TC data for each sampling event.

The average values of $c_J\theta$ for the different types of plots were very similar from sampling event to sampling event. The overall average for all 12 events was 1.12×10^{-6} torr. With c_J being ~1 torr cm^3/cm^2, an average value of ~10^{-6} cm^2/cm^3 was estimated for θ. This is very close to the average value estimated by Ligocki and Pankow (1989) for Portland in 1984 and 1985 and to an estimate given by

Table 6.8. Values of $c_J\theta$ for the Target n-Alkanes from the Regression of log A/F vs. log p°_L on QU, QC, TU, and TC Plots[a] for Portland, OR in 1988.

	$c_J\theta \times 10^6$ (torr)											
Plot	2/27	3/16	4/9	7/20	7/26	8/1	8/7	8/19	8/31	11/17	11/23	11/29
QU	2.01	12.6	69.6	1.96	16.7	6.73	5.53	2.43	6.77	0.74	5.20	2.39
QC	0.45	0.40	0.05	1.08	0.76	0.21	1.75	0.88	1.86	0.14	0.43	0.13
TU	1.83	4.89	21.0	0.45	5.17	5.35	2.58	4.43	2.19	1.91	3.28	2.45
TC	0.29	1.51	1.83	0.22	2.65	1.90	1.13	1.16	2.63	0.66	3.52	1.23
AVE[b]	0.37	0.96	0.94	0.65	1.71	1.06	1.44	1.02	1.90	0.40	1.98	0.68

a) the data points that were thought to be subject to nonexchangeable effects (Section 6.2) were excluded from the log A(TSP)/F data sets for each of the plots; b)average of QC and TC only.

Whitby (1975) for Los Angles air of 3.5 x 10^{-6} cm^2/cm^3. It would not be surprising if the value of θ is lower in Portland than in Los Angeles, where photochemical reactions can produce large numbers of submicron particles. Such particles will have a large surface to volume ratio. Their numbers will affect the second moment of the size distribution which gives θ.

Using the estimates of $c_j\theta$ and eq 6.4, ϕ can be parameterized as a function of p°_L. Figures 6.24 - 6.35 provide plots of ϕ vs log p°_L for the 12 samples collected in Portland. Experimental values of ϕ (eq 6.5), using the same types of plots as in Section 6.1.2, are compared with the estimated values of ϕ using eq 6.4 in Figures 6.24 - 6.35.

The data for the corrected plots (QC and TC) fit the estimated data much better than the uncorrected data in almost all cases. Since the most volatile n-alkanes are present almost entirely in the gas phase, gas adsorption to the filter would provide an artificial particulate phase concentration and seem to have a large effect on ϕ. However, the largest differences between the uncorrected and corrected data were observed for ~C20 to C24, not C16 to C19 as might be expected. The reason for this apparent contradiction is that for compounds in the C16 to C19 range, the concentration collected on the PUFs is much larger than the gas phase concentration collected on the filter. The PUFs concentration is so large that any gas phase adsorption to the filter is effectively masked by the high concentration collected on the PUFSs. In the C20 to C24 range, the concentrations in both phases are similar and gas adsorption to the filters in these cases raises ϕ a

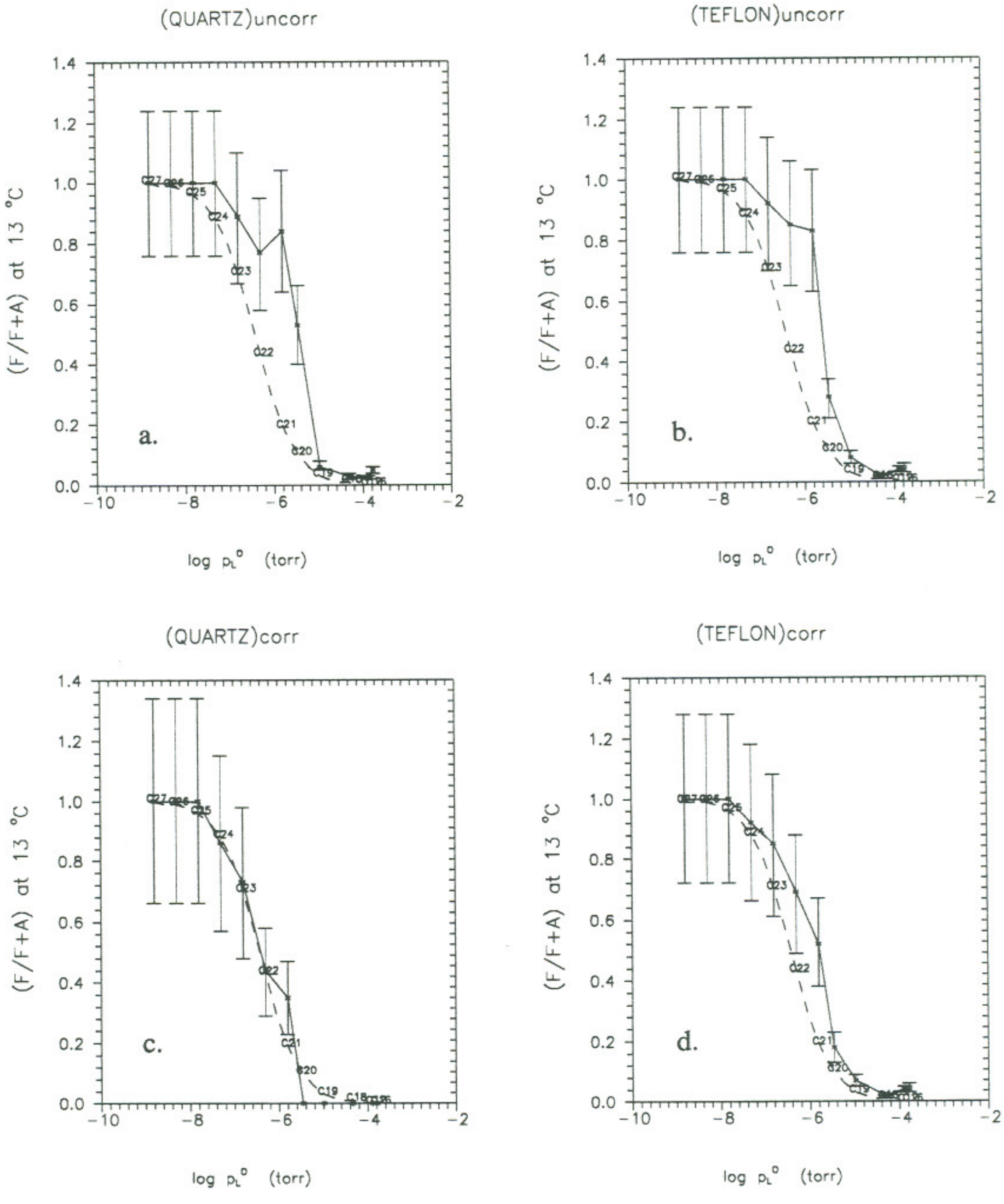

Figure 6.24. ϕ vs. log p°_{L} for n-alkanes from samples collected in Portland, OR on 2/27/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

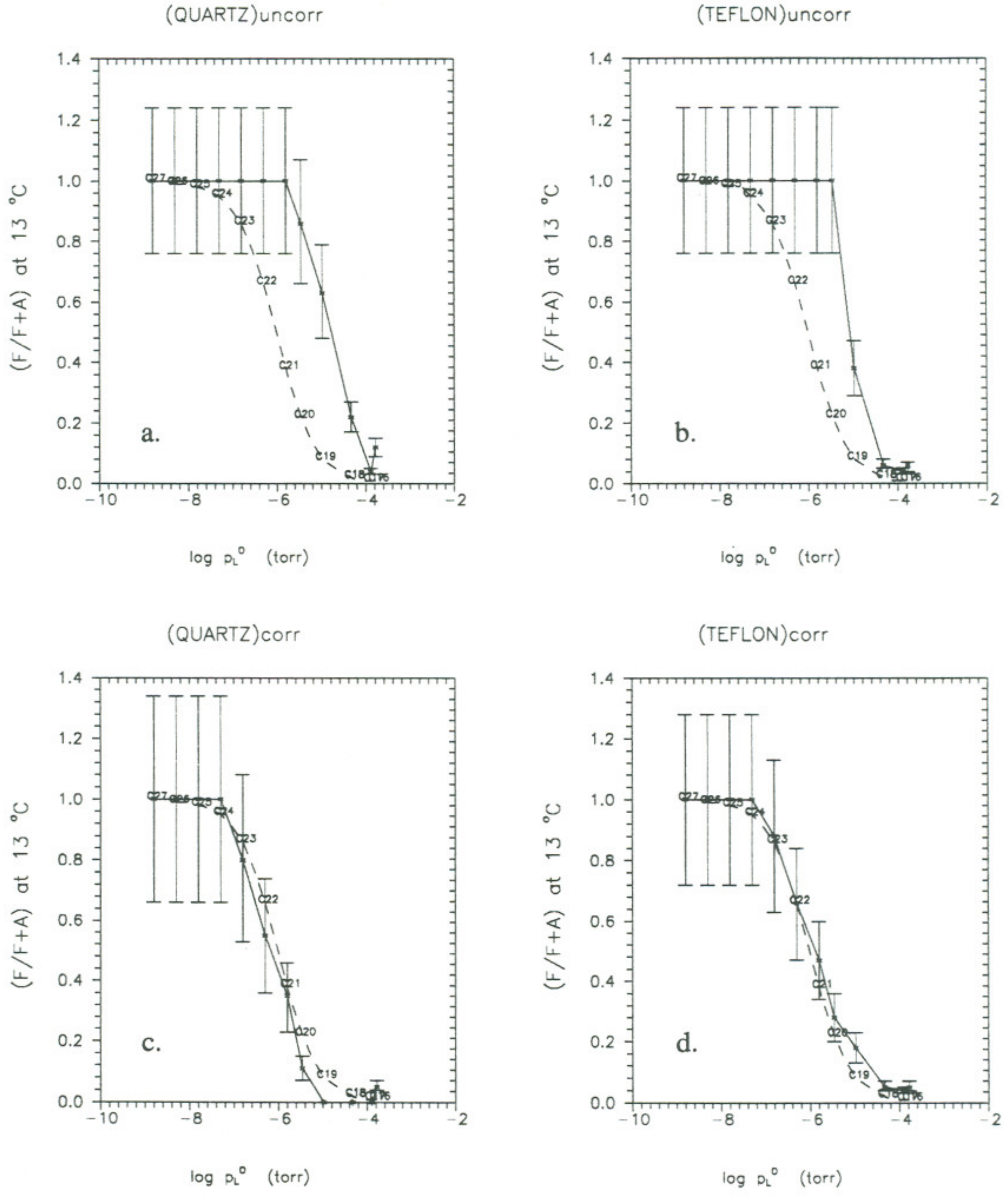

Figure 6.25. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 3/16/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

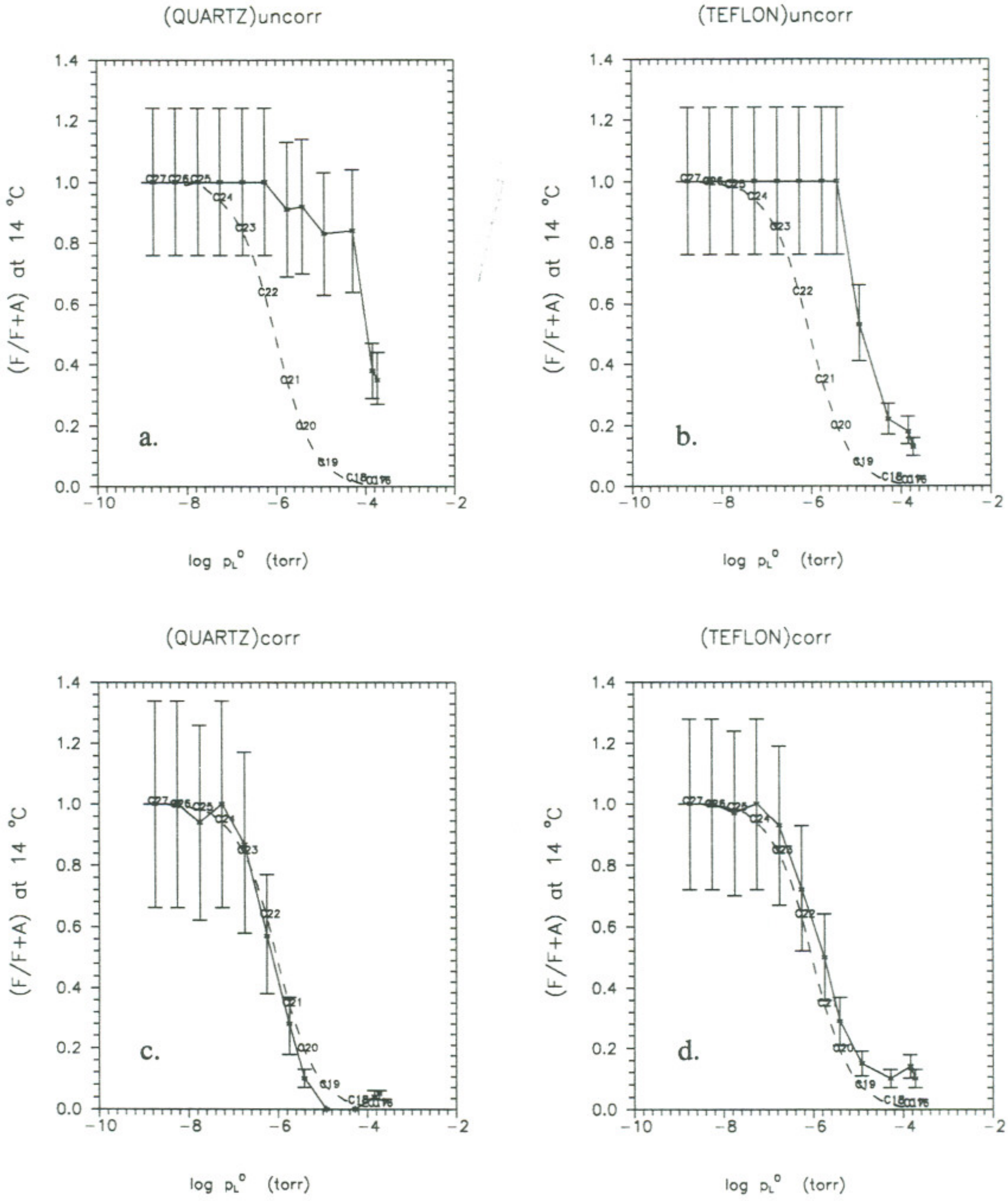

Figure 6.26. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 4/9/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

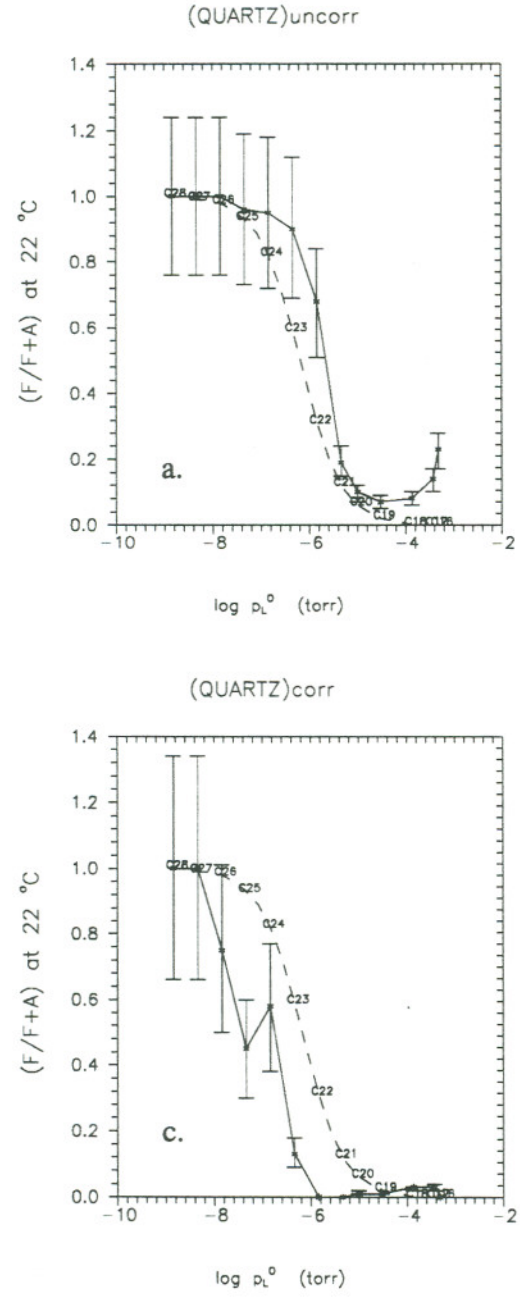

Figure 6.27. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 7/20/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

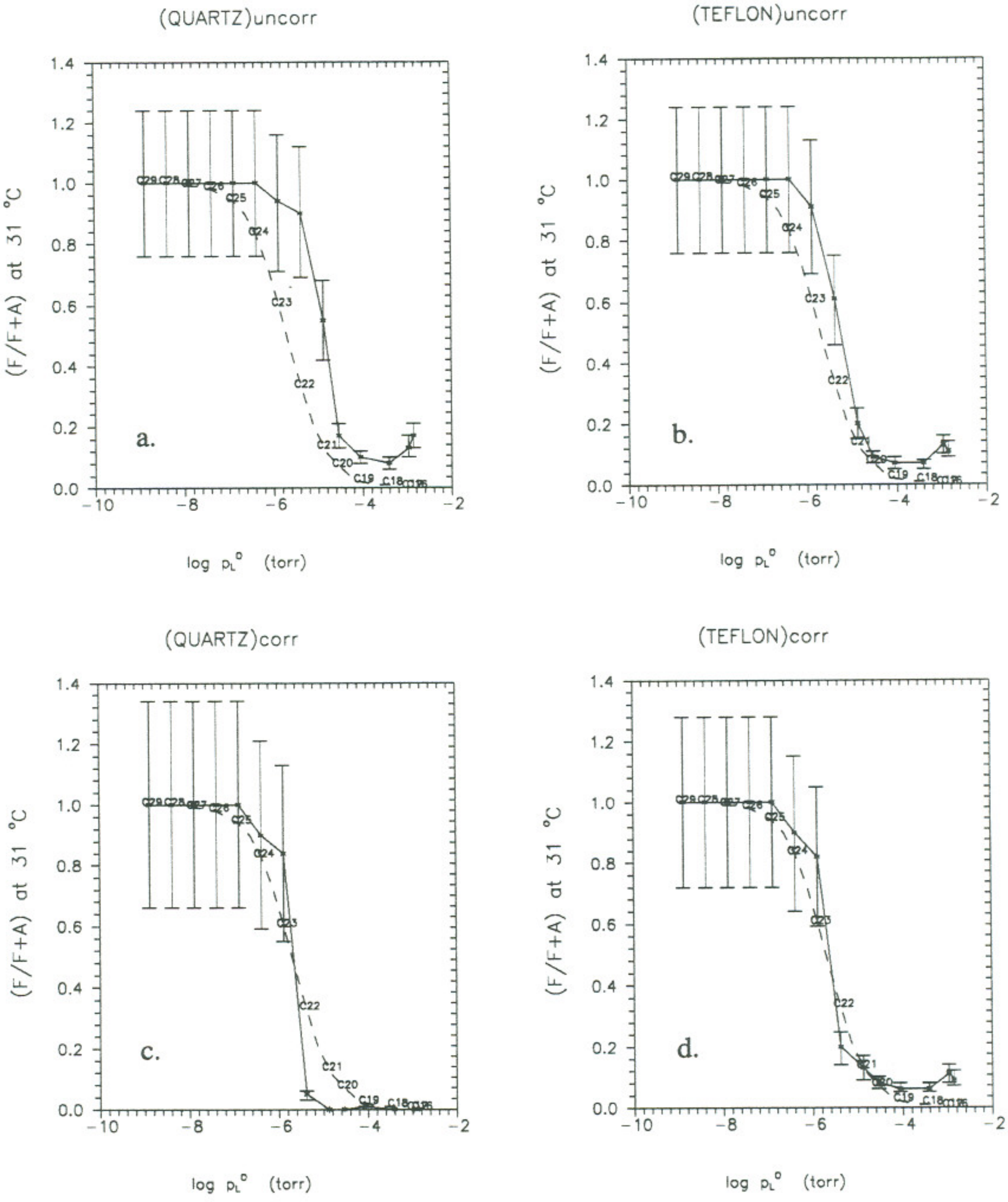

Figure 6.28. ϕ vs. log p^o_L for n-alkanes from samples collected in Portland, OR on 7/26/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

