THE SCAVENGING OF ATMOSPHERIC TRACE ORGANIC COMPOUNDS

BY RAIN

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ABSTRACT

The Scavenging of Atmospheric Trace Organic Compounds
by Rain

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Little is known about the scavenging of organic compounds, parti-
cularly the relative importance of gas and particle scavenging. A
field study of organic compounds in rain and air was conducted in Port-
land, Oregon and at the Oregon coast in order to provide information on
the scavenging process. The samplers collected organic compounds in
the rain dissolved and particulate phases and in the atmospheric vapor
and particulate phases. The rain sampling train consisted of a pre-
filter and filter, followed by two parallel sets of Tenax cartridges
for the adsorption of dissolved organics. The air sampling train con-
sisted of a glass fiber or Teflon membrane filter followed by parallel
sets of adsorbents for the collection of vapors. Polyurethane foam and
Tenax were both used in the air sampler.

Analysis of the rain and air samples proceeded by either solvent
extraction and on-column injection or direct thermal desorption onto a
fused silica capillary column interfaced with a mass spectrometer and
data system (GC/MS/DS). Concentration data were obtained for over 100
organic target compounds including PAHs, phenols, phthalate esters,

alkanes, aromatics, and pesticides. Phenols were the dominant organic compounds found in rain samples, with concentrations in the ug/L range in Portland. PAHs and phthalates were also major constituents. Concentrations at the Oregon coast were generally a factor of 2 to 7 lower than in Portland.

Gas and particle scavenging ratios were obtained from the air and rain concentration data. The gas scavenging ratios (W_g), obtained at ambient temperatures of 3-10°C, ranged from 3 to 10^5 at both sites. W_g values were generally a factor of 3 to 6 higher than the values predicted from the Henry's Law equilibrium, when 25°C literature values were used. However, W_g values for several PAHs agreed well with equilibrium when literature values obtained at the appropriate temperatures were used.

Particle scavenging ratios (W_p) ranged from 10^3 to 10^5 and averaged ~10^4. These values were consistently lower than the 10^5 to 10^6 generally reported for inorganic species. W_p values were significantly lower for the least volatile PAHs than for the other organic compounds. Only alkanes and volatile PAHs exhibited W_p values larger than their W_g values. For the majority of compounds studied, gas scavenging was more important than particle scavenging.

CHAPTER 1   INTRODUCTION

Everyone has probably observed that a good rainstorm "clears the air." There are actually two separate mechanisms at work during this process. The change in air circulation during rainstorms caused by vertical convection currents disperses suspended particles and gaseous pollutants which had been trapped near the ground. Also, both suspended particles and gaseous pollutants may be swept out of the atmosphere by the raindrops themselves. The latter process is referred to as scavenging, and has received much attention lately in connnection with acid rain, where sulfur and nitrogen oxides are the compounds being scavenged. These are not the only compounds which are scavenged by rain, however. Any substance which is present in the atmosphere, whether contaminant or naturally occurring substance, will partition itself into rain in some proportions. Atmospheric particulate material can act as cloud condensation nucleii and also can be scavenged by impaction by falling raindrops. Vapor phase compounds will diffuse rapidly into falling raindrops. The overall extent of partitioning of a substance into rain therefore will depend on the physical form of the compound (vapor or particulate) and its chemical properties such as aqueous solubility and vapor pressure. Understanding the scavenging of atmospheric compounds is of interest to environmental scientists

sents an important mechanism for transporting compounds from the atmosphere to surface ecosystems.

Organic compounds have been largely ignored in past studies of rain scavenging. This may be due in part to the low aqueous solubilities of some organic compounds, leading researchers to assume that rain scavenging was not a significant process for them. Much of the reason, however, is probably due to the magnitude of the task of measuring such a large variety of compounds. In recent years, analytical techniques have been developed to enable the analysis of complex mixtures of trace organic compounds at the levels at which they are found in the environment. At the same time, the presence of trace organic contaminants has become a primary concern in the environmental sciences. Many of these compounds are toxic or carcinogenic and thus represent a potential health risk in the environment. In addition, compounds such as the polychlorinated biphenyls (PCBs) and some pesticides are highly inert chemically and are thus expected to persist for long periods of time. These compounds have been detected in the atmosphere in remote locations such as Enewetok Atoll in the Pacific Ocean (Atlas and Giam, 1981), suggesting that they are now globally distributed in the atmosphere. Preliminary research (Eisenreich et al., 1981) suggests that the atmosphere has in turn become a major source of PCBs to the Great Lakes.

While most early research on the scavenging of organic compounds has focussed on the PCBs, the mechanism of rain scavenging may also be

a significant transport pathway for other classes of organic compounds. Compounds which contain oxygen generally exhibit relatively high water solubilities and low vapor pressures. This is the ideal combination of properties necessary for favorable partitioning of a gaseous compound into rain. While other compounds such as the high molecular weight polycyclic aromatic hydrocarbons (PAHs) may have low water solubilities, they have very low vapor pressures as well. This latter property will cause them to be found predominantly in the atmospheric particulate phase, where scavenging may not depend upon solubility. Thus a variety of organic compounds may be scavenged efficiently from the atmosphere by different mechanisms.

Due to the number of individual organic compounds which are present in the ambient atmosphere, experimental scavenging ratios cannot be obtained for every compound. It is therefore important to use experimental scavenging data to develop general predictive equations for the scavenging of organic compounds. In this manner, the scavenging of compounds which have not been measured in rain can be estimated from their atmospheric concentrations and known chemical properties.

1.1 Objectives

This research project was initiated to investigate the scavenging of atmospheric vapor and particulate phase organic compounds by rain. The first step in this process was to develop sampling and analysis methods to enable the measurement of a wide variety of trace organic compounds in rain and air. A review of such methods is given in

Chapters 2 and 3, along with some theoretical fundamentals. The analytical methods used in this study, and the air and rain concentration data thereby obtained are presented in detail in Chapters 4 and 5. These concentrations have enabled the determination of gas, particle and overall scavenging ratios for each compound. In Chapter 6, these scavenging ratios have in turn been related to the physical and chemical properties of the compounds. This has allowed general statements to be made about the expected behavior of the various classes of organic compounds. In Chapter 7, a model of the scavenging of gases is discussed which examines the mass-transport limitations to the rain/air equilibrium. Finally, in Chapter 8, the scavenging ratios have been compared to information on the other transport and removal mechanisms for organic compounds in order to assess the importance of rain scavenging for each class of compounds.

1.2 Selection of Target Compounds

Due to the vast numbers of naturally occurring organic compounds and organic contaminants which exist in the atmosphere, it is not possible to identify every organic compound found in a rain or air sample. Thus, for this study a list of target compounds was prepared, emphasizing compounds which are EPA priority pollutants. The target compound list evolved over the course of the study, as new compounds were identified in the samples. Some representative target compounds are shown in Figure 1.1. They include PAHs, alkylated PAHs, PAH ketones and
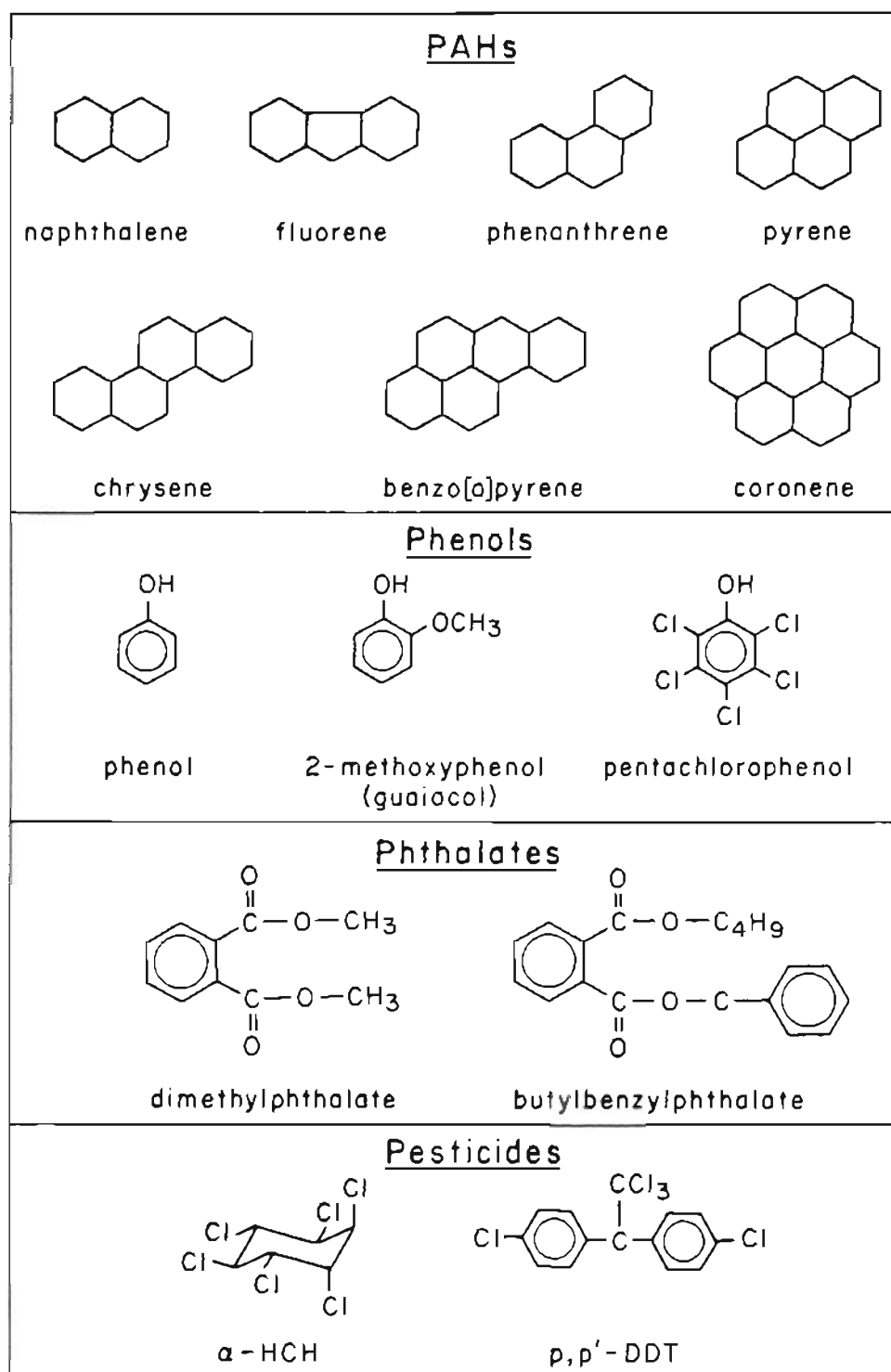
Figure 1.1. Structures of selected target compounds.

quinones, alkylated, nitrated and chlorinated phenols, phthalate esters, chlorinated pesticides, alkanes, alkylated and chlorinated aromatics, and halogenated aliphatics. A complete list of all the compounds measured over the course of the study is given in Table 1.1. PCBs were among the original target compounds. Due to the analytical difficulties inherent in the determination of ambient PCB concentrations, a study of the scavenging of PCBs was considered to be beyond the scope of this study and will be the subject of a subsequent study in this laboratory.