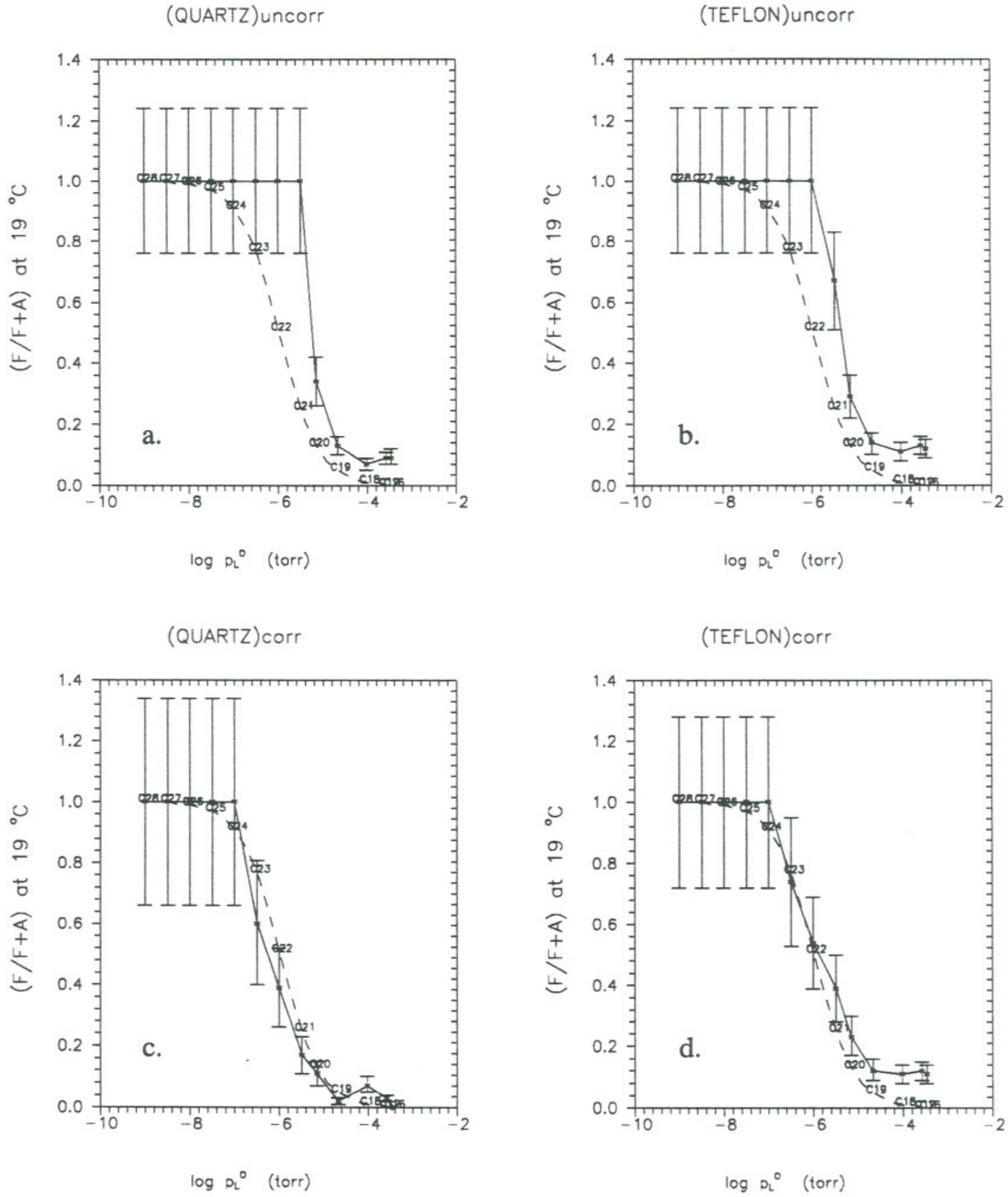

Figure 6.29. ϕ vs. log p°_{L} for n-alkanes from samples collected in Portland, OR on 8/1/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

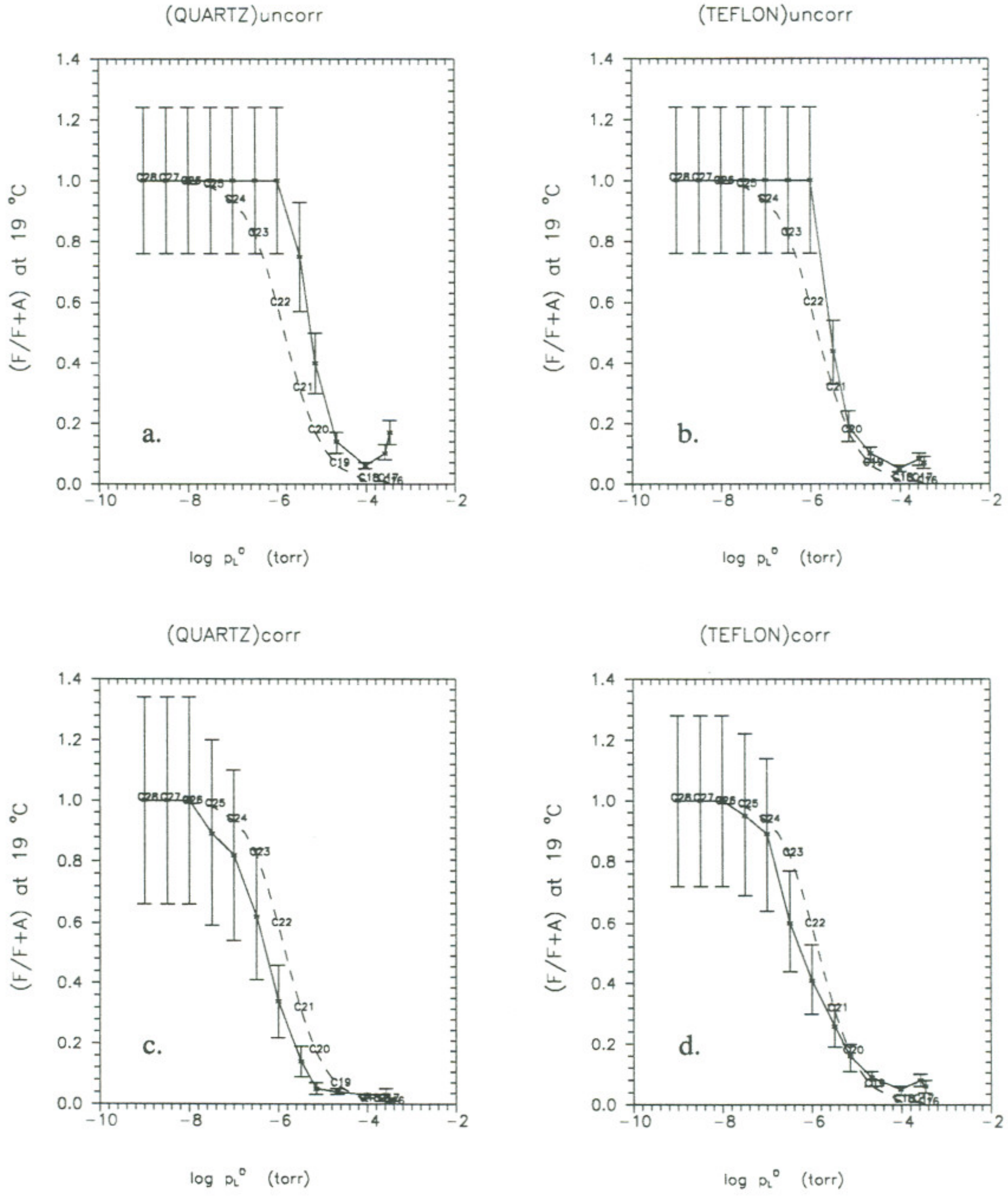

Figure 6.30. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 8/7/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

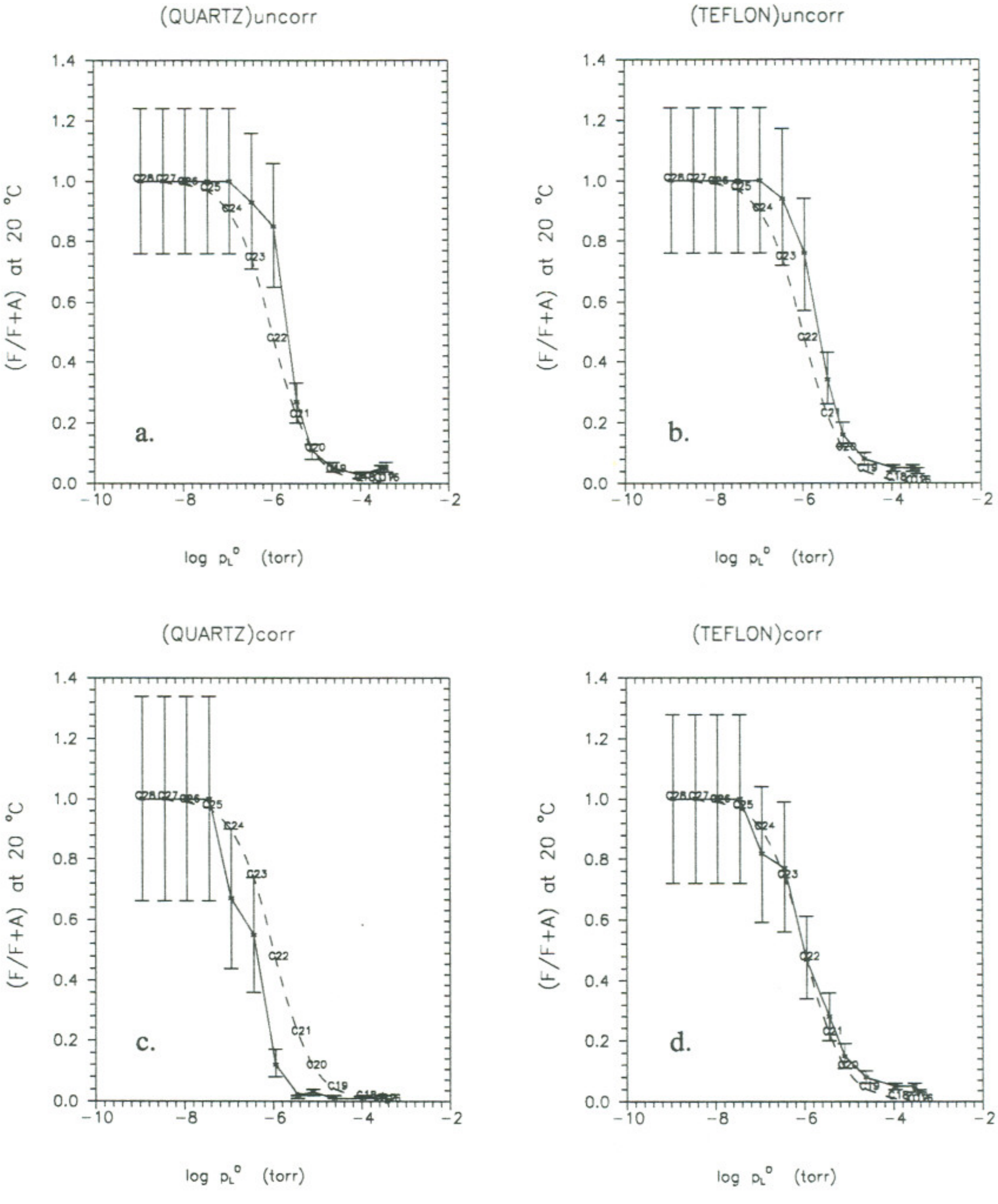

Figure 6.31. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 8/19/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

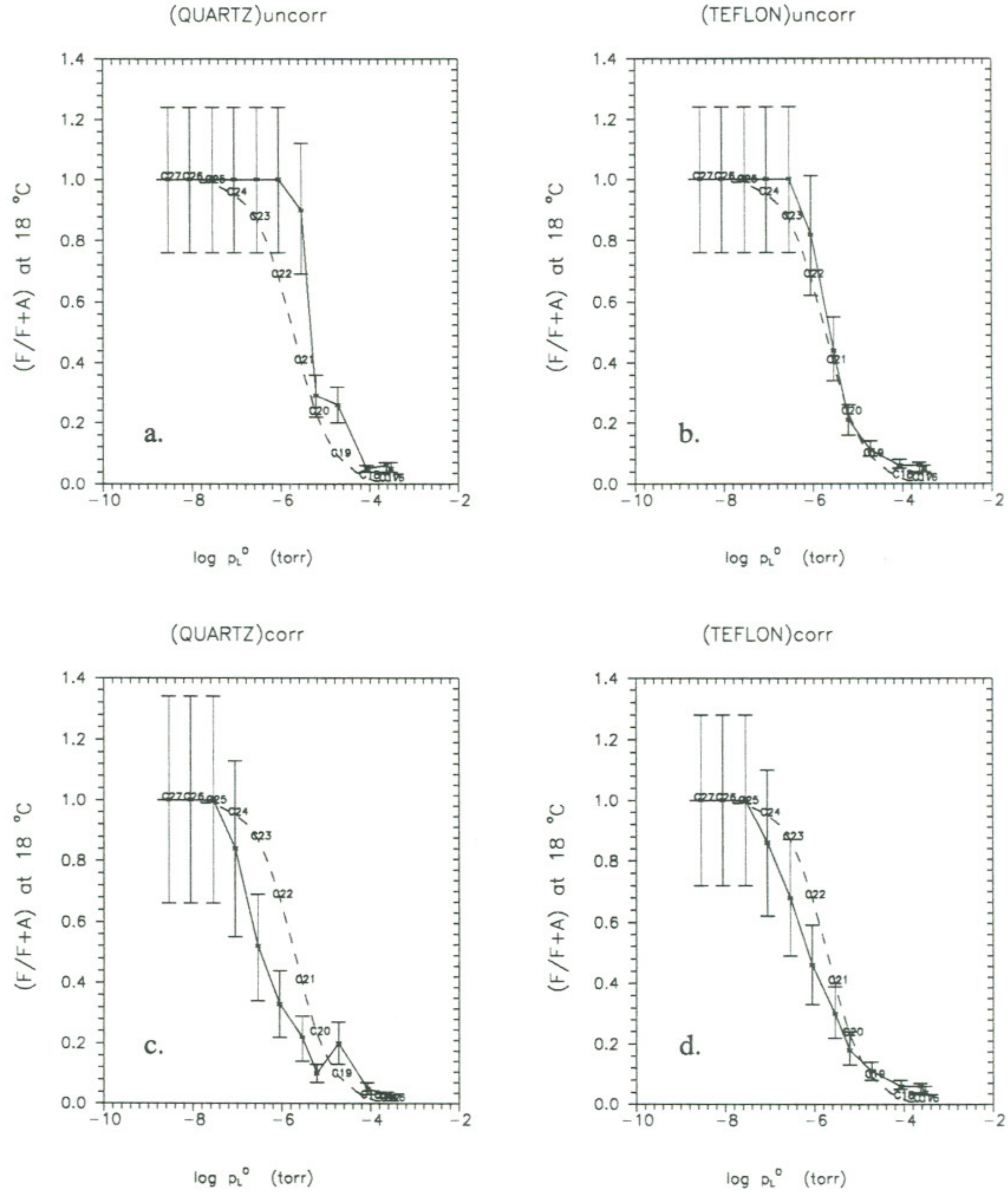

Figure 6.32. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 8/31/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

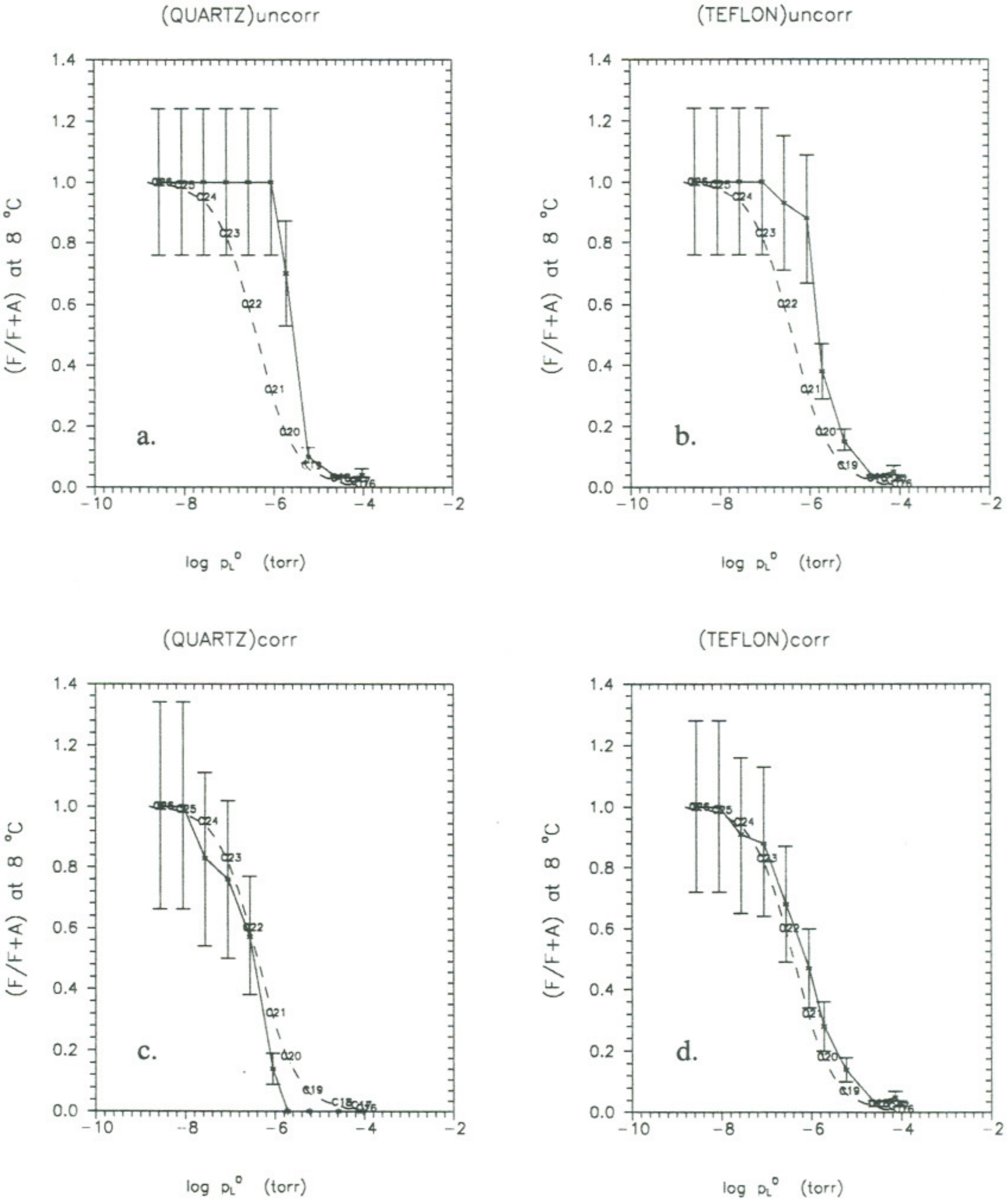

Figure 6.33. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 11/17/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

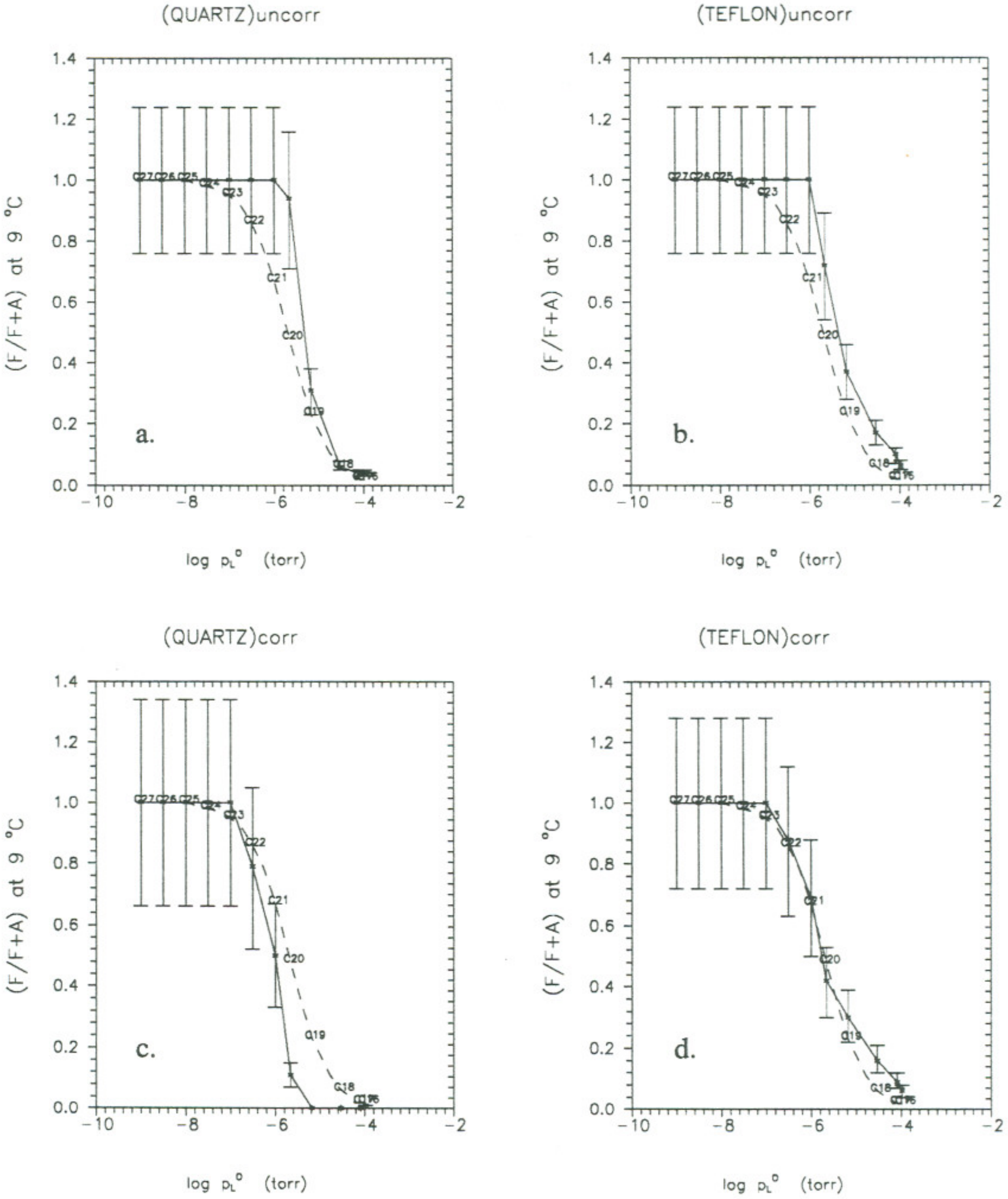

Figure 6.34. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 11/23/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

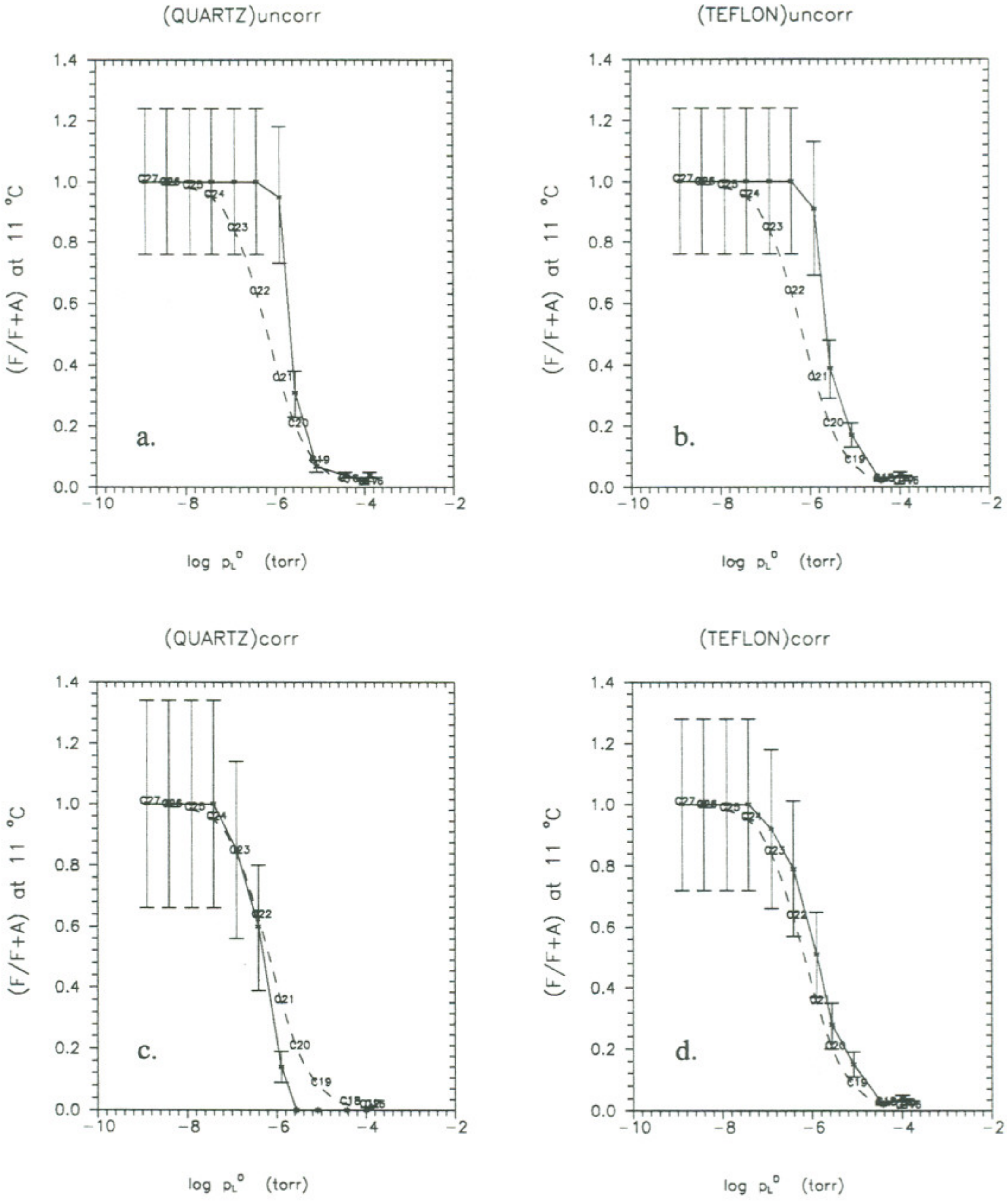

Figure 6.35. ϕ vs. log p°_L for n-alkanes from samples collected in Portland, OR on 11/29/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.8.

substantial amount.

A comparison between the estimated and observed values of ϕ for each event was carried out in two ways. A chi-squared test was first used to see if the differences between the estimated and observed values of ϕ was greater than what would be expected by randomness alone. In the second test, a linear regression analysis between the two data sets was used to determine the correlation and the direction that the predicted and observed data sets deviated from each other, if any.

The results of the chi-squared test were not tabulated as the difference between the observed and estimated data was only significantly different ($P = 0.05$) in one case (QU 4/9) out of a total of 48 did cases. The correlation coefficients from the regression analyses and averages of r^2 for the QU, QC, TU, TC plots are given in Table 6.9. The results of a one-sided t-test indicate that the average degree of fit for the QC data ($r^2_{ave} = 0.95$) was significantly higher than the average degree of fit for the QU data ($r^2_{ave} = 0.82$) at the 95% confidence level. The results from the Teflon sampling train were compared in a similar manner and the average degree of fit for the TC data ($r^2_{ave} = 0.98$) was significantly higher than the results from the average degree of fit of the TU data ($r^2_{ave} = 0.88$). For the sampling conditions encountered during this study, it has been concluded that: 1) in most cases, using either uncorrected or corrected values of ϕ, good agreement was found between experimental values of ϕ and those estimated from Junge's ϕ equation using an average value of $c_j\theta$; and 2) correcting for the sampling artifact of gas adsorption to QFFs provided significantly higher correlations between the

Table 6.9. Values of the Correlation Coefficient (r^2) from Plots of Observed vs. Estimated Values of ϕ for the Target n-Alkanes from Portland, OR in 1988.

	Correlation Coefficients (r^2)											
Plot	2/27	3/16	4/9	7/20	7/26	8/1	8/7	8/19	8/31	11/17	11/23	11/29
QU	0.80	0.68	0.53	0.93	0.85	0.77	0.89	0.99	0.89	0.74	0.88	0.84
QC	0.99	0.99	0.99	0.84	0.96	0.98	0.96	0.94	0.90	0.98	0.94	0.97
TU	0.83	0.67	0.63	0.99	0.95	0.88	0.94	0.96	0.99	0.86	0.94	0.86
TC	0.95	1.00	0.99	0.92	0.97	0.99	0.97	1.00	0.96	0.99	0.99	0.98

AVE[a]	QU	0.82 ± 0.12
AVE	QC	0.95 ± 0.04
AVE	TU	0.88 ± 0.12
AVE	TC	0.98 ± 0.02

a) average value of r^2 for all 12 sampling events.

observed and estimated values of ϕ.

6.3.2. Fraction Associated with the Particulate Phase for the Target PAHs

Values of $c_J\theta$, from the y-intercepts (log $1/c_J\theta$) of log A/F vs. log p°_L plots for the target PAHs are given in Table 6.10. The values of $c_J\theta$ obtained from the plots of the target PAHs were generally higher than the $c_J\theta$ values obtained from the n-alkanes for every sampling event. Over all of the sampling events, the average value of $c_J\theta$ was 5.61×10^{-6} and 1.12×10^{-6} torr (Section 6.3.2) for the target PAHs and n-alkanes, respectively.

The average value of $c_J\theta$ obtained for the PAHs may be overestimated by the relatively large contribution that three of the values has on the average. For example, the average value of $c_J\theta$ with those three points omitted was 1.36×10^{-6} torr which is very close to the estimate obtained from the n-alkanes. The average of the three omitted values was 12.7×10^{-6} torr. It is not clear why these three values are higher. If the median was used, instead of the mean, $c_J\theta$ would be 1.81×10^{-6} torr.

Plots of ϕ vs. log p°_L for QU, QC, TU, and TC (Section 6.1.2) cases are given in Figures 6.36 - 6.43. The dashed lines in each of the four plots from each sampling event was calculated from eq 6.4 and the corresponding estimate of $c_J\theta$ from Table 6.10. The results from the chi-squared analyses revealed that there were no significant differences between the observed and estimated values of ϕ at

Table 6.10. Values of $c_J\theta$ for the Target PAHs from the Regression of log A/F vs. log p°_{L} on QU, QC, TU, and TC plots , for Portland OR, 1988.

	$c_J\theta \times 10^6$ (torr)							
Plot	7/20	7/26	8/7	8/19	8/31	11/17	11/23	11/29
QU	27.7	12.4	5.66	1.40	2.00	1.21	0.77	2.56
QC	27.7	12.4	5.66	1.40	2.00	0.78	0.42	1.61
TU	20.1	6.81	3.48	1.76	1.78	1.87	0.69	1.77
TC	20.1	6.81	3.48	1.76	1.78	1.32	0.61	1.86
AVE[a]	23.9	9.61	4.57	1.58	1.89	1.05	0.52	1.74

a) average of QC and TC only.

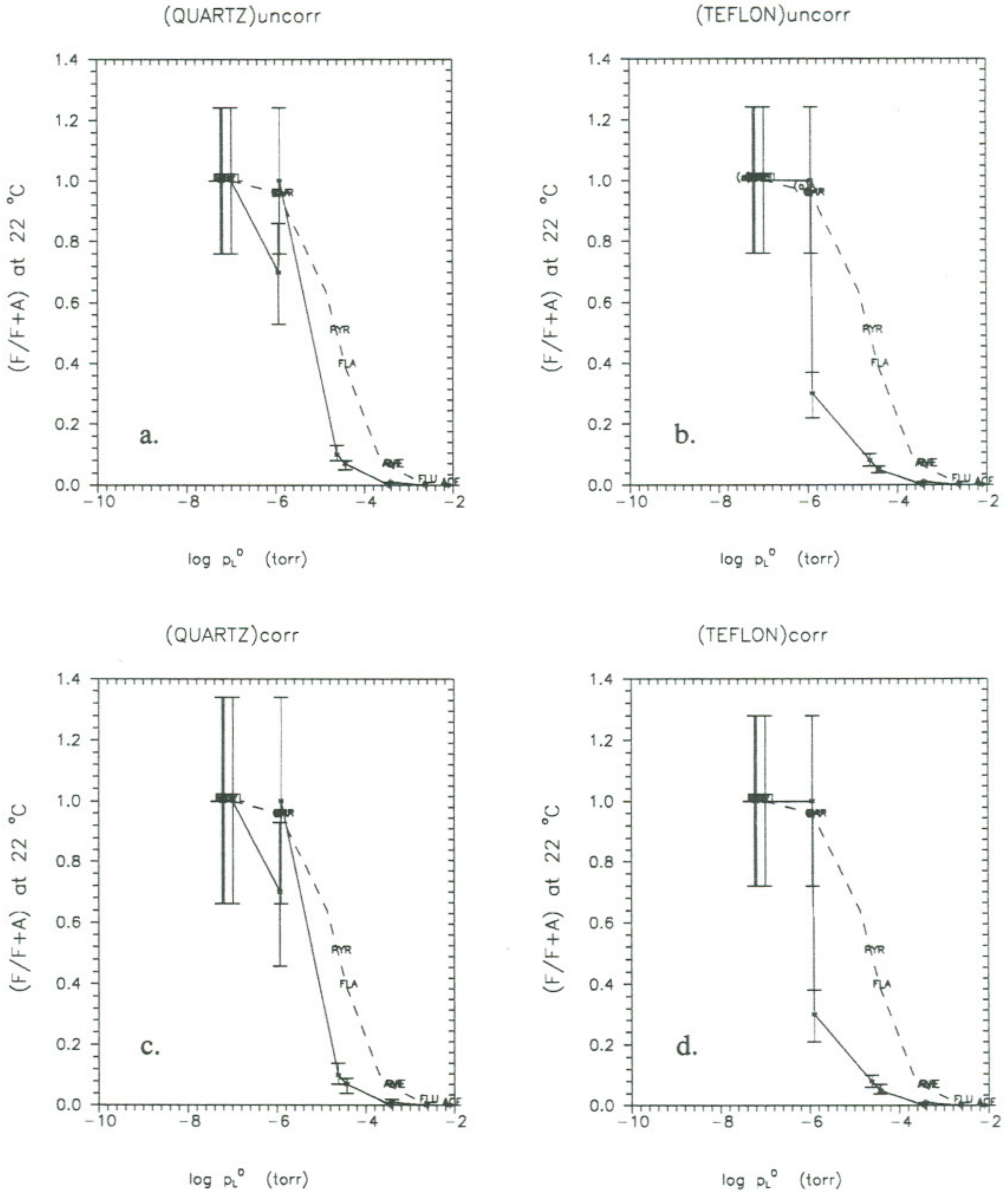

Figure 6.36. ϕ vs. log p°_L for PAHs from samples collected in Portland, OR on 7/20/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

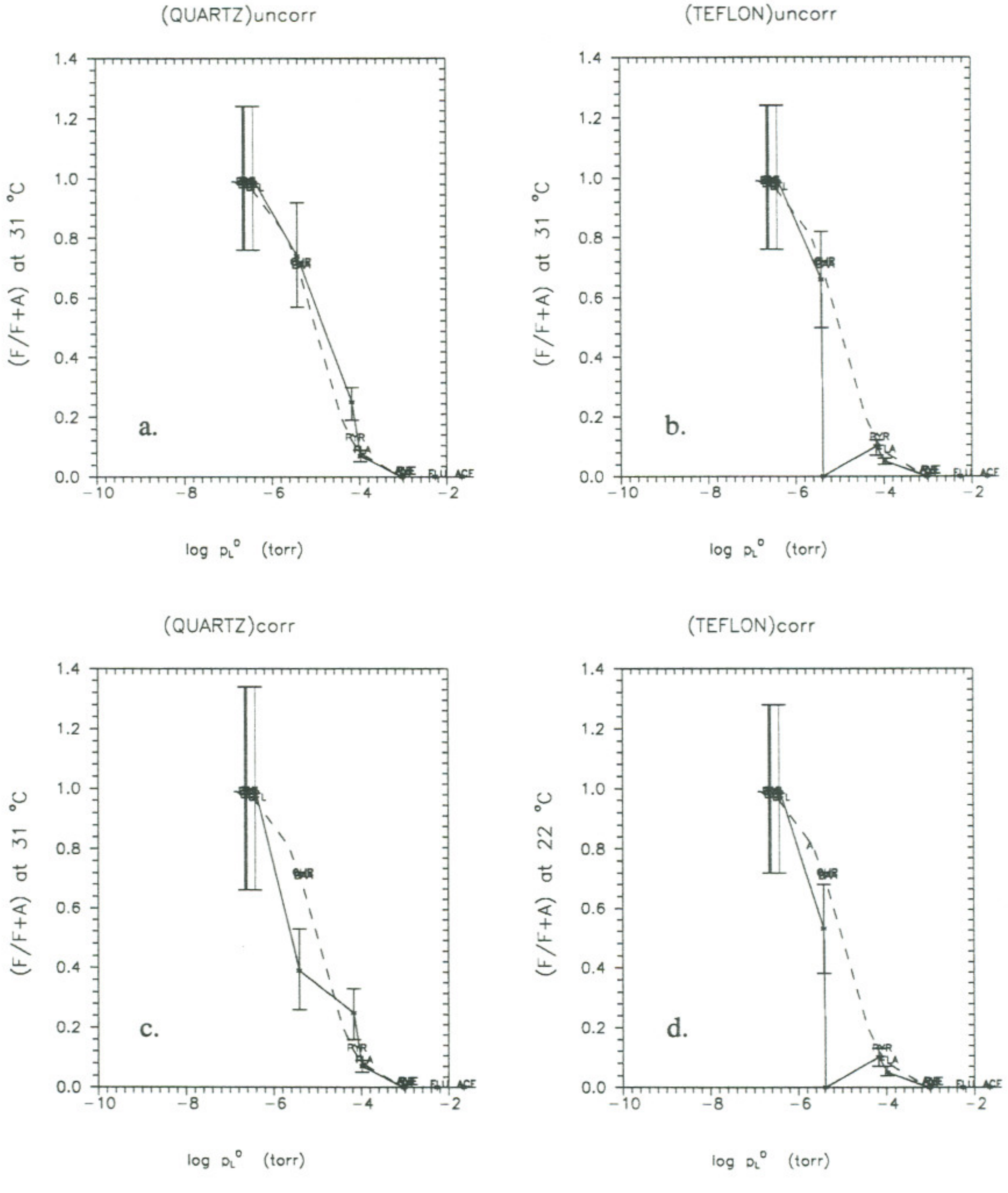

Figure 6.37. ϕ vs. log p°$_L$ for PAHs from samples collected in Portland, OR on 7/26/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