Table 1.1. List of Target Compounds with Chemical Formulae.

Polycyclic Aromatic Hydrocarbons (PAHs)

Naphthalene ($C_{10}H_8$)   Chrysene ($C_{18}H_{12}$)

Biphenyl ($C_{12}H_{10}$)   Benzo[b]fluoranthene ($C_{20}H_{12}$)

Acenaphthylene ($C_{12}H_8$)   Benzo[k]fluoranthene ($C_{20}H_{12}$)

Acenaphthene ($C_{12}H_{10}$)   Benzo{e]pyrene ($C_{20}H_{12}$)

Fluorene ($C_{13}H_{10}$)   Benzo[a]pyrene ($C_{20}H_{12}$)

Phenanthrene ($C_{14}H_{10}$)   Perylene ($C_{20}H_{12}$)

Anthracene ($C_{14}H_{10}$)   Indeno[1,2,3-cd]pyrene ($C_{22}H_{12}$)

Fluoranthene ($C_{16}H_{10}$)   Dibenz[a,c]anthracene ($C_{22}H_{14}$)

Pyrene ($C_{16}H_{10}$)   Dibenz[a,h]anthracene ($C_{22}H_{14}$)

Benzo[a]fluorene ($C_{17}H_{12}$)   Benzo[ghi]perylene ($C_{22}H_{12}$)

Benzo[b]fluorene ($C_{17}H_{12}$)   Coronene ($C_{24}H_{12}$)

Benz[a]anthracene ($C_{18}H_{12}$)

Oxygenated PAHs

1-Indanone (C_9H_8O)   9,10-Anthracenedione ($C_{14}H_8O_2$)

Coumarin ($C_9H_6O_2$)   9,10-Phenanthrenedione ($C_{14}H_8O_2$)

9-Fluorenone ($C_{13}H_8O$)   7-Benz[de]anthracenone ($C_{17}H_{10}O$)

Xanthone ($C_{13}H_8O_2$)   7,12-Benz[a]anthracenedione ($C_{18}H_{10}O_2$)

1,2-Acenaphthenedione ($C_{12}H_8O_2$)

Heterocyclic PAHs

Benzothiazole (C_7H_3OS)   Dibenzothiophene ($C_{12}H_8S$)

Dibenzofuran ($C_{12}H_8O$)

Table 1.1 (cont'd). List of Target Compounds with Chemical Formulae.

Alkylated PAH

1-Methylnaphthalene $(C_{11}H_{10})$ 1-Methylphenanthrene $(C_{15}H_{12})$

2-Methylnaphthalene $(C_{11}H_{10})$ 2-Methylphenanthrene $(C_{15}H_{12})$

1,2-Dimethylnaphthalene $(C_{12}H_{12})$ 3-Methylphenanthrene $(C_{15}H_{12})$

1,3-Dimethylnaphthalene $(C_{12}H_{12})$ 4-Methylphenanthrene $(C_{15}H_{12})$

1,4-Dimethylnaphthalene $(C_{12}H_{12})$ 5-Methylphenanthrene $(C_{15}H_{12})$

1,5-Dimethylnaphthalene $(C_{12}H_{12})$ 2-Methylanthracene $(C_{15}H_{12})$

1,6-Dimethylnaphthalene $(C_{12}H_{12})$ 9-Methylanthracene $(C_{15}H_{12})$

2,3-Dimethylnaphthalene $(C_{12}H_{12})$ 3,6-Dimethylphenanthrene $(C_{16}H_{14})$

2,6-Dimethylnaphthalene $(C_{12}H_{12})$

Phenols

Phenol (C_6H_6O) 2,4-Dichlorophenol $(C_6H_4OCl_2)$

2-Methylphenol (C_7H_8O) 2,6-Dichlorophenol $(C_6H_4OCl_2)$

3-Methylphenol (C_7H_8O) 4-Methyl-2-methoxyphenol $(C_8H_{10}O_2)$

4-Methylphenol (C_7H_8O) 4-Chloro-3-methylphenol (C_7H_8OCl)

2-Methoxyphenol $(C_7H_8O_2)$ 2,3,5-Trimethylphenol $(C_9H_{12}O)$

2-Nitrophenol $(C_6H_5NO_3)$ 2,3,6-Trimethylphenol $(C_9H_{12}O)$

2-Ethylphenol $(C_8H_{10}O)$ 2,4,6-Trimethylphenol $(C_9H_{12}O)$

4-Ethylphenol $(C_8H_{10}O)$ 4-Methyl-2-nitrophenol $(C_7H_8NO_3)$

2,3-Dimethylphenol $(C_8H_{10}O)$ 2,4,5-Trichlorophenol $(C_6H_3OCl_3)$

2,4-Dimethylphenol $(C_8H_{10}O)$ 2,4,6-Trichlorophenol $(C_6H_3OCl_3)$

2,5-Dimethylphenol $(C_8H_{10}O)$ 2,3,4,6-Tetrachlorophenol $(C_6H_2OCl_4)$

Table 1.1 (cont'd). List of Target Compounds with Chemical Formulae.

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Phenols (cont'd)

2,6-Dimethylphenol ($C_8H_{10}O$)   2,4,5,6-Tetrachlorophenol ($C_6H_2OCl_4$)

3,4-Dimethylphenol ($C_8H_{10}O$)   Pentachlorophenol (C_6OCl_5)

Naphthols

1-Naphthol ($C_{10}H_8O$)   2-Naphthol ($C_{10}H_8O$)

Monocyclic Aromatics

Benzene (C_6H_6)   n-Propylbenzene (C_9H_{12})

Toluene (C_7H_8)   2-Chlorotoluene (C_7H_7Cl)

Ethylbenzene (C_8H_{10})   1,2,3-Trimethylbenzene (C_9H_{12})

Chlorobenzene (C_6H_5Cl)   1,2,4-Trimethylbenzene (C_9H_{12})

o-Xylene (C_8H_{10})   1,3,5-Trimethylbenzene (C_9H_{12})

m-Xylene (C_9H_{12})   p-Cymene (C_9H_{12})

p-Xylene (C_9H_{12})   n-Butylbenzene ($C_{10}H_{14}$)

Styrene (C_9H_{10})   1,2,4-Trichlorobenzene ($C_6H_3Cl_3$)

1,2-Dichlorobenzene ($C_6H_4Cl_2$)   Durene ($C_{10}H_{14}$)

1,3-Dichlorobenzene ($C_6H_4Cl_2$)   1,2,3,4-Tetramethylbenzene ($C_{10}H_{14}$)

1,4-Dichlorobenzene ($C_6H_4Cl_2$)   1,2,3,5-Tetramethylbenzene ($C_{10}H_{14}$)

Cumene (C_9H_{12})   Hexachlorobenzene (C_6Cl_6)

Phthalate Esters

Dimethylphthalate ($C_{10}H_{10}O_4$)   Butylbenzylphthalate ($C_{19}H_{20}O_4$)

Diethylphthalate ($C_{12}H_{14}O_4$)   Bis(2-ethylhexyl)phthalate ($C_{24}H_{38}O_4$)

Dibutylphthalate ($C_{16}H_{22}O_4$)   Dioctylphthalate ($C_{24}H_{38}O_4$)

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Table 1.1 (cont'd). List of Target Compounds with Chemical Formulae.

Chlorinated Pesticides

Hexachlorobutadiene (C_4Cl_6) Aldrin $(C_{12}H_8Cl_6)$

Hexachlorocyclopentadiene (C_5Cl_6) Dieldrin $(C_{12}H_8OCl_6)$

α-HCH $(C_6H_6Cl_6)$ p,p-'DDE $(C_{14}H_8Cl_4)$

γ-HCH $(C_6H_6Cl_6)$ p,p'-DDD $(C_{14}H_{10}Cl_4)$

Heptachlor $(C_{10}H_5Cl_7)$ p,p'-DDT $(C_{14}H_9Cl_5)$

Heptachlor epoxide $(C_{10}H_5OCl_7)$

Aldehydes, Ketones and Nitriles

Methylisobutyl ketone $(C_7H_{14}O)$ Benzonitrile (C_7H_5N)

Hexanal $(C_6H_{12}O)$ 2-Tolualdehyde (C_8H_8O)

Furfural $(C_5H_4O_2)$ 3-Tolualdehyde (C_8H_8O)

2-Heptanone $(C_7H_{14}O)$ 4-Tolualdehyde (C_8H_8O)

Heptanal $(C_7H_{14}O)$ Salicylaldehyde $(C_7H_6O_2)$

Benzaldehyde (C_7H_6O) 2,4-Dimethylbenzaldehyde $(C_9H_{10}O)$

Methylfurfural $(C_6H_6O_2)$ 2,5-Dimethylbenzaldehyde $(C_9H_{10}O)$

Alkanes

Octane (C_8H_{18}) Tetradecane $(C_{14}H_{30})$

Nonane (C_9H_{20}) Pentadecane $(C_{15}H_{32})$

Decane $(C_{10}H_{22})$ Hexadecane $(C_{16}H_{34})$

Undecane $(C_{11}H_{24})$ Heptadecane $(C_{17}H_{36})$

Dodecane $(C_{12}H_{26})$ Octadecane $(C_{18}H_{38})$

Tridecane $(C_{13}H_{28})$ Nonadecane $(C_{19}H_{40})$

Table 1.1 (cont'd). List of Target Compounds with Chemical Formulae.