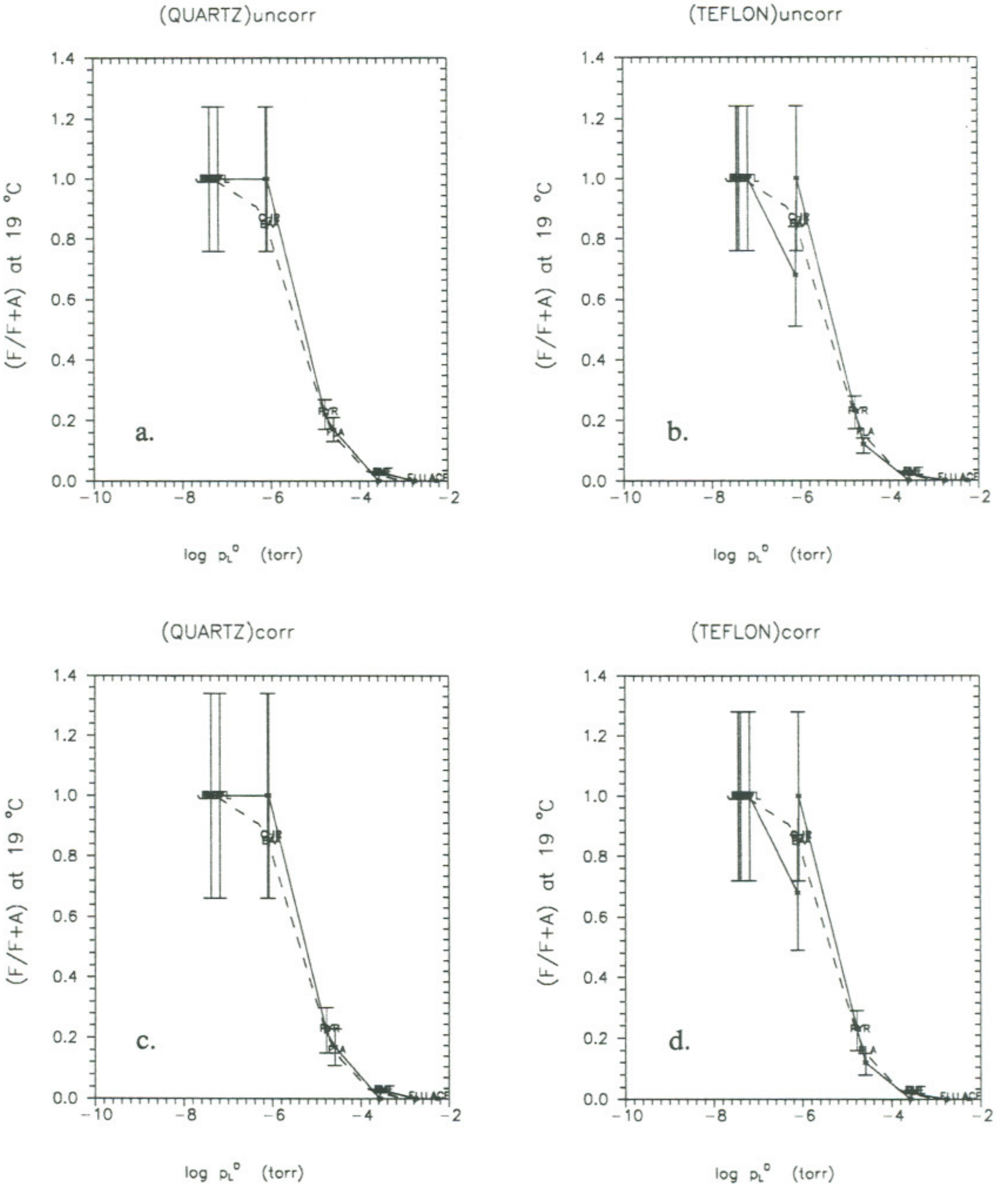

Figure 6.38. ϕ vs. log p°_L for PAHs from samples collected in Portland, OR on 8/7/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

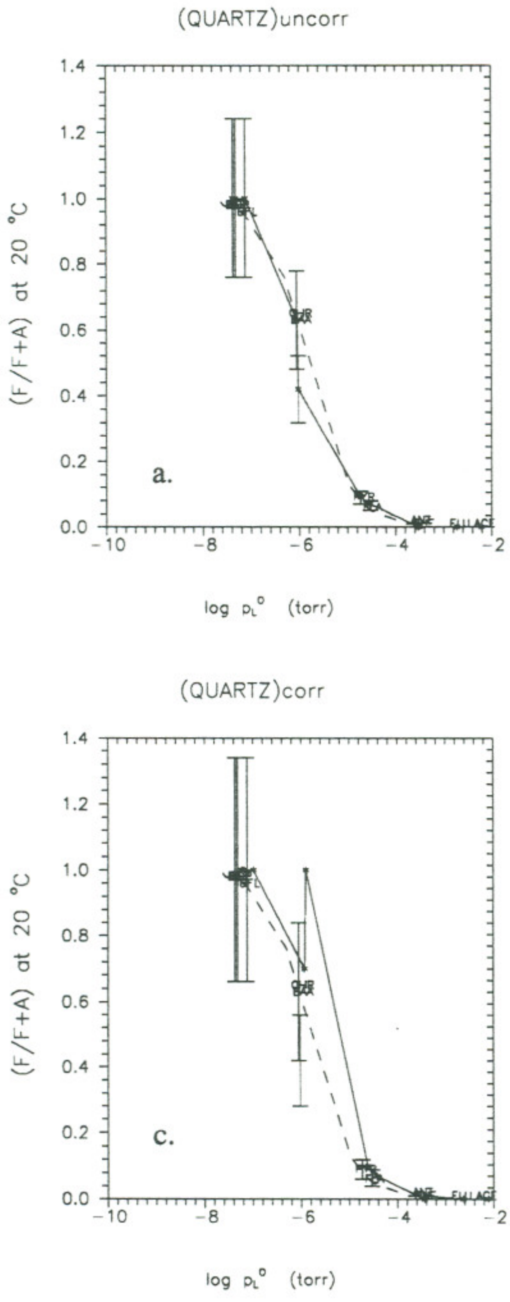

Figure 6.39. ϕ vs. log p°_L for PAHs from samples collected in Portland, OR on 8/19/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

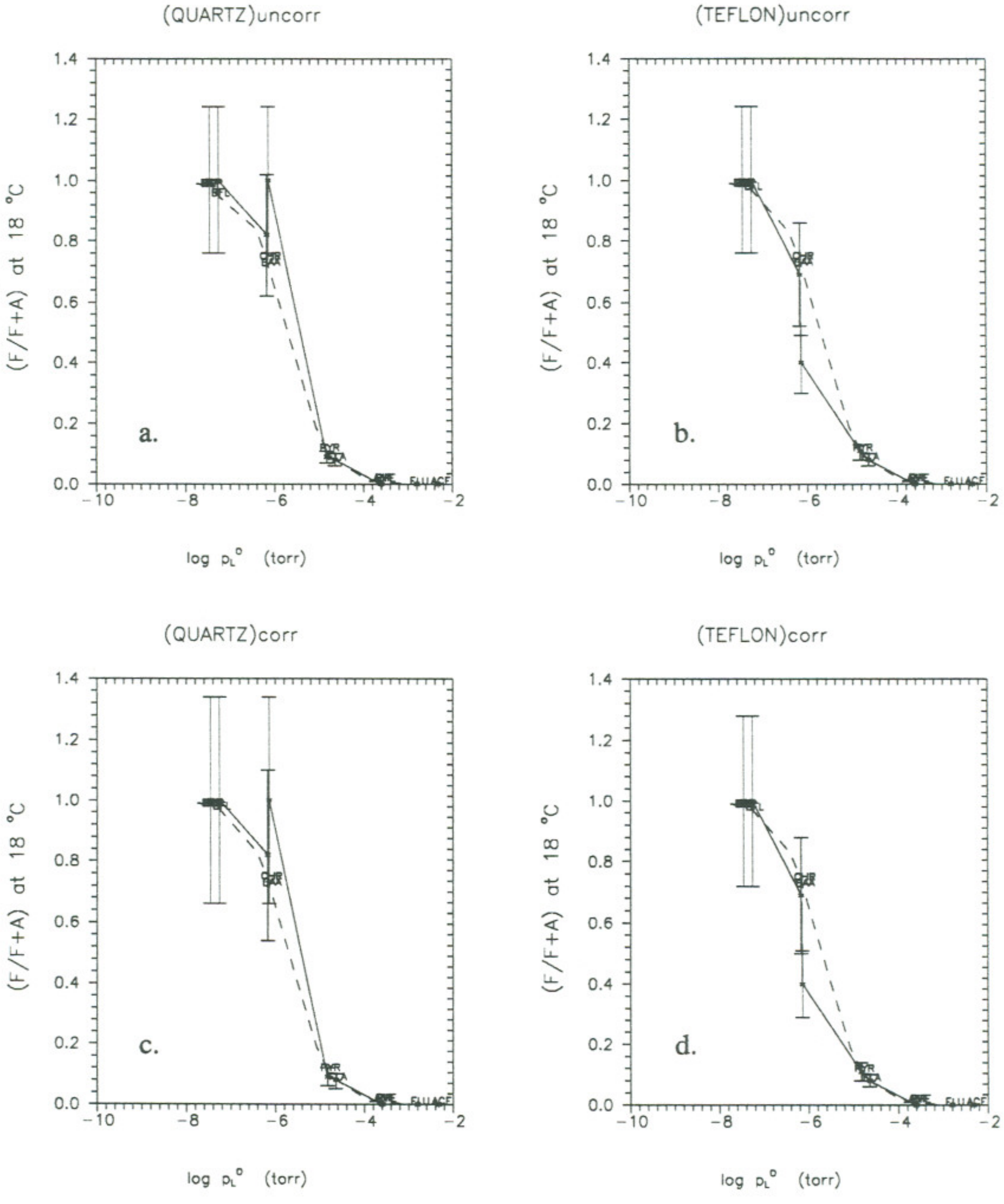

Figure 6.40. ϕ vs. log p°_{L} for PAHs from samples collected in Portland, OR on 8/31/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

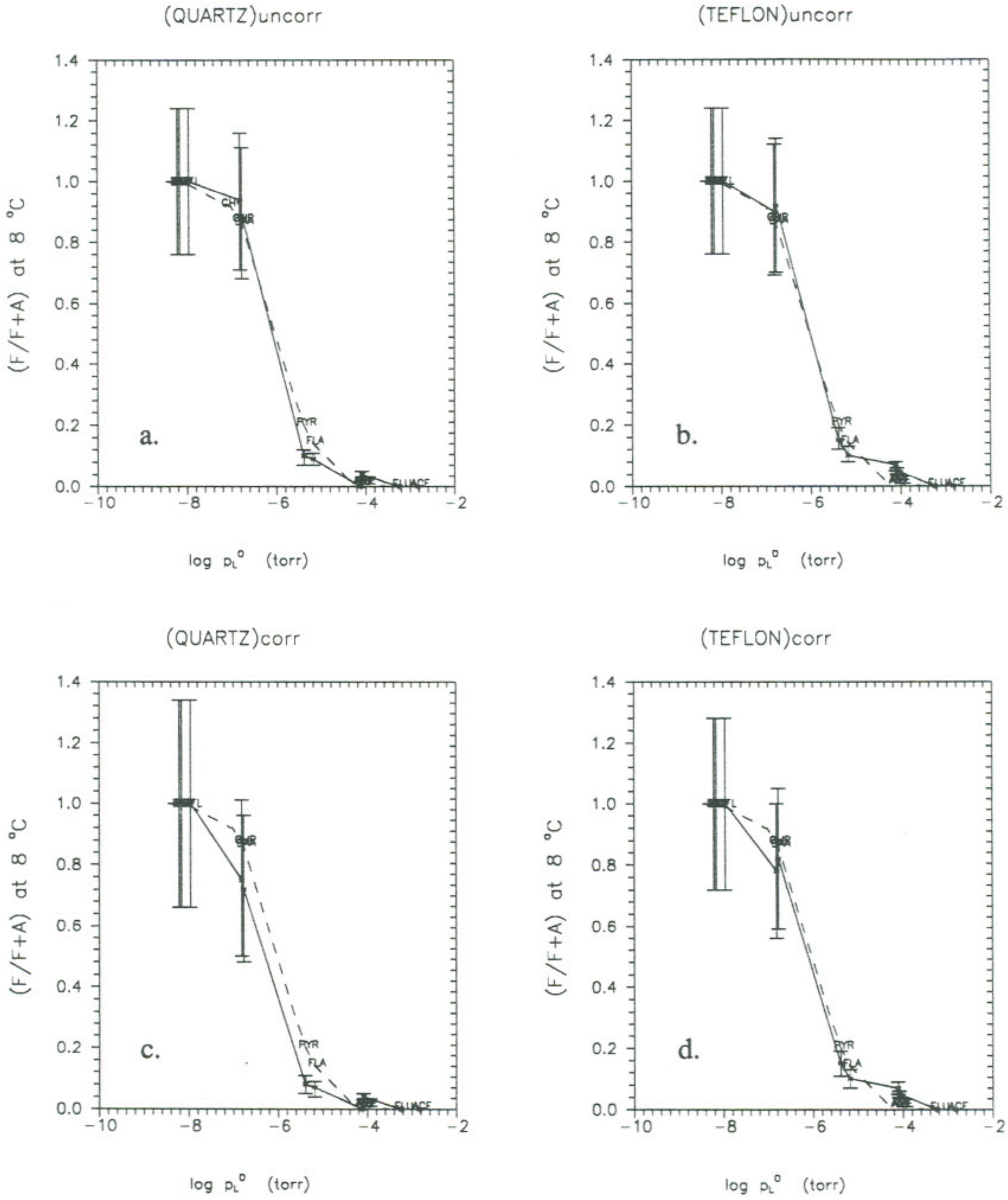

Figure 6.41. Phi vs.. log p°$_L$ for PAHs from samples collected in Portland,, OR on 11/17/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

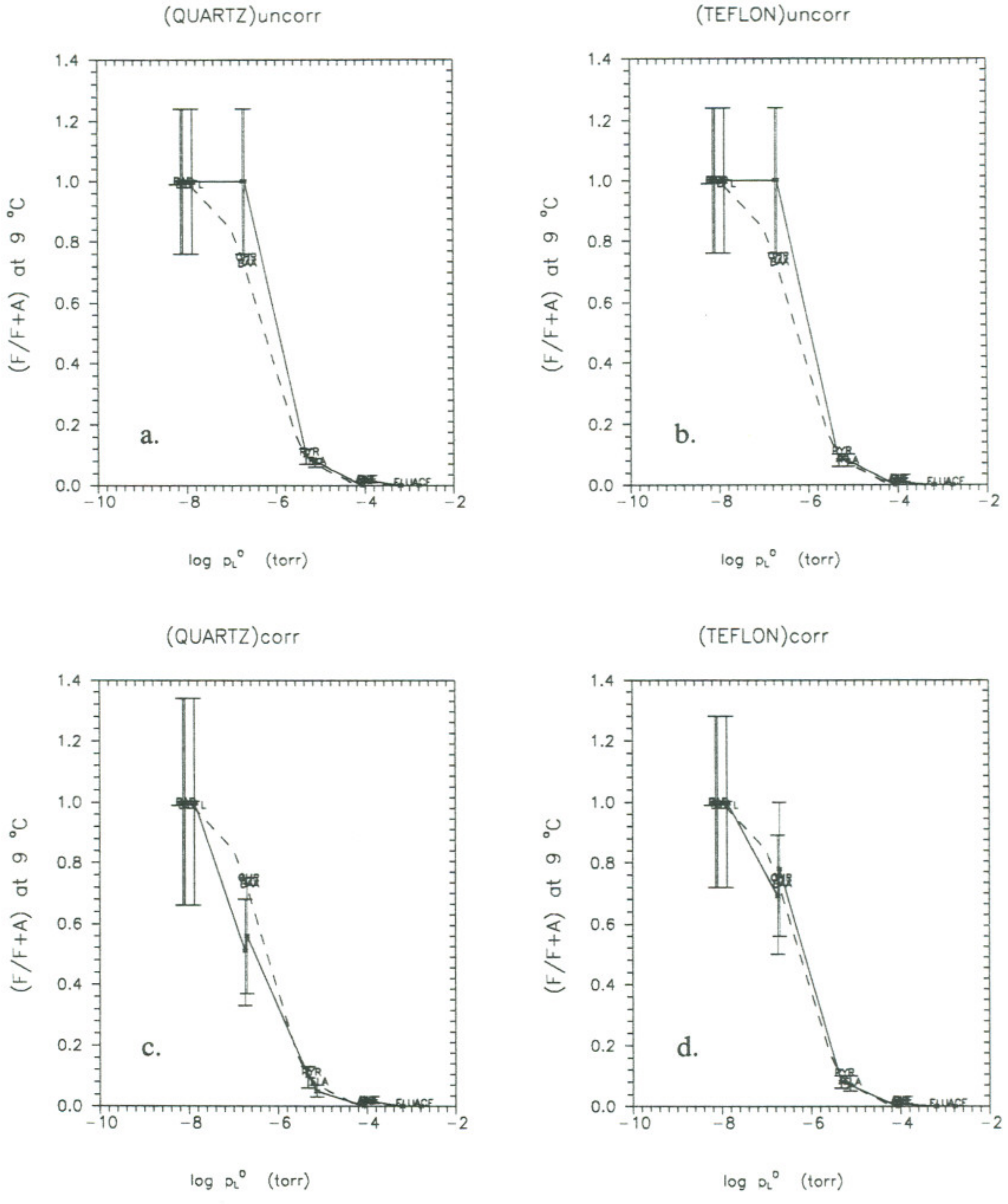

Figure 6.42. ϕ vs. log p°_L for PAHs from samples collected in Portland, OR on 11/23/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