Alkanes (cont'd)

Eicosane ($C_{20}H_{42}$)   Pentacosane ($C_{25}H_{52}$)

Heneicosane ($C_{21}H_{44}$)   Hexacosane ($C_{26}H_{54}$)

Docosane ($C_{22}H_{46}$)   Heptacosane ($C_{27}H_{56}$)

Tricosane ($C_{23}H_{48}$)   Octacosane ($C_{28}H_{58}$)

Tetracosane ($C_{24}H_{50}$)

Halogenated Aliphatics

Trichloroethene (C_2HCl_3)   Dibromochloromethane ($CHBr_2Cl$)

Tetrachloroethene (C_2Cl_4)   1,1,2,2-Tetrachloroethane ($C_2H_2Cl_4$)

1,2-Dichloropropane ($C_3H_5Cl_2$)   Bromoform ($CHBr_3$)

Bromodichloromethane ($CHBrCl_2$)   Hexachloroethane (C_2Cl_6)

1,1,2-Trichloroethane ($C_2H_3Cl_3$)

CHAPTER 2   ORGANIC COMPOUNDS IN THE ATMOSPHERE

In this chapter, the behavior of organic compounds in the atmosphere is discussed. Sampling and analysis methods which have been used for particulate and vapor phase organic compounds are also reviewed.

2.1   Distribution of Atmospheric Organic Compounds between the Vapor and Particulate Phases

In the atmosphere, trace organic compounds are present in both the particulate and vapor phases. For a given compound, the extent of association with particulate matter will depend on its vapor pressure, the ambient temperature, and the amount and type of particulate matter present. The extent of association with particulate matter can be approximated by the relation developed by Junge (1977):

$$\phi = \frac{c\theta}{P + c\theta} \qquad\qquad 2.1$$

where ϕ is the fraction of the atmospheric concentration which is associated with particles:

$$\phi = \frac{[air,particulate]}{[air,total]} \qquad\qquad 2.2$$

P is the vapor pressure of the compound (torr), θ is the total particulate surface area concentration (cm^2/cm^3), and c is an adsorption constant. While this relationship is useful for demonstrating the general trend of increasing association with particles with decreasing vapor pressure, it is only an approximation. It describes only physical, non-site specific adsorption. Furthermore, the value of c is different for each organic compound. The actual extent of association with particles may also depend on the physical form in which the compound was emitted to the atmosphere. For example, polycyclic aromatic hydrocarbons (PAHs) are emitted from combustion sources in conjunction with soot particles, for which they have a high affinity. Thus, PAHs with relatively high vapor pressures are often found on particles even when Equation 2.1 suggests that they would be present purely in the vapor phase. In addition to providing only qualitative predictions, Equation 2.1 also has a practical drawback. The aerosol surface area concentration θ is generally not a parameter measured in air sampling and, in fact, is difficult to measure.

Because θ is likely to be lower in remote locations than in urban areas, the value of ϕ, according to Equation 2.1, should also be lower there. The vapor/particle distribution should thus be shifted towards the vapor phase in remote locations. However, the rate at which equilibrium is achieved between the vapor and particulate phases is not known. If the rate is slow, the vapor/particle distribution in both urban and remote locations may reflect a global average θ value.

2.2 Measurement of Atmospheric Organic Compounds

2.2.1 Review of Sampling Methods

Sampling techniques for vapor and particulate phase organic compounds have, until recently, developed separately. Collection of particles simply involved the passage of large volumes of air through particle filters. Glass fiber filters were chosen most often. Lockhart et al. (1964) demonstrated that the collection efficiencies of such filters were >99% for 0.3 micron (μm) particles at a variety of flow rates. Since 0.3 μm is near the minimum in the collection efficiency curve for fibrous filters (Friedlander, 1977), larger and smaller particles should be collected with equal or greater efficiency. This conclusion was verified by John and Reischl (1978) who also investigated a number of other filter types. In particular, Teflon membrane filters were found to be satisfactory provided that the pore size was $\leq$ 3 um.

Collection of organic vapor phase compounds initially focussed on volatile compounds which are present in the atmosphere at relatively high concentrations. Even so, some concentration or enrichment of the sample was necessary. Early measurement systems employed cryotrapping, which involves the collection of vapor phase material by condensation in a cold sample loop. The main disadvantage of this method is that large quantities of water are collected along with the organic compounds, making analysis of the sample difficult. In the late 1950's and early 1960's, researchers began to investigate the use of adsorbent

traps for the collection of vapor phase organic compounds. Adsorbent materials included activated carbon (West et al., 1958) and polymer beads coated with silicone oil (Cropper and Kaminsky, 1963). The desired properties for adsorbents used in air sampling included a high affinity for the organic compounds to be trapped, a low affinity for water, a low degree of reactivity with atmospheric gases, and low blank levels. Furthermore, the adsorbed organic compounds must be easily removeable during analysis either by heating or by solvent extraction. Many organic compounds are not easily removeable from activated carbon.

Beginning in the late 1960's, some new types of adsorbents were investigated which were already in use as chromatographic packing materials. One of the earliest studies used Porapak Q and S for the determination of halogenated hydrocarbons (Williams and Umstead, 1968). Sorbents in the Chromosorb series were also tested (Dravnieks et al., 1971). The most popular packing material soon turned out to be Tenax-GC, a 2,6-diphenyl phenylene oxide resin which exhibits lower blank levels and higher thermal stability than the other sorbents (Zlatkis et al., 1973; Bertsch et al., 1974; Parsons and Mitzner 1975; Pellizzari et al., 1975; Russell, 1975). Solid sorbent vapor samplers have been reviewed by Crisp (1980).

Recently, several investigations of the chromatographic behavior of organic compounds collected on Tenax and the other adsorbents have been presented (Tanaka, 1978; Brown and Purnell, 1979; Bertoni et al., 1981; Krost et al., 1982). Adsorbent cartridges may be considered

to be short chromatographic columns. Analytes enter the cartridge and are trapped, then subsequently migrate down the cartridge in a succession of desorptions and re-adsorptions. Eventually, when the breakthrough volume is reached, the analytes will begin to elute off of the cartridge. For quantitative trapping of analytes in air samples, therefore, the breakthrough volumes must be known for the compounds of interest, and the sample volumes must be kept substantially below those volumes.

The reactivity of Tenax-GC has also been studied extensively (Hanson et al., 1981; Pellizzari et al., 1984; Walling et al., 1986). Bunch and Pellizzari (1979) reported that degradation of the sorbent does take place during ambient sampling. The degradation products of Tenax-GC are now fairly well-known. Less well understood is the extent to which adsorbed compounds can degrade during sampling. There are some indications that reactions might occur between sorbed analytes and reactive atmospheric gases (Bunch and Pellizzari, 1979; Pellizzari and Krost, 1984). This remains a serious concern.

Tenax and the other adsorbents are most suited to situations where a relatively small volume of air is being sampled. For the measurement of such compounds as pesticides and PCBs, much larger air volumes are required. Plugs of porous polyurethane foam (PUF) were tested and found to be suitable for this application (Bidleman and Olney, 1974; Turner and Glotfelty, 1977; Lewis, 1977). These researchers incorporated PUF plugs into standard high-volume particulate air samplers. Feng and Bidleman (1984) and Bidleman et al. (1984) have reported

breakthrough volumes for a number of compounds on polyurethane foam.

Samplers which utilized a filter followed by an adsorbent trap soon came into use for the measurement of organic compounds other than pesticides and PCBs. In particular, after Pupp et al. (1974) suggested that not all PAHs are present in the particulate phase, several investigations of the vapor/particle distribution of PAHs and other types of organic compounds were reported (Cautreels and Van Cauwenberghe, 1978; Thrane and Mikalsen 1981; Yamasaki et al., 1982; Keller and Bidleman 1984). Yamasaki et al. (1982) and Keller and Bidleman (1984) used total suspended particulate mass (TSP) as the particle concentration parameter in an empirical relation similar to Junge's equation (Section 2.1), and observed reasonable degrees of correlation of the vapor/particle distributions to this modified relationship.

While polyurethane foam has the advantages of being convenient to handle and inexpensive, volatile compounds tend to break through rapidly (Billings and Bidleman, 1980). For this reason large Tenax cartridges have also been used behind filters in high-volume sampling (Billings and Bidleman, 1980). However, although Tenax-GC exhibits less breakthrough, large adsorbent beds may be difficult to integrate into existing samplers and may also be prohibitively expensive for many applications. In addition, the possible degradation of Tenax-GC and sorbed analytes during sampling may limit its utility. Neither PUF nor Tenax-GC is thus the ideal sorbent for atmospheric sampling, although both are quite satisfactory for a wide range of compounds.

A complete sampling scheme for atmospheric organic compounds must therefore include a filter followed by an adsorbent such as PUF or Tenax. Provided that the breakthrough volume of the compound is not exceeded, this system provides a measure of the total atmospheric concentration. It may not, unfortunately, provide an accurate distinction between particulate and vapor phase material. Because adsorption of organics onto particles is a reversible process, researchers now wonder whether some volatilization of adsorbed material might take place while the particles were trapped on the filter. Similarly, there is concern that glass fiber filters might act as an adsorbent for organic vapors. Finally, there is a possibility that some adsorbed compounds might react with photochemical oxidants while on the filter.

This issue has not been resolved to date. A number of things are now known, however. Van Vaeck et al. (1984) measured the degree of volatilization from filters for a number of PAHs and alkanes. They found significant (50%) losses for compounds such as phenanthrene, but less volatilization for the less volatile compounds. Appel et al. (1983) have described a sampler for particulate matter which may eliminate this problem. In the Appel sampler, organic vapors are removed from the airstream before the air is passed through a filter and adsorbent. The amount of material collected on the adsorbent is thus a measure of the volatilization artifact only. Other studies indicate that adsorbed organic carbon may account for 15-20% of total organic carbon on quartz fiber filters (McDow, 1986). Several studies have shown that compounds such as benzo[a]pyrene will degrade on filters

under a variety of conditions (Peters and Seiffert, 1975; Pitts et al., 1978). Potentially mutagenic oxygenated and nitro derivatives were found in the latter study.