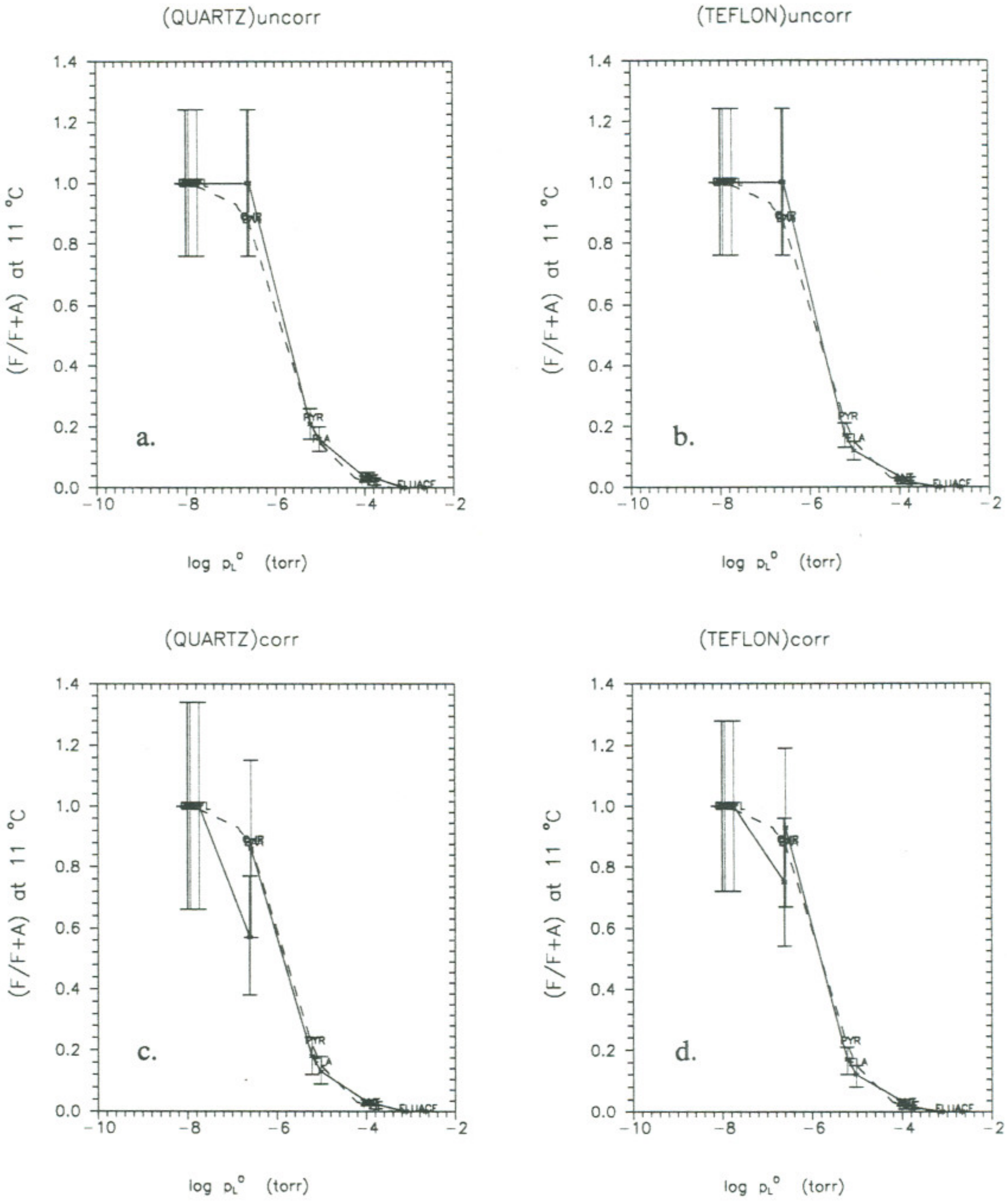

Figure 6.43. ϕ vs. log $p°_L$ for PAHs from samples collected in Portland, OR on 11/29/88. a) QU - uncorrected for gas phase adsorption; b) QC - corrected for gas phase adsorption; c) TU - uncorrected for gas phase adsorption; d) TC - corrected for gas phase adsorption. See Figure 6.2. Dashed line is from equation 6.4 and Table 6.10.

the 95% confidence level.

Since there was very little gas adsorption to the QFFs for the target PAHs, there were very little differences between the uncorrected and corrected values of ϕ in most of the sampling events. Thus, there were only small differences in r^2 between the uncorrected and corrected values of ϕ in a regression analysis of observed vs. predicted values of ϕ. The average value of r^2 was > 0.94 in all four types of plots investigated for the events sampled.

Chapter 7. Summary and Conclusions

A method has been developed for the determination of the gas and particulate phase concentrations of n-alkanes and PAHs in air samples in a manner that minimizes sampling artifacts. Ambient gas and particulate phase concentrations were determined for samples obtained at an urban residential site in Portland, OR during 1988. The ambient temperatures ranged between 7 - 31°C. The concentrations were used to determine equilibrium distribution constants between the gas and particulate phase (K). Distribution constants of this type can be used as primary inputs for compartmental models used to predict the fate of an organic compound in the environment.

The air samplers used to obtain the data were designed to differentiate between the gas and particulate phases as well as minimize the potential for sampling artifacts. Two potential sampling artifacts were considered in the design of the sampler; gas adsorption to a filter collecting suspended particulate matter, and volatilization of the organic compounds associated with the particulate matter collected on the filter.

For each sampling event, gas adsorption to the filter collecting the particulate material was corrected for by placing a second filter behind the front filter. The second filter provided a measure of the amount of adsorption from the gas phase that occurred onto the front filter. Volatilization artifacts were minimized by operating at a relatively high volumetric flow rate over a relatively short sampling period (6 hr). Thus, both fluctuations in temperature and air parcel heterogeneity were minimized.

Gas adsorption to the filters was studied using two identical samplers. One of the samplers utilized two QFFs, one after the other. The second utilized a Teflon membrane filter (TMF) followed by a QFF. Since the surface area of the TMFs is much less than that of the QFFs, if physical adsorption is responsible for the gas adsorption to filters, then the backup QFF (TQB) in the Teflon sampling train will provide a better estimate of gas adsorption to a primary filter. Polyurethane foam sheets (PUFSs) and Tenax-TA air desorption cartridges (ADCs) were used to collect the target compounds in the gas phase for both samplers.

Partitioning between the gas and particulate phases was examined experimentally by computing values of A(TSP)/F, where A and F represent the measured gas and particulate phase concentrations, respectively, and TSP is the total suspended particulate concentration. For a given compound and sampling event, experimental values of K were calculated four ways: 1) A and F measurements from the quartz sampling train using QFFs and PUFSs; 2) A and F measurements from the quartz sampling train corrected for gas adsorption by adding the concentration measured on the TQB to the PUFSs and subtracting the concentration measured on the TQB from the primary QFF; 3) A and F measurements from the Teflon sampling train using TMF and PUFSs; and 4) A and F measurements from the Teflon sampling train corrected for gas adsorption by adding the TQB concentration to the concentration measured on the PUFSs. Experimental values of K for the n-alkanes and PAHs were examined as a function of a compound's subcooled vapor pressure (p°_{L}) within the framework of equilibrium adsorption theory. Equilibrium adsorption theory was then recast by examining values of ϕ for the target n-alkanes and PAHs as a function of p°_{L}.

Gas adsorption to the QFFs was found to be a significant sampling artifact for the n-alkanes (C16 to C23) and three of the PAHs (phenanthrene, anthracene, and fluoranthene). The TQB filter provided the best estimate of the magnitude of gas adsorption to the QFFs. Depending on the sampling conditions and information needed from the experiment, gas adsorption to QFFs should be considered when designing atmospheric filtration experiments for compounds that have vapor pressures in the 10^{-3} - 10^{-6} torr range.

For the n-alkanes and PAHs, the correlation between log K vs. log p°_{L} and what would be predicted from equilibrium adsorption theory was generally quite high. However, for all events, the correlation between log K vs. log p°_{L} was significantly better when the values of K were corrected for gas adsorption. The agreement between the functionality of log K and log p°_{L} and that predicted from equilibrium adsorption theory was also much better.

Negative deviations from what would be expected from equilibrium adsorption theory were observed for compounds that have high values of p°_{L}. The negative deviation may be caused by a fraction of each compound being bound in the particulate phase and nonexchangeable with the gas phase. The nonexchangeable percent for hexadecane, the target compound with the highest percentage of nonexchangeable material, was estimated to be ~2 - 6%.

The fraction of a compound's concentration in the particulate phase (ϕ) was examined within the framework of equilibrium adsorption theory as a function of a compounds p°_{L}. For the n-alkanes in the range of C19 to C24, gas adsorption had a significant effect on the values of ϕ. Without corrections for gas adsorption by filters, it was not uncommon for ϕ to be overestimated by a factor of ~2 to 3, and up to a factor of ~8 during the sampling events in this study. The PAHs exhibited significantly less gas adsorption to the filters. Thus, there was not much difference in the values of ϕ between the uncorrected and corrected values of ϕ.

In light of the results of this study, three recommendations can now be made for future studies on partitioning in the atmosphere: 1) gas adsorption of the volatile compounds to QFFs must be considered when designing a sampling strategy; 2) gas adsorption to TMFs should be examined in a detailed manner to determine if there is an artifact associated with the use of these filters; 3) the effect of relative humidity on partitioning should be examined for studies in the laboratory and in the field.

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APPENDICES

In Appendix 1, the procedure for identification and quantification of target compounds on the Finnigan GC/MS Incos data system are presented. In Appendix 2, the atmospheric gas and particulate phase concentrations from the quartz and Teflon sampling trains in Portland, OR in 1988 are presented.

```
          *SETN
THRCR1
          *
          GETN
          ISFD1
                    *SET IS;GETL #1;SEAR/V (I;$;&;N1,100,100;D-50,50;E)
                    *
          SETL IS
          GETL #1
          SEAR/V (I;$;&;N1,100,100;D-50,50;E)
SETL S1
THRCR2
                    *GETL; SET1 !17;CHRO (I;-;/;%;#;H-40,40;E);LOOP
                    *
                    GETL
                    SET1 !17
                    CHRO (I;-;/;%;#;H-40,40;E)
                    LOOP
          ISFD2
                    *SET IS;GETL #2;SEAR/V (I;$;&;N1,100,100;D-50,50;E)
                    *
          SETL IS
          GETL #2
          SEAR/V (I;$;&;N1,100,100;D-50,50;E)
SETL S2
THRCR2
                    *GETL; SET1 !17;CHRO (I;-;/;%;#;H-40,40;E);LOOP
                    *
                    GETL
                    SET1 !17
                    CHRO (I;-;/;%;#;H-40,40;E)
                    LOOP
          LOOP
```

Figure A1.1 Trace of target compound identification procedure THRECR, written in Finnigan's operating system, Pankow (1986).

```
SETN
QSLRNM
      *GETN
      SETQ DUMMY
      SETS $
      SETL
      EDQL $ (-;W;E)
      QSLRN1
            *
            EDQL (-;W;E)
            GETS
            GETL
      QSLRN2
            *
            QSLRN3
                  *
                  QSLRN4
                        *
                        IF !1, QSLRN3 #1
                        CHRO (I;-;R;#;$;G-1,1;N1,2;A>4,1;D-40,40;H;E)
                        EDQL $ (A;E)
                        RETU QSLRN2
                  EDQL $ (-;N;#;A;E)
            LOOP
      LOOP
```

Figure A1.2. Trace of target compound integration and quantification procedure QUSLRN, written in Finnigan's operating system, Pankow (1986).

Table A2.1a. Atmospheric Concentrations of Target SOCs from Portland, OR on 2/27/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.27 ± 0.15	1.21 ± 0.15	12.46 ± 1.36	12.99 ± 1.42
C17	0.61 ± 0.07	0.90 ± 0.14	15.88 ± 2.01	9.64 ± 1.12
PRI	0.76 ± 0.10	1.20 ± 0.14	5.99 ± 0.76	6.05 ± 0.61
C18	0.48 ± 0.06	1.39 ± 0.18	11.98 ± 1.16	2.93 ± 0.44
PHY	3.83 ± 0.46	2.42 ± 0.36	40.94 ± 4.57	15.34 ± 1.67
C19	1.04 ± 0.10	3.47 ± 0.40	11.32 ± 1.24	4.27 ± 0.49
C20	2.57 ± 0.25	ND[f]	2.02 ± 0.25	0.25 ± 0.04
C21	3.29 ± 0.37	0.21 ± 0.03	0.62 ± 0.05	ND
C22	3.98 ± 0.41	ND	1.22 ± 0.16	ND
C23	4.57 ± 0.51	0.22 ± 0.03	0.59 ± 0.07	ND
C24	5.10 ± 0.68	ND	ND	ND
C25	6.06 ± 0.78	ND	ND	ND
C26	4.24 ± 0.46	ND	ND	ND
C27	5.37 ± 0.64	ND	ND	ND
C28	3.38 ± 0.39	ND	ND	ND
C29	6.86 ± 0.67	ND	ND	ND
C30	4.18 ± 0.86	ND	ND	ND
C31	7.66 ± 0.66	ND	ND	ND

Table A2.1a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 2/27/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	NA[g]	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	1.89 ± 0.23	ND	11.57 ± 1.13	3.01 ± 0.35
PYR	NA	NA	NA	NA
BaA	2.91 ± 0.33	ND	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	2.47 ± 0.25	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS in quartz/quartz combination. e) PQB = backup PUFS in quartz/quartz combination. f) ND = not detected. g) NA = not analyzed.

Table A2.1b. Atmospheric Concentrations of Target SOCs from Portland, OR on 2/27/88.

	Concentrations (ng/m³)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	1.53 ± 0.18	1.20 ± 0.19	18.47 ± 2.05	14.37 ± 1.56
C17	0.84 ± 0.09	0.81 ± 0.09	10.65 ± 1.31	10.44 ± 1.26
PRI	0.98 ± 0.12	0.63 ± 0.07	16.60 ± 1.89	5.22 ± 0.68
C18	0.29 ± 0.05	0.62 ± 0.08	12.46 ± 1.43	5.54 ± 0.61
PHY	5.63 ± 0.86	4.46 ± 0.47	46.44 ± 6.01	22.11 ± 3.01
C19	1.65 ± 0.21	1.21 ± 0.19	12.85 ± 1.39	6.68 ± 0.76
C20	1.32 ± 0.16	2.60 ± 0.30	3.05 ± 0.41	0.39 ± 0.06
C21	2.04 ± 0.22	1.43 ± 0.19	0.42 ± 0.06	ND[f]
C22	4.17 ± 0.53	1.19 ± 0.15	0.71 ± 0.09	ND
C23	4.94 ± 0.43	0.46 ± 0.05	0.44 ± 0.05	ND
C24	4.70 ± 0.59	0.39 ± 0.06	ND	ND
C25	5.91 ± 0.63	ND	ND	ND
C26	4.50 ± 0.49	ND	ND	ND
C27	5.41 ± 0.61	ND	ND	ND
C28	3.47 ± 0.41	ND	ND	ND
C29	6.35 ± 0.74	ND	ND	ND
C30	5.22 ± 0.58	ND	ND	ND
C31	8.43 ± 0.97	ND	ND	ND

Table A2.1b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 2/27/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	NA[g]	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	1.78 ± 0.22	0.52 ± 0.06	14.06 ± 1.59	4.00 ± 0.53
PYR	NA	NA	NA	NA
BaA	2.75 ± 0.34	ND	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	2.60 ± 0.29	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS in Teflon/quartz filter combination. e) PTB = backup PUFS in Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.2a. Atmospheric Concentrations of Target SOCs from Portland, OR on 3/16/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	2.47 ± 0.25	1.17 ± 0.16	11.67 ± 1.35	6.10 ± 0.76
C17	0.62 ± 0.07	1.92 ± 0.72	12.08 ± 1.41	3.52 ± 0.46
PRI	2.68 ± 0.29	2.96 ± 0.36	4.09 ± 0.53	1.76 ± 0.19
C18	1.54 ± 0.18	4.61 ± 0.58	4.83 ± 0.49	0.64 ± 0.07
PHY	0.36 ± 0.04	0.53 ± 0.06	ND[f]	ND
C19	4.02 ± 0.46	3.56 ± 0.42	2.33 ± 0.26	ND
C20	4.11 ± 0.49	ND	ND	0.64 ± 0.07
C21	3.46 ± 0.42	ND	ND	ND
C22	2.63 ± 0.28	ND	ND	ND
C23	2.42 ± 0.29	ND	ND	ND
C24	3.07 ± 0.41	ND	ND	ND
C25	3.37 ± 0.38	ND	ND	ND
C26	1.86 ± 0.21	ND	ND	ND
C27	2.49 ± 0.29	ND	ND	ND
C28	1.26 ± 0.18	ND	ND	ND
C29	1.45 ± 0.16	ND	ND	ND
C30	2.23 ± 0.27	ND	ND	ND
C31	2.29 ± 0.24	ND	ND	ND

Table A2.2a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 3/16/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	NA[g]	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	1.27 ± 0.15	1.47 ± 0.16	0.93 ± 0.13	ND
PYR	NA	NA	NA	NA
BaA	1.02 ± 0.16	ND	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	0.95 ± 0.14	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.2b. Atmospheric Concentrations of Target SOCs from Portland, OR on 3/16/88.

Compound	Concentrations (ng/m^3)[a]			
	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.98 ± 0.11	1.30 ± 0.09	11.49 ± 0.56	5.00 ± 0.11
C17	0.64 ± 0.07	1.35 ± 0.15	11.21 ± 0.13	2.72 ± 0.14
PRI	0.66 ± 0.05	1.47 ± 0.10	5.44 ± 0.18	2.66 ± 0.09
C18	0.50 ± 0.08	1.53 ± 0.12	7.11 ± 0.45	0.55 ± 0.12
PHY	ND[f]	0.41 ± 0.09	0.52 ± 0.07	ND
C19	1.65 ± 0.21	4.87 ± 0.33	2.74 ± 0.16	ND
C20	1.24 ± 0.12	3.23 ± 0.26	ND	ND
C21	1.49 ± 0.18	1.68 ± 0.23	ND	ND
C22	1.46 ± 0.12	0.76 ± 0.09	ND	ND
C23	1.94 ± 0.22	0.20 ± 0.05	ND	ND
C24	1.72 ± 0.24	ND	ND	ND
C25	3.02 ± 0.15	ND	ND	ND
C26	1.60 ± 0.19	ND	ND	ND
C27	2.63 ± 0.21	ND	ND	ND
C28	1.67 ± 0.09	ND	ND	ND
C29	4.87 ± 0.53	ND	ND	ND
C30	0.92 ± 0.13	ND	ND	ND
C31	2.87 ± 0.24	ND	ND	ND

Table A2.2b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 3/16/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	NA	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	0.61 ± 0.08	0.78 ± 0.06	3.48 ± 0.23	ND
PYR	NA	NA	NA	NA
BaA	0.67 ± 0.05	0.31 ± 0.04	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	1.07 ± 0.12	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS TEflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.3a. Atmospheric Concentrations of Target SOCs from Portland, OR on 4/9/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	2.23 ± 0.21	2.13 ± 0.16	3.33 ± 0.35	0.77 ± 0.45
C17	2.10 ± 0.26	4.06 ± 0.56	2.95 ± 0.22	0.45 ± 0.06
PRI	1.97 ± 0.07	4.60 ± 0.34	ND[f]	ND
C18	2.05 ± 0.12	3.78 ± 0.39	0.40 ± 0.06	ND
PHY	0.44 ± 0.05	ND	ND	ND
C19	3.87 ± 0.49	0.65 ± 0.04	0.80 ± 0.11	ND
C20	2.71 ± 0.13	ND	0.23 ± 0.06	ND
C21	3.08 ± 0.21	ND	0.31 ± 0.04	ND
C22	1.60 ± 0.12	ND	ND	ND
C23	3.04 ± 0.34	ND	ND	ND
C24	1.61 ± 0.18	ND	ND	ND
C25	7.27 ± 1.01	ND	ND	ND
C26	1.13 ± 0.04	ND	ND	ND
C27	7.63 ± 0.98	ND	ND	ND
C28	0.81 ± 0.12	ND	ND	ND
C29	7.50 ± 1.24	ND	ND	ND
C30	1.87 ± 0.23	ND	ND	ND
C31	6.66 ± 0.75	ND	ND	ND