2.2.2 Review of Analytical Methods

Organic compounds are generally removed from sampling materials either by solvent extraction or by thermal desorption. Other methods, such as vacuum distillation, have been used less frequently. Solvent extraction of sampling materials is usually accomplished either by Soxhlet extraction or sonication. In either case, a substantial solvent volume reduction step is required before the sample is analyzed. This requirement makes the method best suited for the pre-concentration of relatively non-volatile compounds. In the thermal desorption process, heat is used rather than solvents to remove the analytes. Thermal desorption is an attractive analytical method because high sensitivity can be attained and minimal sample handling is involved. This method is best suited to the analysis of volatile compounds, since they often can be removed from the sorbent at relatively low temperatures. Polyurethane foam has been used exclusively with solvent extraction, while Tenax-GC has been used with both thermal desorption (Pellizzari et al., 1975; Pankow et al., 1982) and solvent extraction (Billings and Bidleman, 1980, 1983; Leuenberger and Pankow, 1984). Fibrous filters have been thermally desorbed (Greaves et al., 1985; McDow, 1986) but are most commonly solvent extracted.

Once the sample has been pre-concentrated, the determination of specific organic compounds in air samples requires an analytical method which is capable of separating individual components out of the resultant complex mixture. Gas chromatography (GC) and high performance liquid chromatography (HPLC) have been the main methods of separation. Generally, at least one cleanup or separation step is required in order to isolate the compounds of interest from other compounds which might interfere. GC with electron capture detection (GC/ECD) is a very sensitive means of analysis for PCBs and other chlorinated compounds (e.g. Giam et al., 1980). High performance liquid chromatography (HPLC) with fluorescence detection has been widely used for the analysis of PAHs (e.g. Keller and Bidleman, 1984). Probably the most versatile and accurate methods, however, is gas chromatography with detection by mass spectrometry (GC/MS). This technique has enabled the determination of even very minor species in the atmosphere without the use of extensive separation techniques (e.g., Eichelberger et al., 1974; Cautreels and Van Cauwenberghe, 1978).

CHAPTER 3   ORGANIC COMPOUNDS IN RAIN

In this chapter, the scavenging behavior of organic compounds is discussed and the gas, particle, and overall scavenging ratios are defined.   Sampling and analytical methods for the determination of organic concentrations in rain are reviewed.   Finally, the application of scavenging ratios to studies of the transport and fate of organic compounds is discussed.

3.1   Scavenging of Atmospheric Organic Compounds

Because organic compounds may be present in the atmosphere in both the vapor and particulate phases, both gas and particle scavenging may be important for a given compound.   The total degree of scavenging of a given compound can be expressed as:

$$W = W_g \ (1-\phi) + W_p \ \phi \qquad\qquad 3.1$$

where W is the overall scavenging ratio:

$$W = \frac{[rain,total]}{[air,total]} \qquad\qquad 3.2$$

W_g is the gas scavenging ratio:

$$W_g = \frac{[\text{rain,dissolved}]}{[\text{air,vapor}]} \qquad 3.3$$

W_p is the particle scavenging ratio:

$$W_p = \frac{[\text{rain,particulate}]}{[\text{air,particulate}]} \qquad 3.4$$

and ϕ is the fraction of the atmospheric concentration which is associated with particles as described in Section 2.1.

3.1.1 Gas Scavenging

The equilibrium distribution of a substance between the vapor and aqueous phases is described by Henry's Law for dilute solutions. The conditions under which an atmospheric vapor would be in equilibrium with falling raindrops were determined by Hales (1972). He found that the time required for equilibrium to be established depended on the Henry's Law constant, the size of the raindrop and the vertical concentration gradients. Slinn et al. (1978) have estimated that atmospheric vapors will reach equilibrium with falling raindrops within a few tens of meters of fall distance if they do not undergo chemical reactions within the drop. Thus, most non-reactive atmospheric trace organics would be expected to partition into rain according to Henry's Law. The validity of this approximation will be examined in detail in Chapter 7.

The equation for the equilibrium distribution between the air and rain is

$$W_g = \alpha = RT/H \qquad\qquad 3.5$$

where α is referred to as the solubility coefficient, and can be thought of as a non-dimensionalized form of the Henry's Law constant; H is the Henry's Law constant; T is the absolute temperature; and R is the gas constant. For compounds which are only slightly soluble in water this relationship becomes:

$$W_g = RTS/P \qquad\qquad 3.6$$

where S is the solubility of the compound and P is its vapor pressure. Both solubility and vapor pressure are functions of temperature. The application of laboratory solubility and vapor pressure data to rain scavenging ratio predictions requires that the measurements be available at the appropriate ambient temperature. In most cases, S and P data are only available at $25^{\circ}C$, a temperature which is inappropriate for the modeling of rain scavenging in the Pacific Northwest in the wintertime. A compilation of S and P data at $25^{\circ}C$ and the resulting α values for a number of organic compounds is presented in Table 3.1.

The presence of organic surface films on raindrops would affect the scavenging of vapors in two ways. A film would slow down the rate of transfer of material between the vapor and dissolved phases, possibly resulting in a lack of equilibrium between the phases. Also, a film would increase the overall scavenging of organic vapors by raindrops, because many organic compounds would partition into the film. If the film-bound organics were measured as dissolved organics, an artificially high value for W_g would be obtained. However, Gill et al. (1983) have

Table 3.1. Solubilities, Vapor Pressures and α Values for Organic Compounds at 25°C.

Compound	S (mg/L)	ref	P (torr)	ref	α
PAHs and Derivatives					
Naphthalene	32	a	7.8 E-2	b	59
1-Methylnaphthalene	29	c	6.6 E-2	d	56
2-Methylnaphthalene	25	c	6.8 E-2	d	48
1,3-Dimethylnaphthalene	8.0	c			
1,4-Dimethylnaphthalene	11.4	c	7.5 E-3	e	180
1,5-Dimethylnaphthalene	3.4	c			
2,3-Dimethylnaphthalene	3.0	c	2.2 E-3	f	160
2,6-Dimethylnaphthalene	2.0	c	1.5 E-3	f	160
Acenaphthylene	3.9	a	6.7 E-3	b	72
Acenaphthene	4.5	c	2.15 E-3	b	250
Biphenyl	7.1	c			
Dibenzofuran	6.6	c	1.8 E-3	f	410
Fluorene	1.85	c	6.0 E-4	b	350
Dibenzothiophene	1.04	c	6.2 E-5	f	1700
Phenanthrene	1.28	c	1.21 E-4	b	1100
Anthracene	4.5 E-2	a	6.0 E-6	b	680
1-Methylphenanthrene	2.7 E-1	c	6.5 E-5		400
Fluoranthene	2.4 E-1	c	9.2 E-6	b	2400
Pyrene	1.4 E-1	c	4.5 E-6	b	2900

Table 3.1 (cont'd). Solubilities, Vapor Pressures and α Values for Organic Compounds at 25°C.

Compound	S (mg/L)	ref	P (torr)	ref	α
Benzo[a]fluorene	4.5 E-2	c	2.85 E-7	g	14000
Benzo[b]fluorene	2.0 E-3	c			
Benz[a]anthracene	1.1 E-2	c	2.1 E-7	b	4300
Chrysene	1.8 E-3	a	9.1 E-9	g	16000
Benzo[b]fluoranthene	1.5 E-3	c	6.3 E-9	g	18000
Benzo[k]fluoranthene	7.6 E-4	c	6.0 E-9	g	9400
Benzo[e]pyrene	6.2 E-3	c	5.7 E-9	g	80000
Benzo[a]pyrene	1.5 E-3	h	5.6 E-9	a	20000
Perylene	3.0 E-4	c			
Benzo[ghi]perylene	2.6 E-4	c	1.0 E-10	a	1.8 E5
Coronene	1.4 E-4	c	1.5 E-12	q	5.8 E6
Phthalate Esters					
Diethylphthalate	1.28 E3	i	3.5 E-3	a	31000
Dibutylphthalate	11.1	i	1.0 E-5	a	74000
Butylbenzylphthalate	2.9	a	8.6 E-6		20000
Bis[2-ethylhexyl]phthalate	0.4	a	2 E-7	a	90000
Dioctylphthalate	0.285	j			

Table 3.1 (cont'd). Solubilities, Vapor Pressures and α Values for Organic Compounds at 25°C.

Compound	S (mg/L)	ref	P (torr)	ref	α
Monocyclic Aromatics					
Toluene	535	a	28.7	a	3.7
Ethylbenzene	167	d	9.5	d	3.0
m-Xylene	162	d	8.25	d	3.4
p-Xylene	179	d	8.8	d	3.5
o-Xylene	186	d	6.6	d	4.8
1,4-Dichlorobenzene	79	a	1.18	a	8.2
1,2-Dichlorobenzene	134	d	1.49	d	11
Mesitylene	73	d	2.46	d	4.5
1,2,4-Trimethylbenzene	56	d	2.03	d	4.2
1,2,4-Trichlorobenzene	30	a	0.29	a	10.6
Phenols					
Phenol	8.2 E4	j	0.34	k	47000
2-Methylphenol	2.6 E4	j	0.29	k	15000
3-Methylphenol	2.3 E4	j	0.14	k	28000
4-Methylphenol	1.8 E4	j	0.12	k	26000
2-Methoxyphenol	1.6 E4	i	0.13	k	18000
2-Nitrophenol	1.4 E3		0.18	f	1000
2,6-Dimethylphenol	5.9 E3	n	0.18	k	5000
2,4-Dimethylphenol	6.2 E3	n	0.098	k	9600

Table 3.1 (cont'd). Solubilities, Vapor Pressures and α Values for Organic Compounds at 25°C.