Table A2.3a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 4/9/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	NA	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	1.38 ± 0.19	0.80 ± 0.11	ND	ND
PYR	NA	NA	NA	NA
BaA	0.93 ± 0.11	ND	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	0.74 ± 0.09	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.3b. Atmospheric Concentrations of Target SOCs from Portland, OR on 4/9/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.82 ± 0.11	1.85 ± 0.21	3.99 ± 0.42	1.37 ± 0.23
C17	0.98 ± 0.08	1.78 ± 0.15	3.76 ± 0.25	0.58 ± 0.07
PRI	0.23 ± 0.04	3.24 ± 0.26	ND[f]	ND
C18	0.44 ± 0.05	2.53 ± 0.37	1.56 ± 0.19	ND
PHY	ND	0.83 ± 0.11	ND	ND
C19	0.83 ± 0.06	4.00 ± 0.36	0.72 ± 0.06	ND
C20	0.88 ± 0.05	2.19 ± 0.30	ND	ND
C21	1.66 ± 0.21	1.67 ± 0.15	ND	ND
C22	1.14 ± 0.09	0.43 ± 0.08	ND	ND
C23	2.68 ± 0.32	0.21 ± 0.06	ND	ND
C24	1.08 ± 0.09	ND	ND	ND
C25	7.13 ± 1.12	0.21 ± 0.05	ND	ND
C26	1.12 ± 0.13	ND	ND	ND
C27	9.11 ± 1.08	ND	ND	ND
C28	0.94 ± 0.06	ND	ND	ND
C29	7.00 ± 0.86	ND	ND	ND
C30	2.92 ± 0.32	ND	ND	ND
C31	8.95 ± 0.96	ND	ND	ND

Table A2.3b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 4/9/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	NA	NA	NA	NA
FLU	NA	NA	NA	NA
PHE	NA	NA	NA	NA
ANT	NA	NA	NA	NA
FLA	0.68 ± 0.08	0.95 ± 0.08	0.42 ± 0.07	ND
PYR	NA	NA	NA	NA
BaA	0.69 ± 0.11	ND	ND	ND
CHR	NA	NA	NA	NA
BFL	NA	NA	NA	NA
BeP	NA	NA	NA	NA
BaP	0.55 ± 0.10	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS TEflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.4a. Atmospheric Concentrations of Target SOCs from Portland, OR on 7/20/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-alkanes				
C16	2.86 ± 0.33	3.00 ± 0.21	3.74 ± 0.42	5.92 ± 0.43
C17	2.96 ± 0.21	3.25 ± 0.48	7.99 ± 0.67	10.50 ± 1.13
PRI	0.72 ± 0.09	0.91 ± 0.07	1.51 ± 0.13	1.59 ± 0.17
C18	1.70 ± 0.20	1.45 ± 0.19	9.85 ± 1.10	10.45 ± 0.89
PHY	0.75 ± 0.12	0.44 ± 0.06	1.59 ± 0.17	2.35 ± 0.31
C19	1.62 ± 0.17	1.53 ± 0.03	13.51 ± 1.32	8.09 ± 1.23
C20	1.48 ± 0.09	1.82 ± 0.22	10.70 ± 0.89	3.26 ± 0.42
C21	2.23 ± 0.26	4.64 ± 0.53	8.10 ± 0.63	1.19 ± 0.16
C22	3.18 ± 0.21	6.18 ± 0.25	1.52 ± 0.12	ND[f]
C23	9.95 ± 1.12	4.39 ± 0.49	1.05 ± 0.19	ND
C24	5.99 ± 0.85	ND	0.31 ± 0.04	ND
C25	9.08 ± 1.16	ND	0.40 ± 0.05	ND
C26	4.77 ± 0.56	ND	ND	ND
C27	9.90 ± 1.07	ND	ND	ND
C28	4.90 ± 0.43	ND	ND	ND
C29	10.17 ± 0.86	ND	ND	ND
C30	5.08 ± 0.59	ND	ND	ND
C31	13.54 ± 1.21	ND	ND	ND

Table A2.4a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 7/20/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	0.34 ± 0.04	0.32 ± 0.05
FLU	ND	ND	3.51 ± 0.39	5.10 ± 0.61
PHE	0.23 ± 0.02	ND	14.68 ± 1.09	4.67 ± 0.63
ANT	ND	ND	1.24 ± 0.16	0.29 ± 0.04
FLA	0.38 ± 0.05	ND	5.05 ± 0.62	0.26 ± 0.05
PYR	0.24 ± 0.05	ND	2.13 ± 0.23	ND
BaA	0.22 ± 0.07	ND	ND	ND
CHR	0.60 ± 0.08	ND	0.26 ± 0.05	ND
BFL	1.81 ± 0.25	ND	ND	ND
BeP	0.77 ± 0.06	ND	ND	ND
BaP	0.28 ± 0.05	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.4b. Atmospheric Concentrations of Target SOCs from Portland, OR on 7/20/88.

	Concentrations (ng/m³)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	1.38 ± 0.17	3.51 ± 0.16	4.12 ± 0.44	6.57 ± 0.52
C17	1.99 ± 0.24	2.22 ± 0.12	8.31 ± 0.74	11.16 ± 0.99
PRI	ND[f]	0.98 ± 0.09	2.71 ± 0.19	2.15 ± 0.21
C18	1.46 ± 0.11	1.12 ± 0.09	9.36 ± 1.13	11.34 ± 0.99
PHY	ND	0.55 ± 0.04	0.99 ± 0.06	1.83 ± 0.23
C19	1.36 ± 0.14	1.38 ± 0.13	16.86 ± 1.11	10.04 ± 0.99
C20	1.23 ± 0.16	1.29 ± 0.17	11.27 ± 1.32	3.88 ± 0.55
C21	2.18 ± 0.26	2.89 ± 0.22	9.82 ± 1.12	2.49 ± 0.29
C22	2.05 ± 0.18	4.22 ± 0.45	5.27 ± 0.23	0.75 ± 0.10
C23	5.39 ± 0.68	7.46 ± 0.89	2.75 ± 0.31	1.32 ± 0.15
C24	5.51 ± 0.41	1.50 ± 0.17	1.05 ± 0.12	ND
C25	6.22 ± 0.69	3.34 ± 0.42	0.91 ± 0.11	ND
C26	3.93 ± 0.45	0.67 ± 0.08	0.22 ± 0.03	ND
C27	8.21 ± 1.00	ND	0.29 ± 0.03	ND
C28	4.43 ± 0.52	ND	ND	ND
C29	9.04 ± 1.14	ND	ND	ND
C30	4.21 ± 0.06	ND	ND	ND
C31	16.12 ± 1.96	ND	ND	ND

Table A2.4b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 7/20/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	0.49 ± 0.06	ND
FLU	ND	ND	3.74 ± 0.45	5.56 ± 0.86
PHE	0.21 ± 0.04	ND	15.92 ± 2.05	5.72 ± 0.08
ANT	ND	ND	0.89 ± 0.13	0.37 ± 0.05
FLA	0.32 ± 0.05	ND	5.44 ± 0.07	0.32 ± 0.05
PYR	0.22 ± 0.03	ND	2.46 ± 0.04	ND
BaA	0.22 ± 0.04	ND	0.53 ± 0.06	ND
CHR	0.53 ± 0.07	ND	ND	ND
BFL	1.58 ± 0.19	ND	ND	ND
BeP	0.76 ± 0.08	ND	ND	ND
BaP	0.40 ± 0.06	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.5a. Atmospheric Concentrations of Target SOCs from Portland, OR on 7/26/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.35 ± 0.17	1.24 ± 0.14	2.86 ± 0.31	3.59 ± 0.42
C17	1.86 ± 0.23	1.53 ± 0.18	5.61 ± 0.72	6.41 ± 0.76
PRI	0.39 ± 0.06	0.33 ± 0.05	0.95 ± 0.12	1.19 ± 0.09
C18	1.03 ± 0.16	0.64 ± 0.08	6.34 ± 0.75	5.65 ± 0.46
PHY	0.29 ± 0.03	0.22 ± 0.03	0.76 ± 0.08	0.82 ± 0.09
C19	1.22 ± 0.16	0.89 ± 0.12	8.02 ± 0.96	3.07 ± 0.65
C20	1.29 ± 0.15	1.95 ± 0.25	5.17 ± 0.68	1.06 ± 0.15
C21	3.15 ± 0.42	4.60 ± 0.45	2.36 ± 0.03	0.20 ± 0.03
C22	4.29 ± 0.47	1.20 ± 0.18	0.47 ± 0.07	ND[f]
C23	9.53 ± 1.21	0.24 ± 0.05	0.20 ± 0.04	ND
C24	4.00 ± 0.53	ND	ND	ND
C25	6.68 ± 0.86	ND	ND	ND
C26	1.60 ± 0.18	ND	ND	ND
C27	7.88 ± 0.98	ND	ND	ND
C28	1.75 ± 0.23	ND	ND	ND
C29	8.78 ± 0.88	ND	ND	ND
C30	1.14 ± 0.16	ND	ND	ND
C31	9.76 ± 1.28	ND	ND	ND

Table A2.5a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 7/26/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	0.35 ± 0.05	0.34 ± 0.06
FLU	ND	ND	3.08 ± 0.35	3.22 ± 0.09
PHE	ND	ND	11.33 ± 1.35	3.61 ± 0.08
ANT	ND	ND	8.38 ± 0.97	2.62 ± 0.35
FLA	0.42 ± 0.06	ND	5.34 ± 0.64	0.34 ± 0.04
PYR	0.54 ± 0.07	ND	1.66 ± 0.21	ND
BaA	ND	ND	ND	ND
CHR	1.16 ± 0.17	0.23 ± 0.03	0.40 ± 0.05	ND
BFL	2.94 ± 0.34	ND	ND	ND
BeP	1.13 ± 0.13	ND	ND	ND
BaP	0.23 ± 0.03	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.5b. Atmospheric Concentrations of Target SOCs from Portland, OR on 7/26/88.

Compound	Concentrations (ng/m^3)[a]			
	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.84 ± 0.10	1.84 ± 0.22	2.72 ± 0.38	3.89 ± 0.22
C17	1.76 ± 0.26	2.24 ± 0.26	5.76 ± 0.52	6.59 ± 0.79
PRI	ND[f]	0.53 ± 0.07	0.96 ± 0.11	1.48 ± 0.16
C18	0.89 ± 0.13	1.03 ± 0.09	6.80 ± 0.76	5.46 ± 0.63
PHY	ND	0.38 ± 0.05	1.11 ± 0.15	1.26 ± 0.16
C19	0.79 ± 0.09	1.12 ± 0.13	7.42 ± 0.81	2.89 ± 0.34
C20	0.73 ± 0.09	1.50 ± 0.26	5.97 ± 0.52	1.31 ± 0.16
C21	1.20 ± 0.18	3.22 ± 0.41	4.53 ± 0.56	0.32 ± 0.04
C22	1.12 ± 0.17	3.87 ± 0.51	0.73 ± 0.09	ND
C23	4.40 ± 0.55	0.53 ± 0.06	0.43 ± 0.04	ND
C24	1.79 ± 0.23	0.21 ± 0.03	ND	ND
C25	5.59 ± 0.64	ND	0.21 ± 0.04	ND
C26	1.40 ± 0.16	ND	ND	ND
C27	8.38 ± 0.93	ND	ND	ND
C28	1.41 ± 0.18	ND	ND	ND
C29	9.77 ± 1.01	ND	ND	ND
C30	1.92 ± 0.19	ND	ND	ND
C31	10.94 ± 1.11	ND	ND	ND

Table A2.5b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 7/26/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	0.30 ± 0.05	0.38 ± 0.05
FLU	ND	ND	3.29 ± 0.45	3.46 ± 0.29
PHE	ND	ND	13.14 ± 1.69	3.43 ± 0.46
ANT	ND	ND	0.34 ± 0.05	0.29 ± 0.04
FLA	0.35 ± 0.05	ND	6.23 ± 0.75	0.26 ± 0.05
PYR	0.23 ± 0.06	ND	2.10 ± 0.24	ND
BaA	ND	ND	0.31 ± 0.06	ND
CHR	1.06 ± 0.21	0.39 ± 0.03	0.53 ± 0.08	ND
BFL	2.53 ± 0.32	ND	ND	ND
BeP	1.17 ± 0.20	ND	ND	ND
BaP	0.28 ± 0.04	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.6a. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/1/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	0.37 ± 0.04	0.22 ± 0.03	1.87 ± 0.32	1.65 ± 0.22
C17	0.47 ± 0.06	0.38 ± 0.04	2.79 ± 0.31	2.15 ± 0.25
PRI	ND[f]	ND	0.73 ± 0.09	0.85 ± 0.09
C18	0.29 ± 0.04	0.22 ± 0.03	2.59 ± 0.28	1.15 ± 0.23
PHY	ND	ND	0.56 ± 0.07	0.33 ± 0.05
C19	0.39 ± 0.05	0.27 ± 0.04	2.16 ± 0.26	0.46 ± 0.07
C20	0.65 ± 0.08	0.37 ± 0.05	1.29 ± 0.16	ND
C21	0.89 ± 0.11	0.76 ± 0.09	ND	ND
C22	0.94 ± 0.13	ND	ND	ND
C23	1.08 ± 0.09	ND	ND	ND
C24	0.84 ± 0.09	ND	ND	ND
C25	1.18 ± 0.15	ND	ND	ND
C26	0.58 ± 0.08	ND	ND	ND
C27	1.48 ± 0.16	ND	ND	ND
C28	0.64 ± 0.08	ND	ND	ND
C29	2.37 ± 0.32	ND	ND	ND
C30	0.65 ± 0.07	ND	ND	ND
C31	2.87 ± 0.37	ND	ND	ND

Table A2.6a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/1/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	ND	ND
FLU	ND	ND	0.87 ± 0.11	0.37 ± 0.05
PHE	ND	ND	1.78 ± 0.21	ND
ANT	ND	ND	0.21 ± 0.04	ND
FLA	ND	ND	0.51 ± 0.06	ND
PYR	ND	ND	0.35 ± 0.04	ND
BaA	ND	ND	ND	ND
CHR	ND	ND	ND	ND
BFL	ND	ND	ND	ND
BeP	ND	ND	ND	ND
BaP	ND	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.6b. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/1/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.48 ± 0.05	0.39 ± 0.05	1.66 ± 0.23	1.74 ± 0.22
C17	0.71 ± 0.09	0.30 ± 0.04	2.80 ± 0.33	2.13 ± 0.30
PRI	ND[f]	ND	0.80 ± 0.09	0.78 ± 0.09
C18	0.47 ± 0.06	ND	2.65 ± 0.29	1.12 ± 0.17
PHY	ND	ND	0.57 ± 0.07	0.37 ± 0.05
C19	0.43 ± 0.05	0.32 ± 0.04	2.25 ± 0.32	0.48 ± 0.06
C20	0.47 ± 0.07	0.39 ± 0.05	1.16 ± 0.13	ND
C21	0.58 ± 0.08	0.63 ± 0.07	0.29 ± 0.04	ND
C22	0.48 ± 0.06	0.21 ± 0.05	ND	ND
C23	0.75 ± 0.09	0.23 ± 0.04	ND	ND
C24	1.22 ± 0.08	0.20 ± 0.04	ND	ND
C25	1.11 ± 0.17	ND	ND	ND
C26	0.65 ± 0.07	ND	ND	ND
C27	1.71 ± 0.24	ND	ND	ND
C28	0.88 ± 0.12	ND	ND	ND
C29	2.87 ± 0.35	ND	ND	ND
C30	0.84 ± 0.09	ND	ND	ND
C31	3.70 ± 0.42	ND	ND	ND

Table A2.6b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/1/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	ND	ND
FLU	ND	ND	0.83 ± 0.11	0.40 ± 0.06
PHE	ND	ND	1.96 ± 0.23	ND
ANT	ND	ND	0.26 ± 0.04	ND
FLA	ND	ND	0.47 ± 0.06	ND
PYR	ND	ND	0.34 ± 0.06	ND
BaA	ND	ND	ND	ND
CHR	ND	ND	ND	ND
BFL	ND	ND	ND	ND
BeP	ND	ND	ND	ND
BaP	ND	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.7a. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/7/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.39 ± 0.19	0.68 ± 0.09	3.10 ± 0.33	3.84 ± 0.45
C17	1.27 ± 0.23	0.78 ± 0.08	5.66 ± 0.72	5.26 ± 0.56
PRI	0.35 ± 0.05	0.24 ± 0.03	2.49 ± 0.30	1.84 ± 0.19
C18	0.46 ± 0.07	0.33 ± 0.05	5.05 ± 0.62	2.15 ± 0.26
PHY	0.21 ± 0.03	ND[f]	2.22 ± 0.24	0.63 ± 0.08
C19	0.90 ± 0.10	0.52 ± 0.07	5.06 ± 0.66	0.57 ± 0.06
C20	0.74 ± 0.08	0.65 ± 0.07	1.10 ± 0.13	ND
C21	1.90 ± 0.23	2.22 ± 0.19	0.64 ± 0.09	ND
C22	2.45 ± 0.29	0.53 ± 0.07	ND	ND
C23	4.31 ± 0.52	ND	ND	ND
C24	4.04 ± 0.45	ND	ND	ND
C25	5.57 ± 0.62	ND	ND	ND
C26	4.94 ± 0.61	ND	ND	ND
C27	7.59 ± 0.74	ND	ND	ND
C28	6.24 ± 0.70	ND	ND	ND
C29	8.75 ± 1.01	ND	ND	ND
C30	4.90 ± 0.56	ND	ND	ND
C31	11.11 ± 1.23	ND	ND	ND

Table A2.7a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/7/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	1.29 ± 0.14	0.48 ± 0.06
FLU	ND	ND	3.22 ± 0.41	1.66 ± 0.14
PHE	0.20 ± 0.03	ND	6.95 ± 0.81	0.78 ± 0.09
ANT	ND	ND	0.79 ± 0.08	ND
FLA	0.48 ± 0.06	ND	2.32 ± 0.26	ND
PYR	0.30 ± 0.05	ND	1.04 ± 0.15	ND
BaA	0.30 ± 0.04	ND	ND	ND
CHR	1.10 ± 0.16	ND	0.52 ± 0.06	ND
BFL	2.22 ± 0.30	ND	ND	ND
BeP	0.73 ± 0.09	ND	ND	ND
BaP	ND	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.7b. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/7/88.