Compound	S (mg/L)	ref	P (torr)	ref	α
2,5-Dimethylphenol	4.6 E3	m	0.10	f	6600
3,4-Dimethylphenol	5.1 E3	m	0.027	f	29000
3,5-Dimethylphenol	4.8 E3	m	0.035	f	21000
2,4-Dichlorophenol	4.5 E3	j	0.089	m	5700
2,4,5-Trichlorophenol	1.2 E3	j	0.022	m	5100
1-Naphthol			7.9 E-3	f	
2-Naphthol			6.8 E-3	f	
Pesticides					
α-HCH	1.63	a	2.5 E-5	a	4200
γ-HCH	7.8	a	1.6 E-4	a	3100
p,p'-DDE	0.04	a	6.5 E-6	a	360
p,p'-DDD	0.02	a	1.0 E-6	a	1200
p,p'-DDT	5.5 E-3	a	1.9 E-7	a	1500
Ketones					
Methylisobutyl ketone	1.95 E4	o	7.1	m	510
2-Heptanone	4.3 E3	o	1.4	m	500
Chlorinated Aliphatics					
Trichloroethene	1.1 E3	a	57.9	a	2.6
Tetrachloroethene	200	a	14	a	1.6

Table 3.1 (cont'd). Solubilities, Vapor Pressures and α Values for Organic Compounds at 25°C.

Compound	S (mg/L)	ref	P (torr)	ref	α
Alkanes					
Eicosane	1.9 E-3	d	1.8 E-4	p	0.7
Heneicosane			6.8 E-5	p	
Docosane			2.9 E-5	p	
Tricosane			1.3 E-5	p	
Tetracosane			5.5 E-6	p	
Pentacosane			2.5 E-6	p	
Hexacosane	1.7 E-3	d	1.1 E-6	p	79
Heptacosane			4.9 E-7	p	
Octacosane			2.2 E-7	p	

a Mabey et al., 1982. b Sonnefeld et al., 1983. c Pearlman et al., 1984. d Mackay and Shiu, 1981. e estimated from the KLH equation given in Mackay et al., 1982. f Chao et al., 1983. g Yamasaki et al., 1984. h Whitehouse,1984. i Schwarz and Miller, 1980. j Verschueren, 1983. k Erichsen and Dobbert, 1955. l Andon et al., 1960. m Weast, 1973. n Korenman et al., 1978. o Hansch et al., 1968. p estimated from Equation 14-14 of Lyman et al., 1982. q Murray et al., 1974.

reported that the quantities of surface-active organic material in rain are not sufficient for monolayer surface coverage. Experimental evidence of the existence of equilibrium gas scavenging would thus provide additional evidence that surface films do not exist on raindrops.

3.1.2 Particle Scavenging

Much of the research on rain scavenging of atmospheric pollutants has focused on the process of particle scavenging. This complex process is now known to depend on the meteorology and cloud physics of each storm event as well on as the size and chemical composition of the particles. The simplest model for in-cloud particle scavenging involves nucleation scavenging followed by coalescence of the cloud droplets into raindrops. In this process, cloud droplets form around hygroscopic aerosol particles which then collide and coalesce into raindrops. Of the order of 10^6 10 μm cloud droplets must combine to form one 1 mm raindrop. Hence, scavenging ratios under these conditions are expected to be of the order of 10^6. However, this process alone seldom produces precipitation. In cold clouds, ice crystals and cloud droplets coexist. The ice crystals generally form around clay particles. They grow initially by vapor accretion. Since "clean" water is added to the nucleus, no scavenging takes place during this process. Once the crystals become large enough, they will begin to fall and may grow by collection of supercooled droplets (riming). Scavenging ratios for this cold-cloud process may be considerably lower than 10^6, depending on the relative importance of vapor accretion and riming to the growth of the droplet.

In the case of below-cloud scavenging, W_p values are estimated to be 10^3 to 10^5 for 0.01 to 1.0 μm particles (Slinn et al., 1978). From this limited information, one may expect to observe overall particle scavenging ratios in the range 10^3 - 10^6.

3.2 Measurement of Organic Compounds in Rain

Measurement of organic compounds in aqueous samples has traditionally been accomplished by collection of a volume of water followed by liquid:liquid extraction with a solvent such as methylene chloride. Due to the difficulty of minimizing contamination of very large sample volumes, this method is better suited to the analysis of relatively polluted samples than to rain samples. Alternatively, adsorbents such as XAD resins and Tenax-GC have been used to determine organic concentrations in natural waters (Leoni et al., 1975, 1976) and tap water (Van Rossum and Webb, 1978). XAD resins have excellent retention capabilities for all classes of organic compounds (Junk et al., 1974), but suffer from high blank levels. Tenax exhibits excellent collection efficiencies for neutral organics (Pankow and Isabelle, 1982; Agostiano, 1983; Leuenberger and Pankow 1984), but not for polar compounds such as phenols.

In aqueous sampling with adsorbent cartridges, breakthrough may depend upon parameters other than sample volume. For example, at high sample flow rates, breakthrough due to incomplete time for diffusion to the sorbent surface may occur (Pankow et al., 1982). Breakthrough volumes for compounds with high water solubilities may be low because of unfavorable partitioning of the analyte between the aqueous and sorbent

phases.

One of the earliest surveys of trace organic compounds in rain was conducted in Norway by Lunde et al. (1977). They used large aluminum cans for the collection of rain and snow samples, then passed the water or meltwater through glass fiber filters and activated carbon in the laboratory. They identified a number of PAHs, alkanes, carboxylic acid esters and phthalate esters. The presence of such compounds in relatively remote areas of Norway indicated that long-range transport of combustion products was occurring. In the 1980's, several researchers have reported on the concentrations of various organic compounds in rain and snow samples collected throughout the United States, Europe and Japan (Matsumoto and Hanya, 1980; Meyers and Hites, 1982; Georgii and Schmitt, 1983; Kawamura and Kaplan, 1983; Quaghebeur et al., 1983). The methods used in these studies all involved collection of a rainwater sample in a glass, aluminum or stainless steel vessel followed by liquid:liquid extraction and analysis by GC, GC/MS or HPLC. Generally, however, the concentrations of these compounds were not measured in the air. Thus while fluxes of pollutants could be calculated, no conclusions could be drawn about the scavenging process.

Atkins and Eggleton (1971) examined the scavenging ratios for three pesticides by comparing air and rain data from the literature. They found that the scavenging ratios of DDT were too high to be explained by equilibrium gas scavenging alone, and thus concluded that a portion of the DDT must be present on particles. Bidleman and Christensen (1979) measured high molecular weight organochlorine compounds in rain and air.

They collected rain in stainless steel basins and extracted it with methylene chloride to recover the organics. From this information they were able to calculate scavenging ratios. They concluded that PCBs and DDT were scavenged primarily by particle scavenging despite the fact that the majority of these compounds were present in the vapor phase. Atlas and Giam (1981) measured air and rain concentrations of α- and γ-HCH and dibutyl- and bis(2-ethylhexyl)-phthalate over the Pacific Ocean. The resultant scavenging ratios agreed reasonably well with equilibrium gas scavenging values for these compounds (Pankow et al., 1984). Simmonds (1984) measured several volatile halogenated compounds in rain and air. His analytical method involved the introduction of the rain and air samples directly into a purge and trap apparatus. He found good agreement with equilibrium values for several compounds, but significant deviations from equilibrium for other chemically similar compounds.

In 1984, two automated rain samplers were described in the literature. Strachan and Hunneault developed a stainless-steel/Teflon sampler with collection area of 0.2 m^3. At the same time, Pankow et al. developed an aluminum/Teflon sampler with collection area 0.8 m^3. Both samplers were designed to open only during periods of rainfall, and thus avoid problems due to contamination of samples from dry deposition. Both samplers also featured in-situ adsorption columns for the immediate pre-concentration of organic compounds. This was an important concern because of the possibility of volatilization, wall losses, and chemical and biological degradation of some organic compounds before they could be processed in the laboratory.

These samplers were operated at ground level. Ground level sampling is completely appropriate for the determination of gas scavenging ratios, because the existence of rain/air equilibrium or near-equilibrium means that the ground level air and rain concentrations will be related regardless of how they differ from the concentrations which existed in the cloud. The same is not true for particle scavenging ratios, however. If in-cloud scavenging is occurring, and if the concentrations in the cloud are very different than those at ground level, then the particle scavenging ratios obtained at ground level may have little meaning. Fortunately, the degree of vertical convective motion which occurs during most rainstorms ensures that the air masses at ground level and in the cloud will not be too different. In this case, while sampling in-cloud would still be preferable, ground level sampling, especially for preliminary studies, will provide valuable information.

3.3 The Role of Rain Scavenging in Environmental Fate Calculations

In determining the fate of organic compounds in the environment, the rate of removal of such compounds from the atmosphere due to rain scavenging is an important piece of information. Because rain scavenging is a mechanism which transports material from one environmental reservoir to another, it can be viewed either as a removal mechanism for atmospheric compounds, or as a source for aquatic compounds. In the following sections these two approaches are discussed. The best approach for understanding the ocean/atmosphere system in particular,

however, is a dynamic, integrated approach such as presented by Mackay et al. (1986).

3.3.1 Atmospheric Lifetimes of Organic Compounds

The residence time, or lifetime, of a compound in the atmosphere will depend upon the mechanisms and rates of removal of that compound. Removal mechanisms include chemical reactions, rain scavenging, dry deposition, and advective transport. The total rate of removal will include contributions from each of these mechanisms. Compounds with long lifetimes (months to years) will become globally distributed, while those with short lifetimes will be found only near their sources.

The lifetime T, in years, of a compound which is at steady-state in the atmosphere is given by the relation

$$T = Q/R \qquad\qquad 3.7$$

where Q is the total atmospheric burden in grams and R is the total removal rate in grams per year. Lifetimes due to each individual removal mechanism can be defined and compared as to the relative importance of each. The total lifetime is then given by

$$1/T = 1/T_1 + 1/T_2 + .\ .\ . \qquad\qquad 3.8$$

For compounds which exist exclusively in the vapor phase, the lifetime due to wet deposition may be obtained from the gas scavenging ratio and the total amount of rainfall. To calculate the lifetime, a vertical concentration profile must be assumed. Because of the variation of

pressure with altitude, the density of air, and hence the density of a well-mixed vapor phase compound, decreases exponentially with altitude. The concentration profile of such a compound is given by the equation

$$c = c_o \exp[-z/z_o] \qquad 3.9$$

where c_o is the concentration of the compound at ground level (g/m^3), z is altitude (m) and z_o is the altitude at which the density of air has dropped to 1/e times its original concentration. The column abundance C (g/m^2) of the compound is then given by

$$C = \int_0^h c(z)dz = \int_0^h c_o \exp[-z/z_o] \, dz \qquad 3.10$$

This is integrated over the height of the mixed layer, which can range from hundreds of meters to the height of the troposphere. The following calculation is carried out for the latter case. The value of z_o is roughly 10 km, which is also the approximate height of the troposphere. Thus

$$C - 6000 \, c_o \qquad 3.11$$

The removal rate R (g/yr) due to gas scavenging is equal to the precipitation rate P (in m/yr) multiplied by the concentration in the rain (g/m^3) and some reference area A (m^2)

$$R = P \, A \, c_{rain} = P \, A \, W_g \, c_o \qquad 3.12$$

From this it can be seen that the approximate lifetime is given by

$$T = Q/R = AC/R = \frac{6000 \ A \ c_o}{P \ A \ W_g \ c_o} = \frac{6000}{P \ W_g} \qquad 3.13$$

It should be emphasized that Equation 3.13 is a rough approximation only, since: 1) the steady-state assumption may not be appropriate for many compounds, and 2) rainfall does not occur at a continuous, steady rate. (Not even in Oregon.)

For a situation where $P = 1$ m/yr and $W_g = 6000$, the lifetime given by Equation 3.13 would be 1 year. Since few atmospheric organic compounds exhibit gas scavenging ratios greater than 20000, lifetimes due to gas scavenging will generally be on the order of months or years.

An analogous expression can be derived for the lifetime due to particle scavenging:

$$T_{part} = \frac{6000}{P \ W_p} \qquad 3.14$$

For a W_p value of 10^5 and $P = 1$ m/yr, the lifetime would be about 3 weeks. However, there is some question as to the validity of this expression. Unlike gas scavenging, particle scavenging is not an equilibrium process. Hence there is no guarantee that W_p is a constant with respect to rainfall amount. Several researchers (Gatz, 1976; Strachan et al., 1980; van Noort et al., 1985) have suggested that the value of W_p is much greater at the beginning of a storm, and that particle scavenging is therefore a non-linear process. In that case the flux of scavenged material would depend more on the number of storm events than on the amount of rainfall.

3.3.2 Wet Deposition as a Source of Organic Compounds to Ecosystems

Fluxes of organic compounds due to gas and particle scavenging, termed "wet deposition," are of interest in determining the inputs of atmospheric compounds to aqueous systems. The flux due to wet deposition (F_{wet}) can be expressed very simply as

$$F_{wet} = [rain,total] \; P \qquad\qquad 3.15$$

where F_{wet} is in $g/(m^2 \; yr)$ and P is the precipitation rate in m/yr. In terms of scavenging ratios,

$$F_{wet} = [air,total] \; W \; P \qquad\qquad 3.16$$

These fluxes can then be compared to other known sources of material to the ecosystem. This will be discussed further in Chapter 8.

Several extensive studies on wet deposition to the Great Lakes have been conducted. Eisenreich (1981) estimated the inputs of PCBs to Lake Superior from wet and dry deposition as well as from industrial sources. He concluded that the increase in concentration of PCBs in the lake was due to wet and dry deposition. Murphy (1981) studied the input of PCBs to Lakes Huron and Michigan by sampling rain and air concurrently with polyurethane foam. By comparing wet deposition to other known inputs of PCBs, he found the atmosphere to be the major source, with wet and dry deposition approximately equal. Andren and Strand (1981) concluded that the ratio of wet to dry deposition for PAHs to Lake Michigan was 9:1. Bidleman et al. (1981) found wet deposition to be more important than dry deposition for toxaphene inputs to the South Atlantic Bight. Thus

the careful measurement of gas and particle scavenging ratios for a wide variety of organic compounds would be of use to the understanding of sources of these compounds to various sensitive ecosystems.

CHAPTER 4 AIR SAMPLING FOR ORGANIC COMPOUNDS

This chapter presents the description of the sampling apparatus used to determine organic concentrations in the atmospheric vapor and particulate phases. The methods of extracting the analytes from the sample matrix and analyzing the samples are then described, followed by the resulting concentrations obtained from two years of air sampling in Portland and one at the Oregon coast. The comparison of these data to the concurrent rain data is presented in Chapter 6.

4.1 Experimental Procedure

4.1.1 Sampling Apparatus

The air sampler which was developed for this study has the capability to collect organic compounds ranging in volatility from trichloro-ethene to coronene, in both the vapor and particulate phases. The air sampler (Figure 4.1) utilized 102 mm glass fiber filters (GFFs) or Teflon membrane filters (TMFs) followed by two or three parallel vapor sampling channels. GFFs with backup GFFs were utilized during the 1984 sampling season. For four events in 1985, duplicate samplers were run, one with a GFF and one with a TMF. TMFs were used for the remaining 1985 events. No backup filters were utilized in 1985.
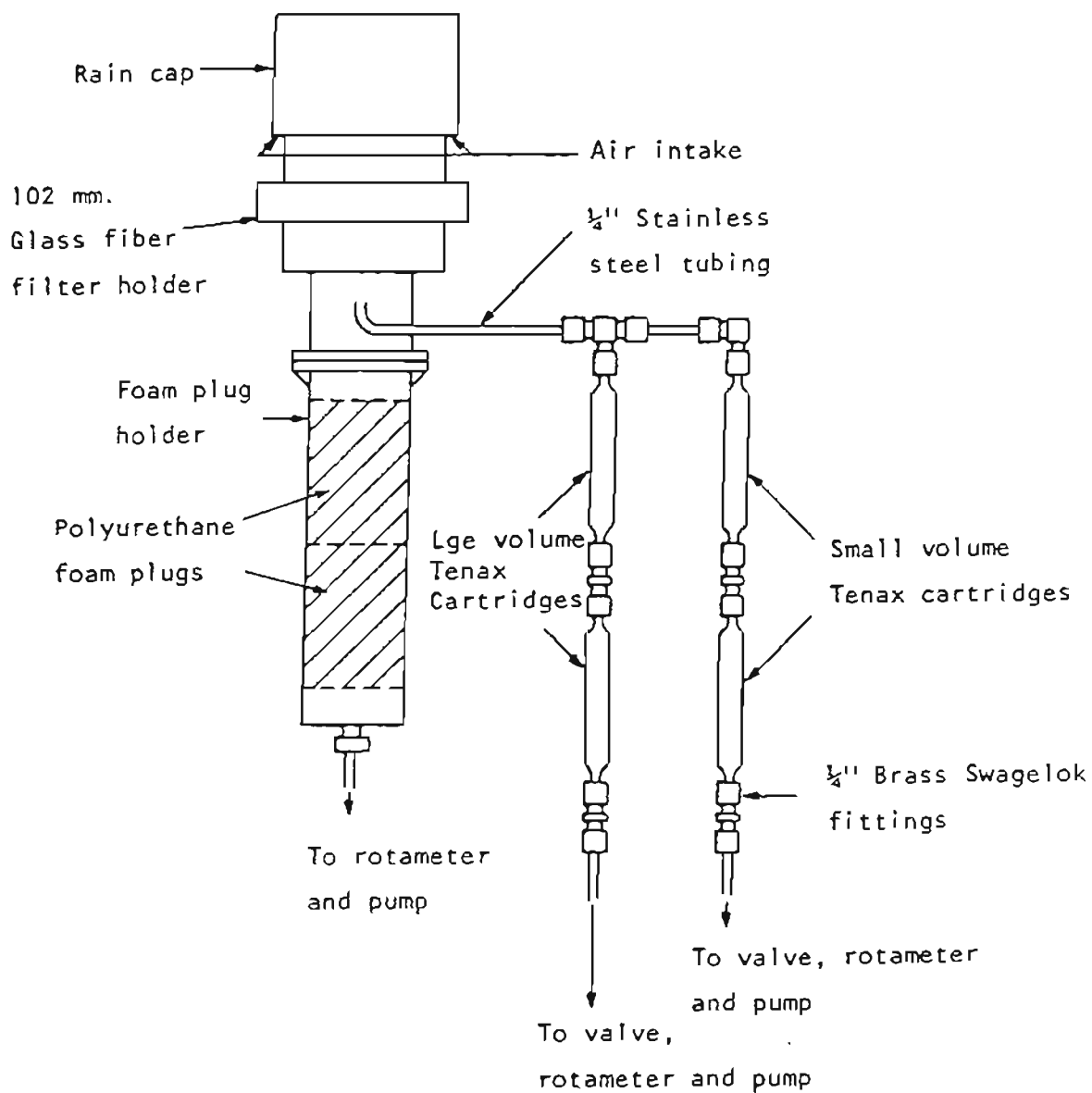
Figure 4.1. Air sampler used to collect organic compounds in the vapor and particulate phases.

The air sampler processed 100-190 L/min of air through the filter. Over 99% of the total flow continued directly through a polyurethane foam plug (PUFP) 7.6 cm long and 5.1 cm in diameter. The PUFPs were used for the determination of low volatility organic vapors. During the 1984 sampling season, flows of 40 mL/min and 600 mL/min were diverted through two air desorption cartridges, ADC-1 and -2, respectively. The ADCs were used for the determination of high-to-intermediate volatility compounds. The ADC-1s were eliminated in 1985 when the most volatile compounds were removed from the list of target compounds. Each channel was equipped with a backup adsorbent. All adsorbents were shielded from light during sampling, transport and storage. An overall flow rate of 150 L/min was provided by a Gast 1022 or 822 oil-less carbon vane pump (Gast Manufacturing Corp., Benton Harbor, MI). The pump was housed in a noise-reducing box approximately 3 meters from the sampler in a direction which was downwind of the sampler during the prevailing south winds. The pump was actuated by the sensor for the rain sampler, allowing air sampling only during periods of rain sampling. The total sampling time was recorded. The flow rate through each of the channels was measured with a laboratory-calibrated rotameter (Dwyer Instruments, Michigan City, IN).

The ADC bodies were constructed of Pyrex glass, with o.d. 1.1 cm, bed length 8.0 cm, and bed volume 5.7 cm^3, and packed with 0.79 g of 35/60 mesh Tenax-GC or Tenax-TA. (Tenax-GC was used in the 1984 sampling season. Tenax-TA, a new type of Tenax developed specifically for use as an adsorbent, was used in the 1985 sampling season. Henceforth,

the term "Tenax" will be used to refer collectively to both Tenax-GC and Tenax-TA.) The Tenax was held in place with silanized glass wool plugs. The ends of the cartridges were constructed of precision 0.25 in (0.64 cm) o.d. tubing which could be sealed with Teflon ferrules into brass Swagelok fittings for sampling and airtight storage.