	Concentrations (ng/m³)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-alkanes				
C16	0.59 ± 0.07	1.34 ± 0.19	3.39 ± 0.50	4.35 ± 0.51
C17	1.01 ± 0.14	0.82 ± 0.06	6.21 ± 0.76	4.68 ± 0.46
PRI	ND[f]	0.32 ± 0.04	2.09 ± 0.32	2.47 ± 0.31
C18	0.40 ± 0.05	0.26 ± 0.03	5.82 ± 0.78	2.10 ± 0.24
PHY	ND	0.21 ± 0.04	1.51 ± 0.19	0.95 ± 0.12
C19	0.57 ± 0.08	0.63 ± 0.07	4.96 ± 0.59	0.35 ± 0.05
C20	0.59 ± 0.08	0.61 ± 0.06	2.52 ± 0.31	ND
C21	0.86 ± 0.11	1.35 ± 0.15	1.12 ± 0.16	ND
C22	0.85 ± 0.09	1.21 ± 0.14	ND	ND
C23	1.52 ± 0.18	1.00 ± 0.12	ND	ND
C24	3.11 ± 0.41	0.39 ± 0.06	ND	ND
C25	6.07 ± 0.74	0.31 ± 0.04	ND	ND
C26	4.14 ± 0.52	ND	ND	ND
C27	6.51 ± 0.66	ND	ND	ND
C28	5.78 ± 0.62	ND	ND	ND
C29	7.87 ± 0.89	ND	ND	ND
C30	5.16 ± 0.63	ND	ND	ND
C31	10.37 ± 1.32	ND	ND	ND

Table A2.7b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/7/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	0.47 ± 0.06	0.57 ± 0.06
FLU	ND	ND	3.76 ± 0.49	1.99 ± 0.24
PHE	0.22 ± 0.03	ND	8.78 ± 0.99	1.06 ± 0.14
ANT	ND	ND	1.02 ± 0.15	ND
FLA	0.33 ± 0.05	ND	2.56 ± 0.29	ND
PYR	0.28 ± 0.04	ND	0.97 ± 0.16	ND
BaA	0.34 ± 0.04	ND	ND	ND
CHR	0.80 ± 0.11	ND	0.38 ± 0.06	ND
BFL	2.37 ± 0.28	ND	ND	ND
BeP	0.87 ± 0.12	ND	ND	ND
BaP	0.84 ± 0.13	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS TEflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.8a. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/19/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	0.74 ± 0.09	0.42 ± 0.06	6.13 ± 0.67	6.59 ± 0.76
C17	0.81 ± 0.10	0.51 ± 0.08	8.89 ± 0.98	6.91 ± 0.81
PRI	0.25 ± 0.04	ND[f]	1.71 ± 0.23	2.53 ± 0.33
C18	0.38 ± 0.05	0.20 ± 0.03	8.12 ± 0.99	3.83 ± 0.56
PHY	0.21 ± 0.03	ND	1.48 ± 0.19	1.15 ± 0.13
C19	0.57 ± 0.07	0.26 ± 0.04	7.89 ± 0.84	2.15 ± 0.31
C20	0.70 ± 0.08	0.36 ± 0.05	5.03 ± 0.61	0.77 ± 0.09
C21	1.02 ± 0.16	1.33 ± 0.15	2.77 ± 0.34	ND
C22	1.63 ± 0.21	1.53 ± 0.14	0.28 ± 0.04	ND
C23	2.86 ± 0.43	0.23 ± 0.03	0.20 ± 0.02	ND
C24	2.06 ± 0.17	ND	ND	ND
C25	2.85 ± 0.31	ND	ND	ND
C26	1.54 ± 0.17	ND	ND	ND
C27	2.41 ± 0.31	ND	ND	ND
C28	1.17 ± 0.19	ND	ND	ND
C29	3.57 ± 0.47	ND	ND	ND
C30	1.07 ± 0.13	ND	ND	ND
C31	3.91 ± 0.45	ND	ND	ND

Table A2.8a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/19/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	1.16 ± 0.17	1.51 ± 0.16
FLU	ND	ND	5.43 ± 0.62	3.27 ± 0.33
PHE	ND	ND	19.50 ± 1.78	3.34 ± 0.39
ANT	ND	ND	1.25 ± 0.14	ND
FLA	0.79 ± 0.10	ND	10.19 ± 1.31	0.78 ± 0.09
PYR	0.50 ± 0.07	ND	4.87 ± 0.06	0.29 ± 0.03
BaA	0.56 ± 0.07	ND	0.78 ± 0.09	ND
CHR	2.68 ± 0.33	ND	1.58 ± 0.20	ND
BFL	7.03 ± 0.61	ND	ND	ND
BeP	2.92 ± 0.35	ND	ND	ND
BaP	3.27 ± 0.33	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.8b. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/19/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.53 ± 0.07	0.70 ± 0.08	6.05 ± 0.81	7.98 ± 0.94
C17	0.80 ± 0.09	0.54 ± 0.07	7.70 ± 0.94	7.70 ± 0.81
PRI	ND[f]	0.28 ± 0.04	2.16 ± 0.33	3.71 ± 0.45
C18	0.63 ± 0.08	0.23 ± 0.02	7.87 ± 0.89	4.16 ± 0.23
PHY	ND	ND	1.59 ± 0.25	1.37 ± 0.16
C19	0.86 ± 0.11	0.43 ± 0.07	7.39 ± 0.79	2.34 ± 0.35
C20	1.04 ± 0.14	0.47 ± 0.06	4.61 ± 0.56	0.83 ± 0.09
C21	1.46 ± 0.19	0.93 ± 0.15	2.56 ± 0.31	0.23 ± 0.04
C22	1.58 ± 0.16	1.24 ± 0.18	0.51 ± 0.07	ND
C23	3.31 ± 0.45	0.76 ± 0.09	0.20 ± 0.03	ND
C24	1.79 ± 0.20	0.21 ± 0.04	ND	ND
C25	2.30 ± 0.21	ND	ND	ND
C26	1.50 ± 0.19	ND	ND	ND
C27	2.78 ± 0.33	ND	ND	ND
C28	1.57 ± 0.17	ND	ND	ND
C29	4.11 ± 0.64	ND	ND	ND
C30	0.98 ± 0.12	ND	ND	ND
C31	4.88 ± 0.52	ND	ND	ND

Table A2.8b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/19/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	1.07 ± 0.16	1.77 ± 0.23
FLU	ND	ND	5.27 ± 0.64	4.30 ± 0.46
PHE	ND	ND	18.74 ± 2.14	3.87 ± 0.41
ANT	ND	ND	1.85 ± 0.24	ND
FLA	0.83 ± 0.13	ND	10.28 ± 1.02	0.63 ± 0.08
PYR	0.54 ± 0.07	ND	5.00 ± 0.62	0.30 ± 0.05
BaA	0.64 ± 0.07	ND	0.53 ± 0.07	ND
CHR	2.87 ± 0.39	ND	1.48 ± 0.16	ND
BFL	7.57 ± 0.84	ND	ND	ND
BeP	3.38 ± 0.36	ND	ND	ND
BaP	2.86 ± 0.31	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.9a. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/31/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	0.78 ± 0.09	0.43 ± 0.06	6.87 ± 0.78	6.62 ± 0.72
C17	0.84 ± 0.08	0.57 ± 0.08	8.38 ± 0.94	5.47 ± 0.65
PRI	0.28 ± 0.04	0.27 ± 0.03	3.04 ± 0.35	3.47 ± 0.43
C18	0.47 ± 0.06	0.36 ± 0.05	6.40 ± 0.71	2.49 ± 0.36
PHY	ND[f]	ND	1.52 ± 0.19	0.77 ± 0.09
C19	2.37 ± 0.35	0.68 ± 0.09	5.66 ± 0.63	1.05 ± 0.15
C20	0.97 ± 0.14	1.78 ± 0.21	2.33 ± 0.36	ND
C21	1.93 ± 0.26	1.58 ± 0.15	0.21 ± 0.02	ND
C22	2.17 ± 0.34	ND	ND	ND
C23	2.23 ± 0.26	ND	ND	ND
C24	2.76 ± 0.33	ND	ND	ND
C25	2.41 ± 0.30	ND	ND	ND
C26	2.78 ± 0.40	ND	ND	ND
C27	1.06 ± 0.15	ND	ND	ND
C28	1.26 ± 0.18	ND	ND	ND
C29	3.75 ± 0.46	ND	ND	ND
C30	1.55 ± 0.21	ND	ND	ND
C31	4.79 ± 0.49	ND	ND	ND

Table A2.9a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/31/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	1.04 ± 0.17	1.46 ± 0.16
FLU	ND	ND	4.02 ± 0.45	1.74 ± 0.26
PHE	ND	ND	6.34 ± 0.70	1.14 ± 0.13
ANT	ND	ND	5.27 ± 0.65	ND
FLA	0.34 ± 0.04	ND	3.97 ± 0.43	ND
PYR	0.20 ± 0.03	ND	2.06 ± 0.25	ND
BaA	0.26 ± 0.04	0.25 ± 0.04	0.58 ± 0.07	ND
CHR	1.91 ± 0.24	ND	0.42 ± 0.07	ND
BFL	3.28 ± 0.44	ND	ND	ND
BeP	1.27 ± 0.16	ND	ND	ND
BaP	ND	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.9b. Atmospheric Concentrations of Target SOCs from Portland, OR on 8/31/88.

Compound	Concentrations (ng/m^3)[a]			
	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	0.42 ± 0.05	0.50 ± 0.06	4.17 ± 0.53	4.38 ± 0.49
C17	0.66 ± 0.09	0.38 ± 0.06	5.96 ± 0.76	4.63 ± 0.46
PRI	ND[f]	0.25 ± 0.03	1.82 ± 0.26	2.35 ± 0.32
C18	0.54 ± 0.06	ND	5.27 ± 0.66	2.54 ± 0.41
PHY	ND	ND	1.55 ± 0.19	1.12 ± 0.16
C19	0.75 ± 0.09	0.43 ± 0.05	4.73 ± 0.58	1.15 ± 0.18
C20	0.85 ± 0.14	0.58 ± 0.08	2.89 ± 0.29	0.31 ± 0.04
C21	1.15 ± 0.17	1.20 ± 0.13	1.44 ± 0.18	ND
C22	1.15 ± 0.17	1.10 ± 0.14	0.26 ± 0.03	ND
C23	1.51 ± 0.26	0.71 ± 0.09	ND	ND
C24	1.51 ± 0.18	0.24 ± 0.15	ND	ND
C25	2.15 ± 0.26	ND	ND	ND
C26	1.29 ± 0.18	ND	ND	ND
C27	2.56 ± 0.27	ND	ND	ND
C28	1.29 ± 0.18	ND	ND	ND
C29	2.98 ± 0.33	ND	ND	ND
C30	1.39 ± 0.19	ND	ND	ND
C31	4.11 ± 0.46	ND	ND	ND

Table A2.9b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 8/31/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	0.62 ± 0.08	0.82 ± 0.09
FLU	ND	ND	2.94 ± 0.36	1.66 ± 0.23
PHE	ND	ND	4.40 ± 0.56	0.98 ± 0.14
ANT	ND	ND	3.14 ± 0.34	ND
FLA	0.22 ± 0.04	ND	2.55 ± 0.29	ND
PYR	0.21 ± 0.03	ND	1.75 ± 0.19	ND
BaA	0.25 ± 0.04	ND	0.38 ± 0.06	ND
CHR	1.74 ± 0.26	ND	0.23 ± 0.04	ND
BFL	2.12 ± 0.28	ND	ND	ND
BeP	0.85 ± 0.11	ND	ND	ND
BaP	ND	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.10a. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/17/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.36 ± 0.18	0.33 ± 0.04	13.34 ± 1.62	15.75 ± 1.22
C17	0.93 ± 0.15	0.64 ± 0.07	22.28 ± 3.21	13.24 ± 1.53
PRI	0.66 ± 0.08	1.24 ± 0.16	12.05 ± 1.33	11.72 ± 1.40
C18	0.90 ± 0.14	0.88 ± 0.13	20.27 ± 1.06	5.47 ± 0.76
PHY	0.40 ± 0.06	0.61 ± 0.09	4.38 ± 0.71	1.69 ± 0.19
C19	1.76 ± 0.21	2.44 ± 0.31	13.41 ± 1.47	2.09 ± 0.35
C20	3.59 ± 0.51	0.69 ± 0.09	1.19 ± 0.16	0.33 ± 0.04
C21	5.98 ± 0.74	1.57 ± 0.17	ND[f]	ND
C22	6.43 ± 0.66	0.23 ± 0.02	ND	ND
C23	3.79 ± 0.44	ND	ND	ND
C24	5.32 ± 0.69	ND	ND	ND
C25	5.37 ± 0.65	ND	ND	ND
C26	3.82 ± 0.43	ND	ND	ND
C27	3.25 ± 0.33	ND	ND	ND
C28	2.65 ± 0.39	ND	ND	ND
C29	3.11 ± 0.32	ND	ND	ND
C30	1.94 ± 0.26	ND	ND	ND
C31	3.96 ± 0.47	ND	ND	ND

Table A2.10a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/17/88.

	Concentrations (ng/m³)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	2.38 ± 0.36	2.71 ± 0.34
FLU	ND	ND	16.63 ± 2.12	6.70 ± 0.78
PHE	1.49 ± 0.19	ND	31.62 ± 2.56	3.83 ± 0.65
ANT	ND	ND	10.76 ± 1.21	1.09 ± 0.16
FLA	1.72 ± 0.22	0.33 ± 0.05	17.62 ± 2.01	0.54 ± 0.07
PYR	1.43 ± 0.18	ND	12.89 ± 1.45	0.35 ± 0.05
BaA	4.08 ± 0.55	0.70 ± 0.08	0.49 ± 0.07	ND
CHR	2.90 ± 0.35	ND	0.20 ± 0.04	ND
BFL	7.07 ± 0.75	ND	ND	ND
BeP	1.88 ± 0.23	ND	ND	ND
BaP	1.96 ± 0.21	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.10b. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/17/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-alkanes				
C16	1.26 ± 0.19	1.46 ± 0.21	17.91 ± 2.23	21.25 ± 1.98
C17	2.31 ± 0.32	1.09 ± 0.15	25.44 ± 3.12	16.25 ± 1.96
PRI	0.63 ± 0.08	0.82 ± 0.09	18.26 ± 2.31	16.15 ± 1.87
C18	0.92 ± 0.14	0.90 ± 0.12	19.90 ± 2.25	6.60 ± 0.82
PHY	0.23 ± 0.04	0.45 ± 0.07	4.34 ± 0.59	2.56 ± 0.39
C19	3.68 ± 0.56	1.88 ± 0.27	17.73 ± 2.55	2.79 ± 0.34
C20	4.80 ± 0.49	1.48 ± 0.23	5.82 ± 0.72	2.11 ± 0.27
C21	4.50 ± 0.52	1.48 ± 0.17	0.64 ± 0.08	ND
C22	4.31 ± 0.44	1.74 ± 0.24	0.32 ± 0.04	ND
C23	3.93 ± 0.54	0.63 ± 0.07	ND	ND
C24	5.07 ± 0.63	0.51 ± 0.06	ND	ND
C25	5.56 ± 0.73	ND	ND	ND
C26	3.70 ± 0.45	ND	ND	ND
C27	3.04 ± 0.34	ND	ND	ND
C28	2.25 ± 0.27	ND	ND	ND
C29	2.91 ± 0.35	ND	ND	ND
C30	2.14 ± 0.26	ND	ND	ND
C31	3.71 ± 0.42	ND	ND	ND

Table A2.10b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/17/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	2.28 ± 0.35	2.76 ± 0.29
FLU	ND	ND	14.22 ± 1.76	5.93 ± 0.86
PHE	1.65 ± 0.27	ND	27.06 ± 3.33	5.03 ± 0.67
ANT	0.58 ± 0.07	ND	6.85 ± 0.77	1.03 ± 0.13
FLA	1.89 ± 0.26	0.36 ± 0.05	15.96 ± 2.12	0.54 ± 0.08
PYR	2.17 ± 0.23	0.22 ± 0.03	11.78 ± 1.98	0.35 ± 0.05
BaA	3.55 ± 0.46	0.46 ± 0.16	0.30 ± 0.06	ND
CHR	1.87 ± 0.25	0.32 ± 0.06	0.20 ± 0.04	ND
BFL	6.77 ± 0.75	ND	ND	ND
BeP	1.45 ± 0.19	ND	ND	ND
BaP	2.85 ± 0.36	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS Teflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.11a. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/23/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	0.80 ± 0.09	0.50 ± 0.07	10.56 ± 1.26	7.95 ± 0.94
C17	0.83 ± 0.11	1.04 ± 0.16	13.36 ± 1.45	4.73 ± 0.56
PRI	0.59 ± 0.08	1.27 ± 0.16	9.49 ± 0.97	4.50 ± 0.62
C18	0.77 ± 0.08	1.41 ± 0.21	10.01 ± 1.21	1.33 ± 0.15
PHY	0.33 ± 0.04	1.25 ± 0.15	1.67 ± 0.19	0.23 ± 0.03
C19	1.18 ± 0.20	6.31 ± 0.72	2.66 ± 0.31	ND[f]
C20	3.79 ± 0.45	3.57 ± 0.44	0.25 ± 0.02	ND
C21	3.88 ± 0.39	0.27 ± 0.04	ND	ND
C22	3.14 ± 0.35	ND	ND	ND
C23	3.54 ± 0.41	ND	ND	ND
C24	3.57 ± 0.39	ND	ND	ND
C25	4.44 ± 0.49	ND	ND	ND
C26	2.25 ± 0.29	ND	ND	ND
C27	3.04 ± 0.31	ND	ND	ND
C28	2.25 ± 0.32	ND	ND	ND
C29	3.14 ± 0.39	ND	ND	ND
C30	1.84 ± 0.22	ND	ND	ND
C31	4.25 ± 0.46	ND	ND	ND

Table A2.11a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/23/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	1.27 ± 0.15	1.07 ± 0.16
FLU	ND	ND	0.53 ± 0.07	ND
PHE	0.33 ± 0.05	ND	20.03 ± 3.32	0.90 ± 0.12
ANT	ND	ND	5.29 ± 0.63	0.64 ± 0.09
FLA	0.72 ± 0.09	0.31 ± 0.05	8.53 ± 0.89	0.20 ± 0.04
PYR	0.61 ± 0.07	ND	5.56 ± 0.77	0.23 ± 0.03
BaA	1.83 ± 0.21	ND	ND	ND
CHR	1.44 ± 0.20	ND	ND	ND
BFL	3.00 ± 0.41	ND	ND	ND
BeP	0.93 ± 0.08	ND	ND	ND
BaP	0.56 ± 0.07	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.11b. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/23/88.