4.1.2 Sampling Sites

The Portland site used in both 1984 and 1985 was located at the Oregon Department of Environmental Quality (ODEQ) air monitoring station at 5824 S.E. Lafayette St. The station is in a residential section of southeast Portland. Both the air and rain samplers were situated at ground level with inlets at approximately 2 m. The coastal site used in 1985 was located at Ft. Stevens State Park on the northern Oregon coast. That site was approximately 110 km northwest of Portland and 15 km west of Astoria, at the mouth of the Columbia River. The samplers were placed at ground level in a yard at the park office. The office contained a woodstove and adjoined a garage in which the park vehicles were housed. One other residence was located nearby. In addition, an extensive campground facility was located within 1/2 km of the site. For these reasons the coastal site should not be considered a remote or pristine site. It was chosen because it generally experiences strong winds directly from the Pacific Ocean during rainstorms. The sampling took place in April of 1985, at a time when the park was not used heavily by campers.

4.1.3 Materials

The 102 mm glass fiber filters were obtained from Gelman (Ann Arbor, MI). The 2 μm pore size Teflon-backed Teflon membrane filters (Zefluor) were obtained from Membrana (Pleasanton, CA) in 20.3 by 25.4 cm sheets and were cut into 102 mm disks. Tenax-GC and Tenax-TA were obtained from Alltech Assoc. (Deerfield, IL) with mesh size 35/60. Polyurethane foam of density 0.022 g/cm^3 was obtained from Dayco Northwest (Portland, OR) in sheets of thickness 7.6 cm. Plugs of diameter 5.1 cm were cut from the PUF sheets using a 2.25 inch hole saw operated in reverse. All solvents used were distilled-in-glass grade (Burdick & Jackson, Muskegon, MI). Perdeuterated internal standards were obtained from KOR Isotopes (Cambridge, MA) and MSD Isotopes (Los Angeles, CA). Other standard materials were generally from Chem Service (West Chester, PA).

4.1.4 Preparation of Sampling Materials

The GFFs were pre-cleaned by Soxhlet extraction for 24 h in acetone, air dried, and then baked in a muffle furnace at 400°C for 2 h. The TMFs were pre-cleaned by sonication in 60:40 acetone:hexane for two 10 min periods, then air dried. The air filters were transported to and from the sampling site wrapped in pre-baked aluminum foil.

PUFPs were cleaned by Soxhlet extraction for 24 h in 60:40 acetone:hexane and dried under a stream of pre-purified nitrogen. PUFPs were stored and transported in clean screw-capped glass jars fitted

with TFE Teflon capliners. Teflon tape was wrapped around the threads of the jar to provide an airtight seal. Filled ADCs were cleaned by pumping 2 L of 60:40 acetone:hexane through a series of five cartridges at a rate of 3 mL/min with a Waters HPLC pump. The ADCs were dried, either by vacuum or with a stream of ultrapure helium, and then conditioned by heating at 275°C under a flow of ultrapure helium at a rate of 100 mL/min for 3 hours. If the ADCs were stored for longer than 3-4 weeks after cleaning, the latter step of the cleaning process was repeated immediately prior to sampling. Cartridges were capped with pre-cleaned brass Swagelok caps equipped with Teflon ferrules. The Teflon ferrules and the brass caps were cleaned by sonication in 60:40 acetone:hexane, air dried, and then degassed at 150°C under vacuum prior to assembly. The capped cartridges were stored and transported in clean Pyrex culture tubes.

4.1.5 Recovery Studies

The extraction efficiencies for removal of adsorbed organic material from aerosol particles were determined by analyzing the GFFs before and after extraction using a thermo-optical carbon analyzer (Johnson et al., 1980). Studies of the recovery of the target compounds from PUFPs, both absolute and relative to the internal standard compounds, were conducted by spiking the sampling material with a solution in acetone containing all analytes of interest. The spiked filters and PUFPs were then subjected to the entire extraction, cleanup

and analysis procedure used for the samples. Recoveries were determined after each step in the procedure.

4.1.6 Analysis of samples

All samples were stored at $5^{\circ}C$ in sealed containers which were shielded from light. The filters and PUFPs were extracted within two weeks after sampling and analyzed within two months after extraction; the ADCs were thermally desorbed within two months after sampling.

4.1.6.1 Extraction of Filters

Prior to extraction, GFFs and TMFs were each spiked with 50 μL of an internal standard solution. The internal standard compounds were either deuterated analogs of the target compounds, or other chemically similar compounds. They were added to monitor losses of the target compounds during extraction and subsequent analytical procedures. The internal standard solution (in acetone) had the following composition (ng/μL): naphthalene-d_8 (20); 2,4-dibromophenol (4); acenaphthene-d_{10} (20); fluorene-d_{10} (20); 2,4,6-tribromophenol (4); benzophenone-d_{10} (20); phenanthrene-d_{10} (20); fluoranthene-d_{10} (20); o,p'-DDE (1); o,p'-DDD (1); chrysene-d_{12} (20); perylene-d_{12} (20). The 1985 internal standard solution also contained phenol-d_5 (100 ng/μL) and 2,4-dimethylphenol-d_3 (50 ng/μL). The spiked filters were Soxhlet extracted with 20 mL of 50:50 acetone:methylene chloride for 1.5-2 h. Front and backup filters were extracted separately. The extracts were concentrated to 2 mL in a miniature Kuderna-Danish (K-D)

apparatus. All 1984 air filters were re-extracted with 75:25 toluene: methanol. These extracts were prepared in the same manner as the acetone:methylene chloride extracts.

4.1.6.2 Cleanup of the Filter Extracts

The concentrated extracts from 1984 were separated into acid and base/neutral fractions as follows. An extract was brought up to 10 mL in hexane, placed in a small separatory funnel and extracted with two 15 mL portions of 0.01 $\underline{N}$ NaOH. The organic layer, containing the base/neutrals, was dried over 2 g anhydrous Na_2SO_4. The aqueous layer was acidified to pH 2 with concentrated H_2SO_4, then extracted with two 15 mL portions of methylene chloride. The extracts from 1985 were not fractionated, but were cleaned up by passing them through a column containing 5 mL of 15% deactivated silica gel. The column was eluted with 25 mL of methylene chloride. The resulting extracts were again concentrated to 2 mL in the miniature K-D apparatus, then transferred to a 3 mL Mini-vial (Alltech Assoc., Deerfield, IL). The extracts were again stored at 5°C until they were analyzed by GC/MS.

4.1.6.3 GC/MS Analysis of Filter Extracts

For analysis, the extract volume was further reduced to 200 μL by blowdown with ultrapure helium. During the blowdown step the vial was placed in a block heated to 40°C to counteract evaporative cooling. A 5 μL aliquot of an external standard solution in acetone containing 200·

ng/μL each of 2-bromo-m-xylene, anthracene-d_{10}, and decafluorotri-phenylphosphine was added to the extract just before analysis.

The analysis of the February 1984 extracts utilized a 30 m, 0.32 mm i.d. SE-54 fused silica capillary column with film thickness 0.25 μm (J&W Scientific, Rancho Cordova, CA) in a Finnigan 4000 GC/MS/DS (Sunnyvale, CA). For all subsequent samples, an HP 5790A GC interfaced to the Finnigan MS (Pankow and Isabelle, 1984) was used in place of the Finnigan 9610 GC. The chromatographic conditions for the on-column injections were: carrier gas linear velocity, 50 cm/s (at ambient temperature), provided by an inlet pressure of 8 psi; MS scanning from 60 to 450 amu in 0.75 s; injection and hold for 1 min at 80°C; program to 320°C at 10°C/min. The transfer line, source, and MS manifold temperatures were maintained at 250, 250, and 100°C, respectively. The electron multiplier was set at 1400-1800 volts as required to achieve the needed sensitivity.

Replicate analyses were performed occasionally. In addition, several of the air filter samples were analyzed with the mass spectro-meter in the "multiple ion detection" (MID) mode. In this mode, the mass spectrometer focussed on specific ions rather than scanning the entire range. By specifying the ions of interest, added sensitivity for specific compounds such as the PAHs and pesticides was achieved.

4.1.6.4 Identification and Quantification Procedure for Target Compounds

Identification and quantification of the target compounds was carried out by comparison to standards in the following manner. First,

the retention times and spectra of the target and internal standard compounds in the standard solutions were recorded. These were then compared to peaks in the sample chromatogram using the IDOS procedure THRECR (Appendix 1). Identifications were considered positive if the sample peaks contained the correct masses, in the correct ratios, eluting at the correct retention times. Response curves were then generated from the analysis of standards containing the internal and external standards and varying amounts of the target compounds. A relative response factor for each compound, based on the appropriate internal standard compound, was calculated with the GC/MS/DS software. This software enabled the use of response factors which were a function of analyte concentration. Response factors are given by the formula

$$\text{response factor} = \frac{(\text{area})(\text{internal standard amount})}{(\text{internal standard area})(\text{amount})} \quad\quad 4.1$$

Peaks in the sample chromatograms were integrated using the IDOS procedure QUSLRN (Appendix 1). Once the correct response factors were obtained, the amount of target compound in the sample was calculated by rearranging Equation 4.1 as follows

$$\text{amount} = \frac{(\text{area})(\text{internal standard amount})}{(\text{internal standard area})(\text{response factor})} \quad\quad 4.2$$

4.1.6.5 Analysis of PUFPs

Prior to extraction, the PUFPs were spiked with 50 μL of the internal standard solution described in Section 4.1.6.1. They were Soxhlet extracted with 500 mL of 60:40 acetone:hexane for 3 h (at least 10 Soxhlet cycles). The extracts were concentrated to ~20 mL in a K-D apparatus, then further concentrated to 1 mL in a miniature K-D apparatus. The 1984 extracts were fractionated into acid and base/neutral fractions and the 1985 extracts were cleaned up on silica gel as described in Section 4.1.6.2 for the air filter extracts. A 5 μL aliquot of the external standard solution was added to the extracts just before analysis. GC/MS/DS analysis proceeded as described in Section 4.1.6.3. MID analysis of PUFP extracts was not required because concentrations were generally well above detection limits.