	Concentrations (ng/m³)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	1.12 ± 0.14	0.65 ± 0.08	8.81 ± 0.92	7.81 ± 1.22
C17	1.78 ± 0.23	0.90 ± 0.11	10.61 ± 1.01	5.80 ± 0.76
PRI	0.42 ± 0.05	0.60 ± 0.09	9.62 ± 1.03	4.76 ± 0.59
C18	2.06 ± 0.23	0.74 ± 0.09	8.26 ± 0.97	1.61 ± 0.19
PHY	ND[f]	0.42 ± 0.06	2.03 ± 0.28	0.54 ± 0.08
C19	2.48 ± 0.31	1.54 ± 0.16	3.83 ± 0.27	0.33 ± 0.05
C20	2.99 ± 0.35	2.99 ± 0.46	0.41 ± 0.04	0.78 ± 0.09
C21	2.85 ± 0.37	1.28 ± 0.18	ND	ND
C22	2.68 ± 0.30	0.38 ± 0.06	ND	ND
C23	3.04 ± 0.31	ND	ND	ND
C24	3.28 ± 0.40	ND	ND	ND
C25	3.85 ± 0.46	ND	ND	ND
C26	2.34 ± 0.29	ND	ND	ND
C27	3.10 ± 0.34	ND	ND	ND
C28	2.16 ± 0.27	ND	ND	ND
C29	3.87 ± 0.51	ND	ND	ND
C30	2.21 ± 0.29	ND	ND	ND
C31	4.57 ± 0.59	ND	ND	ND

Table A2.11b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/23/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	1.23 ± 0.19	1.02 ± 0.14
FLU	ND	ND	0.80 ± 0.11	2.53 ± 0.35
PHE	0.26 ± 0.04	ND	18.25 ± 2.26	1.01 ± 0.14
ANT	ND	ND	7.14 ± 0.89	0.93 ± 0.15
FLA	0.62 ± 0.07	0.24 ± 0.03	7.41 ± 0.86	ND
PYR	0.53 ± 0.07	ND	5.90 ± 0.74	0.25 ± 0.03
BaA	1.86 ± 0.24	0.52 ± 0.06	ND	ND
CHR	1.07 ± 0.16	0.47 ± 0.06	ND	ND
BFL	3.18 ± 0.40	ND	ND	ND
BeP	0.98 ± 0.14	ND	ND	ND
BaP	1.26 ± 0.16	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS TEflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.12a. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/29/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	2.65 ± 0.32	0.79 ± 0.10	34.65 ± 4.29	24.83 ± 3.22
C17	1.65 ± 0.23	1.11 ± 0.19	49.21 ± 7.26	23.21 ± 2.98
PRI	0.74 ± 0.08	1.06 ± 0.16	25.18 ± 3.26	14.38 ± 1.78
C18	1.83 ± 0.24	1.72 ± 0.22	29.74 ± 3.99	10.44 ± 1.23
PHY	0.60 ± 0.07	0.73 ± 0.07	8.86 ± 1.00	2.98 ± 0.35
C19	2.57 ± 0.31	2.81 ± 0.37	32.47 ± 3.68	2.05 ± 0.29
C20	4.89 ± 0.56	13.08 ± 2.85	10.21 ± 1.31	0.85 ± 0.09
C21	12.48 ± 1.34	6.01 ± 0.75	0.40 ± 0.06	0.20 ± 0.03
C22	15.14 ± 1.89	1.23 ± 0.19	ND[f]	ND
C23	16.21 ± 1.94	0.50 ± 0.07	ND	ND
C24	16.10 ± 2.13	0.99 ± 0.14	ND	ND
C25	18.79 ± 1.82	0.71 ± 0.09	ND	ND
C26	11.88 ± 1.29	0.43 ± 0.07	ND	ND
C27	10.77 ± 1.61	0.34 ± 0.05	ND	ND
C28	8.17 ± 0.92	0.25 ± 0.03	ND	ND
C29	7.06 ± 0.82	ND	ND	ND
C30	7.07 ± 0.89	ND	ND	ND
C31	11.80 ± 1.29	ND	ND	ND

Table A2.12a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/29/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	0.55 ± 0.07	3.93 ± 0.45	5.42 ± 0.61
FLU	ND	ND	23.86 ± 3.56	15.44 ± 2.31
PHE	1.49 ± 0.16	0.27 ± 0.04	32.21 ± 4.07	6.78 ± 0.86
ANT	0.45 ± 0.07	ND	14.81 ± 1.76	ND
FLA	5.91 ± 0.79	0.80 ± 0.11	30.90 ± 4.35	0.72 ± 0.10
PYR	5.46 ± 0.68	0.59 ± 0.08	20.16 ± 2.94	0.45 ± 0.05
BaA	17.96 ± 1.92	1.56 ± 0.18	ND	ND
CHR	8.48 ± 0.97	0.63 ± 0.08	ND	ND
BFL	17.04 ± 2.01	ND	ND	ND
BeP	5.01 ± 0.68	ND	ND	ND
BaP	5.54 ± 0.59	ND	ND	ND

a) average ± 1s for two replicate injections. b) QQP = quartz/quartz primmary filter combination. c) QQB = quartz/quartz backup filter combination. d) PQP = primary PUFS quartz/quartz filter combination. e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.12b. Atmospheric Concentrations of Target SOCs from Portland, OR on 11/29/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
n-Alkane				
C16	1.88 ± 0.23	2.05 ± 0.32	36.17 ± 3.92	21.82 ± 2.42
C17	3.24 ± 0.35	1.49 ± 0.19	47.66 ± 6.21	23.28 ± 3.11
PRI	0.95 ± 0.13	1.10 ± 0.15	21.15 ± 2.21	13.14 ± 1.45
C18	1.26 ± 0.19	1.83 ± 0.23	40.72 ± 5.34	9.35 ± 1.21
PHY	0.71 ± 0.08	0.63 ± 0.08	8.58 ± 0.97	3.07 ± 0.41
C19	5.86 ± 0.64	3.89 ± 0.54	27.48 ± 3.32	2.06 ± 0.26
C20	8.47 ± 0.94	8.75 ± 0.88	12.55 ± 1.41	0.87 ± 0.12
C21	10.74 ± 1.24	9.29 ± 1.01	1.07 ± 0.12	ND[f]
C22	14.09 ± 1.53	1.83 ± 0.26	ND	ND
C23	15.20 ± 1.67	1.30 ± 0.20	ND	ND
C24	14.90 ± 1.53	ND	ND	ND
C25	20.48 ± 2.76	ND	ND	ND
C26	11.32 ± 1.29	ND	ND	ND
C27	12.93 ± 1.40	ND	ND	ND
C28	5.91 ± 0.75	ND	ND	ND
C29	6.91 ± 0.79	ND	ND	ND
C30	7.51 ± 0.89	ND	ND	ND
C31	10.03 ± 1.41	ND	ND	ND

Table A2.12b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 11/29/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	4.90 ± 0.63	4.76 ± 0.56
FLU	ND	ND	40.96 ± 5.25	14.72 ± 1.86
PHE	1.18 ± 0.14	0.32 ± 0.04	58.81 ± 8.56	7.26 ± 0.88
ANT	0.61 ± 0.09	ND	21.11 ± 2.48	0.27 ± 0.03
FLA	5.53 ± 0.64	0.77 ± 0.09	40.05 ± 5.55	0.90 ± 0.13
PYR	5.05 ± 0.56	0.63 ± 0.06	24.04 ± 2.64	0.72 ± 0.10
BaA	18.51 ± 2.02	1.37 ± 0.16	ND	ND
CHR	6.96 ± 0.86	2.29 ± 0.34	ND	ND
BFL	16.10 ± 1.97	ND	ND	ND
BeP	5.73 ± 0.71	ND	ND	ND
BaP	7.24 ± 0.75	ND	ND	ND

a) average ± 1s for two replicate injections. b) TQP = Teflon/quartz primary filter combination. c) TQB = Teflon/quartz backup filter combination. d) PTP = primary PUFS Teflon/quartz filter combination. e) PTB = backup PUFS TEflon/quartz filter combination. f) ND = not detected. g) NA = not analyzed.

Table A2.13a. Atmospheric Concentrations of Target SOCs from Portland, OR on 12/5/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.60 ± 0.21	0.83 ± 0.09	51.87 ± 7.89	34.06 ± 4.26
C17	1.30 ± 0.18	0.93 ± 0.12	31.14 ± 4.11	27.17 ± 3.28
PRI	0.47 ± 0.06	1.03 ± 0.13	23.02 ± 2.41	19.19 ± 2.01
C18	5.00 ± 0.64	1.39 ± 0.19	21.58 ± 2.37	10.99 ± 0.99
PHY	1.10 ± 0.18	0.58 ± 0.07	7.79 ± 0.85	2.90 ± 0.39
C19	3.13 ± 0.38	3.78 ± 0.41	35.62 ± 4.86	2.74 ± 0.36
C20	7.83 ± 0.88	15.15 ± 1.99	9.88 ± 1.20	0.88 ± 0.09
C21	22.39 ± 3.41	5.65 ± 0.69	0.45 ± 0.07	ND[f]
C22	27.24 ± 3.51	0.88 ± 0.10	ND	ND
C23	23.66 ± 4.29	0.23 ± 0.02	ND	ND
C24	21.01 ± 2.43	ND	0.32 ± 0.05	ND
C25	22.49 ± 2.34	ND	ND	ND
C26	11.18 ± 1.34	ND	ND	ND
C27	19.94 ± 2.28	ND	ND	ND
C28	10.91 ± 1.20	ND	ND	ND
C29	9.40 ± 1.21	ND	ND	ND
C30	8.78 ± 0.97	ND	ND	ND
C31	12.07 ± 1.35	ND	ND	ND

Table A2.13a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 12/5/88.

	Concentrations (ng/m^3)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	0.26 ± 0.03	2.68 ± 0.35
FLU	ND	ND	2.06 ± 0.31	1.19 ± 0.16
PHE	1.45 ± 0.19	0.46 ± 0.04	137.7 ± 17.5	8.11 ± 0.95
ANT	1.04 ± 0.12	ND	83.26 ± 9.21	1.61 ± 0.19
FLA	5.07 ± 0.69	1.28 ± 0.15	37.43 ± 4.28	1.20 ± 0.17
PYR	4.61 ± 0.59	1.09 ± 0.13	24.23 ± 3.01	0.80 ± 0.09
BaA	23.73 ± 3.42	0.52 ± 0.08	ND	ND
CHR	19.88 ± 2.53	0.43 ± 0.06	ND	ND
BFL	34.42 ± 3.89	ND	ND	ND
BeP	17.56 ± 2.03	ND	ND	ND
BaP	10.68 ± 1.13	ND	ND	ND

a) average ± 1s for two replicate injections; b) QQP = quartz/quartz primmary filter combination; c) QQB = quartz/quartz backup filter combination; d) PQP = primary PUFS quartz/quartz filter combination; e) PQB = backup PUFS quartz/quartz filter combination. f) ND = not detected; g) NA = not analyzed.

Table A2.13b. Atmospheric Concentrations of Target SOCs from Portland, OR on 12/5/88.

	Concentrations (ng/m^3)[a]			
Compound	TTP[b]	TTB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	3.08 ± 0.39	3.04 ± 0.31	48.45 ± 5.27	16.20 ± 1.93
C17	3.66 ± 0.38	5.13 ± 0.61	35.62 ± 4.01	15.17 ± 1.89
PRI	2.36 ± 0.29	1.37 ± 0.16	25.85 ± 3.36	15.49 ± 2.07
C18	5.12 ± 0.61	7.73 ± 0.81	25.66 ± 2.91	9.18 ± 1.14
PHY	1.79 ± 0.24	0.63 ± 0.09	8.61 ± 1.01	3.23 ± 0.21
C19	12.66 ± 1.41	10.34 ± 1.27	31.79 ± 4.28	1.45 ± 0.18
C20	16.27 ± 1.95	9.96 ± 1.25	12.67 ± 1.37	1.00 ± 0.14
C21	25.96 ± 3.48	5.41 ± 0.74	2.25 ± 0.24	ND[f]
C22	30.38 ± 3.79	1.95 ± 0.26	0.61 ± 0.08	ND
C23	28.19 ± 2.98	0.25 ± 0.03	ND	ND
C24	23.35 ± 3.95	ND	ND	ND
C25	23.61 ± 2.57	ND	ND	ND
C26	13.75 ± 1.58	ND	ND	ND
C27	19.14 ± 2.27	ND	ND	ND
C28	10.98 ± 1.46	ND	ND	ND
C29	10.84 ± 1.09	ND	ND	ND
C30	7.83 ± 0.09	ND	ND	ND
C31	13.07 ± 1.38	ND	ND	ND

Table A2.13b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 12/5/88.

	Concentrations (ng/m^3)[a]			
Compound	TTP[b]	TTB[c]	PTP[d]	PTB[e]
PAHs	ND	ND	0.26 ± 0.02	2.68 ± 0.33
ACE				
FLU	ND	ND	2.06 ± 0.24	1.19 ± 0.14
PHE	1.64 ± 0.19	0.33 ± 0.04	156.1 ± 19.6	8.11 ± 0.11
ANT	1.05 ± 0.13	0.49 ± 0.06	86.66 ± 10.23	2.15 ± 0.26
FLA	5.18 ± 0.65	0.92 ± 0.13	49.44 ± 5.06	1.19 ± 0.28
PYR	4.78 ± 0.67	0.70 ± 0.08	30.16 ± 4.09	0.88 ± 0.13
BaA	35.13 ± 5.21	0.36 ± 0.06	0.22 ± 0.03	ND
CHR	18.05 ± 2.68	ND	0.56 ± 0.07	ND
BFL	38.10 ± 4.23	ND	ND	ND
BeP	17.40 ± 2.05	ND	ND	ND
BaP	13.49 ± 1.56	ND	ND	ND

a) average ± 1s for two replicate injections; b) TTP = Teflon/Teflon primary filter combination; c) TTB = Teflon/Teflon backup filter combination; d) PTP = primary PUFS Teflon/Teflon filter combination; e) PTB = backup PUFS Teflon/Teflon filter combination; f) ND = not detected; g) NA = not analyzed.

Table A2.14a. Atmospheric Concentrations of Target SOCs from Portland, OR on 12/11/88.

	Concentrations (ng/m³)[a]			
Compound	QQP[b]	QQB[c]	PQP[d]	PQB[e]
n-Alkanes				
C16	1.43 ± 0.17	0.30 ± 0.04	17.01 ± 1.72	12.89 ± 0.89
C17	0.79 ± 0.09	0.48 ± 0.06	16.45 ± 2.12	8.69 ± 0.78
PRI	0.46 ± 0.07	0.87 ± 0.11	14.09 ± 1.49	6.61 ± 0.53
C18	0.69 ± 0.08	1.15 ± 0.19	15.34 ± 1.54	3.09 ± 0.18
PHY	0.31 ± 0.05	0.47 ± 0.06	3.15 ± 0.67	1.00 ± 0.09
C19	2.47 ± 0.28	1.65 ± 0.17	10.62 ± 1.34	1.44 ± 0.08
C20	3.46 ± 0.45	4.25 ± 0.51	3.81 ± 0.35	0.72 ± 0.07
C21	6.43 ± 0.79	2.32 ± 0.34	0.29 ± 0.07	ND[f]
C22	8.10 ± 0.09	ND	0.23 ± 0.03	ND
C23	10.16 ± 1.42	ND	ND	ND
C24	11.49 ± 1.67	ND	ND	ND
C25	13.66 ± 1.89	ND	ND	ND
C26	7.99 ± 0.11	ND	ND	ND
C27	12.43 ± 1.31	ND	ND	ND
C28	5.64 ± 0.70	ND	ND	ND
C29	6.35 ± 0.65	ND	ND	ND
C30	4.80 ± 0.49	ND	ND	ND
C31	6.72 ± 0.86	ND	ND	ND

Table A2.14a (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 12/11/88.

Compound	Concentrations (ng/m^3)[a]			
	QQP[b]	QQB[c]	PQP[d]	PQB[e]
PAHs				
ACE	ND	ND	5.08 ± 0.70	4.71 ± 0.46
FLU	ND	ND	18.30 ± 3.41	5.35 ± 0.64
PHE	0.95 ± 0.14	0.24 ± 0.03	93.23 ± 12.23	3.08 ± 0.50
ANT	0.32 ± 0.05	ND	39.12 ± 4.89	0.72 ± 0.07
FLA	3.31 ± 0.40	0.50 ± 0.07	16.96 ± 2.01	0.33 ± 0.04
PYR	2.30 ± 0.04	0.33 ± 0.04	10.63 ± 1.52	0.20 ± 0.02
BaA	11.15 ± 1.35	0.84 ± 0.08	0.93 ± 0.15	1.01 ± 0.16
CHR	4.10 ± 0.56	0.66 ± 0.08	0.24 ± 0.03	0.24 ± 0.04
BFL	13.40 ± 1.58	ND	ND	ND
BeP	4.92 ± 0.57	ND	ND	ND
BaP	4.18 ± 0.47	ND	ND	ND

a) average ± 1s for two replicate injections; b) QQP = quartz/quartz primmary filter combination; c) QQB = quartz/quartz backup filter combination; d) PQP = primary PUFS quartz/quartz filter combination; e) PQB = backup PUFS quartz/quartz filter combination; f) ND = not detected; g) NA = not analyzed.

Table A2.14b. Atmospheric Concentrations of Target SOCs from Portland, OR on 12/11/88.

	Concentrations (ng/m³)[a]			
Compound	TTP[b]	TTB[c]	PTP[d]	PTB[e]
n-Alkanes				
C16	1.81 ± 0.21	1.90 ± 0.25	16.46 ± 1.83	8.12 ± 0.94
C17	2.66 ± 0.32	2.99 ± 0.35	17.00 ± 1.98	6.53 ± 0.72
PRI	1.08 ± 0.16	0.82 ± 0.09	13.20 ± 1.35	4.80 ± 0.68
C18	3.28 ± 0.45	3.87 ± 0.51	13.49 ± 1.68	1.63 ± 0.19
PHY	0.64 ± 0.07	0.36 ± 0.07	4.08 ± 0.56	0.75 ± 0.09
C19	5.71 ± 0.69	3.94 ± 0.54	9.98 ± 1.23	0.63 ± 0.08
C20	6.46 ± 0.86	3.69 ± 0.46	3.14 ± 0.46	ND[f]
C21	7.08 ± 0.84	1.92 ± 0.23	0.53 ± 0.07	ND
C22	9.03 ± 1.15	0.74 ± 0.08	ND	ND
C23	11.33 ± 1.25	0.24 ± 0.04	ND	ND
C24	12.71 ± 1.36	ND	ND	ND
C25	15.26 ± 1.78	ND	ND	ND
C26	8.97 ± 0.94	ND	ND	ND
C27	14.09 ± 1.58	ND	ND	ND
C28	6.41 ± 0.79	ND	ND	ND
C29	7.42 ± 0.91	ND	ND	ND
C30	5.48 ± 0.68	ND	ND	ND
C31	8.00 ± 0.97	ND	ND	ND

Table A2.14b (cont'd.). Atmospheric Concentrations of Target SOCs from Portland, OR on 12/11/88.

	Concentrations (ng/m^3)[a]			
Compound	TQP[b]	TQB[c]	PTP[d]	PTB[e]
PAHs				
ACE	ND	ND	5.90 ± 0.71	5.13 ± 0.64
FLU	ND	ND	22.61 ± 3.10	5.41 ± 0.62
PHE	1.20 ± 0.19	0.42 ± 0.06	119.3 ± 13.5	2.25 ± 0.34
ANT	0.42 ± 0.08	0.21 ± 0.03	49.43 ± 8.12	ND
FLA	3.71 ± 0.46	0.61 ± 0.07	24.38 ± 2.57	0.34 ± 0.04
PYR	2.53 ± 0.04	0.39 ± 0.05	14.60 ± 1.78	0.25 ± 0.04
BaA	12.50 ± 1.57	0.90 ± 0.14	1.54 ± 0.18	ND
CHR	3.48 ± 0.47	0.43 ± 0.05	0.97 ± 0.13	ND
BFL	15.06 ± 1.78	ND	ND	ND
BeP	4.89 ± 0.59	ND	ND	ND
BaP	5.49 ± 0.63	ND	ND	ND

a) average ± 1s for two replicate injections; b) TTP = Teflon/Teflon primary filter combination; c) TTB = Teflon/Teflon backup filter combination; d) PTP = primary PUFS Teflon/Teflon filter combination; e) PTB = backup PUFS Teflon/Teflon filter combination; f) ND = not detected; g) NA = not analyzed.

VITA

The author was born on June 18, 1960 in Rochester (upstate), New York. He attended primary and secondary school in a small town outside of Rochester and graduated from Greece Olympia High School in 1978. The first turning point in his life was reached when it became painfully evident that he was not big enough to play college football and would have to look elsewhere for enjoyment. Going to college for an education, instead of football, was the chosen option. The second turning point came when he was working on a landscaping crew after his first year of college. This experience convinced him to add chemistry as a second major, since a career in environmental science was his ultimate goal. He graduated with honors from the State University of New York at Brockport with Bachelor of Science degrees in Chemistry (ACS) and Biology in 1983.

The same year he began study at the Oregon Graduate Center in the department of Biological, Chemical, and Environmental Sciences. He completed the requirements for the degree of Doctor of Philosophy in Environmental Science and Engineering at the Oregon Graduate Institute in 1989. The names were changed to protect the innocent.

The author has been married two years to the former Deborah Sue Lohman and they have two children, Kendra and Levi.

He has left OGI to accept a two year appointment at the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG) in Dübendorf, Switzerland.