4.1.6.6 Analysis of ADCs

ADCs were analyzed by thermal desorption and capillary GC/MS/DS. A 2 μL aliquot of an internal standard solution in methanol was injected into the bed of each ADC immediately prior to analysis. The internal standard solution for the 1984 samples contained (ng/μL): benzene-d_6 (40); toluene-d_8 (40); 1,1,2,2-tetrachloroethane-d_2 (10); phenol-d_5 (40); 1,2-dichlorobenzene-d_4 (10); naphthalene-d_8 (10); 2,4-dibromophenol (2); acenaphthene-d_{10} (10); fluorene-d_{10} (10); 2,4,6-tribromophenol (2); phenanthrene-d_{10} (10); and fluoranthene-d_{10} (10). The 1985 internal standard solution also included 2,4-dimethylphenol-d_3

40 ng/μL) and benzophenone-d_{10} (10 ng/μL), but not benzene-d_6 nor 1,2-dichlorobenzene-d_4.

The February 1984 ADC-2 analyses by GC/MS utilized the capillary column described in Section 4.1.6.3 and the Finnigan 9610 GC. All subsequent ADC-2 analyses and all of the ADC-1 analyses took place on the HP 5790A GC interfaced to the Finnigan MS. For analysis, a cartridge was placed in the desorption apparatus and purged for 10 min with a backflow of helium to remove the oxygen and most of the methanol. The ADC-1s were desorbed at 230°C for 20 min under a pressure of 20 psi; the ADC-2s were desorbed at 250°C for 30 min under a pressure of 30 psi. The oven temperature was held at -80°C during the desorption step, then programmed to 250°C at 10°C/min. The MS was scanned from 60 to 350 amu in 0.5 s. Other MS parameters were the same as described in Section 4.1.6.3 for the on-column injection analyses. For the 1984 ADC-1 analyses, an SE-54 capillary column with a 1 μm film thickness (J&W Scientific) was investigated. The oven temperature was programmed at 15°C/min during the runs in which the 1 μm film column was used.

4.2 Atmospheric Concentrations of Organic Compounds

In this section, the results from the air sampling program are presented. First, however, factors such as recoveries, breakthrough, and artifacts, which might influence the quality of the concentration data, are examined.

4.2.1 Results from Recovery Studies

4.2.1.1 Extraction Efficiencies for GFFs

The solvent mixture of 50:50 acetone:methylene chloride was chosen for extraction of the filters because of its excellent extraction characteristics. Individually, acetone and methylene chloride have been shown by others to provide excellent recoveries of PAHs from ambient filter samples (Stanley et al., 1967; Stenberg and Alsberg, 1981). (Samples of fly ash have been found to be much more difficult to extract completely). A binary mixture of the two solvents has also been shown to be more effective for the extraction of organic carbon than either solvent individually (Grosjean, 1975). In preliminary work for this study, 1.5-3 hours were found to be adequate for the extractions. Longer extraction times only resulted in the loss of the solvent as well as the more volatile internal standard compounds. The results of the analyses of total organic carbon of two GFFs before and after extraction showed that an average of 64% of the total organic carbon was removed in the first 2 h acetone:methylene chloride extraction. Because the organic carbon removal was less than 100%, the filters were re-extracted. The solvent mixture of toluene and methanol was chosen for the re-extractions because similar mixtures have been found to extract all of the organic carbon on diesel emission filter samples (Japar et al., 1984). The results from the re-extractions of all rain and air filters in this study showed that detectable quantities of the compounds of interest were found in only one toluene:metha-

nol air filter extract. From this information it was concluded that, while the solvent mix and extraction time chosen in this study did not provide complete recovery of all organic carbon from the filter samples, it did provide good recoveries of the compounds of interest here.

4.2.1.2 Recovery of Target Compounds from PUFPs

In order to simulate the low amounts expected in the sample extracts, the PUFP recovery determinations were carried out so as to produce a final concentrated extract level of 2 ng/μL per component. This is equivalent to an atmospheric concentration of 1-8 ng/m^3 for typical sample volumes. The overall recoveries of the target compounds are presented in Table 4.1. Excluding the phthalates, absolute overall recoveries of all compounds for the extraction/separation procedure were in the range 68-99%, and averaged 77%. Relative recoveries based on the internal standards were all in the range 93-110%. The standard deviations of the relative recoveries averaged 4% for the PAHs, indicating good analytical precision. The standard deviations of the relative recoveries of the other classes of compounds were larger, up to 12% for hexadecane and 15% for aldrin. It is likely that this was due in part to the lack of use of closely related internal standards for these compounds. Phthalates are known to be troublesome compounds to determine at trace levels because of their ubiquitous presence in the laboratory environment. Table 4.1 shows that contamination was observed only for bis(2-ethylhexyl)phthalate.

Table 4.1. Recoveries of Organic Compounds from PUFP Extraction and Separation Procedure[a].

Compound	Internal Standard	Absolute Recovery (%)[b]	Relative Recovery (%)[c]
PAHs and Derivatives			
Acenaphthylene	1	68 ± 4	97 ± 1
Acenaphthene	1	72 ± 3	102 ± 3
Fluorene	2	72 ± 3	99 ± 4
9-Fluorenone	3	71 ± 4	100 ± 3
Dibenzothiophene	4	75 ± 5	103 ± 2
Phenanthrene	4	72 ± 5	101 ± 3
Anthracene	4	71 ± 3	98 ± 5
1-Methylphenanthrene	4	75 ± 8	102 ± 3
9-Methylanthracene	4	74 ± 8	101 ± 5
9,10-Anthracenedione	3	72 ± 9	102 ± 8
Fluoranthene	5	78 ± 10	100 ± 1
Pyrene	5	82 ± 11	105 ± 5
Benz[a]anthracene	6	81 ± 10	97 ± 4
Chrysene	6	84 ± 12	100 ± 7
Benzo[b+k]fluoranthene	7	96 ± 17	103 ± 7
Benzo[a]pyrene	7	90 ± 11	98 ± 10
Perylene	7	99 ± 18	108 ± 8

Table 4.1 (cont'd). Recoveries of Neutral Compounds from PUFP

Extraction and Separation Procedure[a].

Compound	Internal Standard	Absolute Recovery (%)	Relative Recovery (%)
Pesticides and PCBs			
2,6-Dichlorobiphenyl	3	71 ± 3	102 ± 4
α-HCH	4	71 ± 10	97 ± 10
Hexachlorobenzene	4	74 ± 10	100 ± 6
γ-HCH	4	72 ± 8	99 ± 7
2,5,2'-Trichlorobiphenyl	4	75 ± 6	103 ± 12
2,5,4'-Trichlorobiphenyl	4	73 ± 8	100 ± 3
Heptachlor	4	68 ± 11	93 ± 7
2,5,2',5'-Tetrachlorobiphenyl	8	77 ± 12	103 ± 8
Aldrin	8	78 ± 7	106 ± 15
2,5,3',4'-Tetrachlorobiphenyl	8	78 ± 14	104 ± 3
2,4,5,2',5'-Pentachlorobiphenyl	8	82 ± 17	109 ± 2
p,p'-DDE	8	85 ± 19	110 ± 4
Dieldrin	8	81 ± 13	109 ± 6
3,4,3',4'-Tetrachlorobiphenyl	9	81 ± 15	102 ± 6
p,p'-DDD	9	77 ± 20	97 ± 2
2,4,5,2',4',5'-Hexachlorobiphenyl	9	87 ± 20	110 ± 3
p,p'-DDT	9	80 ± 22	99 ± 4

Table 4.1 (cont'd). Recoveries of Neutral Compounds from PUFP
Extraction and Separation Procedure[a].

Compound	Internal Standard	Absolute Recovery (%)	Relative Recovery (%)
Alkanes			
Tetradecane	1	68 ± 4	97 ± 10
Hexadecane	3	72 ± 10	103 ± 12
Eicosane	5	75 ± 14	96 ± 7
Heneicosane	5	78 ± 16	100 ± 9
Phthalates			
Diethylphthalate	3	79 ± 8	113 ± 10
Dibutylphthalate	5	89 ± 10	115 ± 5
Butylbenzylphthalate	6	102 ± 22	121 ± 17
Bis(2-ethylhexyl)phthalate	6	274 ± 50[d]	326 ± 47[d]

[a] ± 1 s values are based on three replicate samples. [b] Absolute recoveries are based on external standard, anthracene-d_{10}. [c] Relative recoveries are based on internal standards: 1) acenaphthene-d_{10}; 2) fluorene-d_{10}; 3) benzophenone-d_{10}; 4) phenanthrene-d_{10}; 5) fluoranthene-d_{10}; 6) chrysene-d_{12}; 7) perylene-d_{12}; 8) o,p'-DDE; 9) o,p'-DDD. [d] Not included in average recovery calculation.

4.2.2 Results from Filter Artifact Studies

Glass fiber filters are known to suffer from artifact problems caused by the adsorption of gaseous material. This adsorption pheno- menon has been well-documented for SO_2 (Byers and Davis, 1970; Coutant, 1977; Appel et al., 1984) and has been observed for organic compounds as well (Eichmann et al., 1979; Cadle et al., 1983; McDow 1986). Two investigations of this problem were conducted in this study, and are described below.

4.2.2.1 The 1984 Backup Filter Study

Backup GFFs were used during the 1984 sampling season in order to quantify the extent of vapor adsorption of the target compounds. Since the GFFs exhibit >99% collection efficiency for all particle sizes (Lockhart, 1964; John and Reischl, 1978), any material found on the backup filter in quantities greater than ~1% of the amount on the pri- mary filter must represent adsorbed vapor. Figure 4.2 shows typical blank, backup, and primary filter chromatograms obtained during the 1984 sampling period. Several points are apparent: 1) the overall level of organic material on the backup filters was low compared to the primary filters; 2) the backup filters occasionally exhibited a small "hump" of unresolved organic compounds which occurred earlier in the chromatogram than the unresolved "hump" in the primary filter chromato- gram.

Target compounds found on the backup filters consisted entirely of compounds with vapor pressures in the range of 10^{-8} - 10^{-4} torr. The
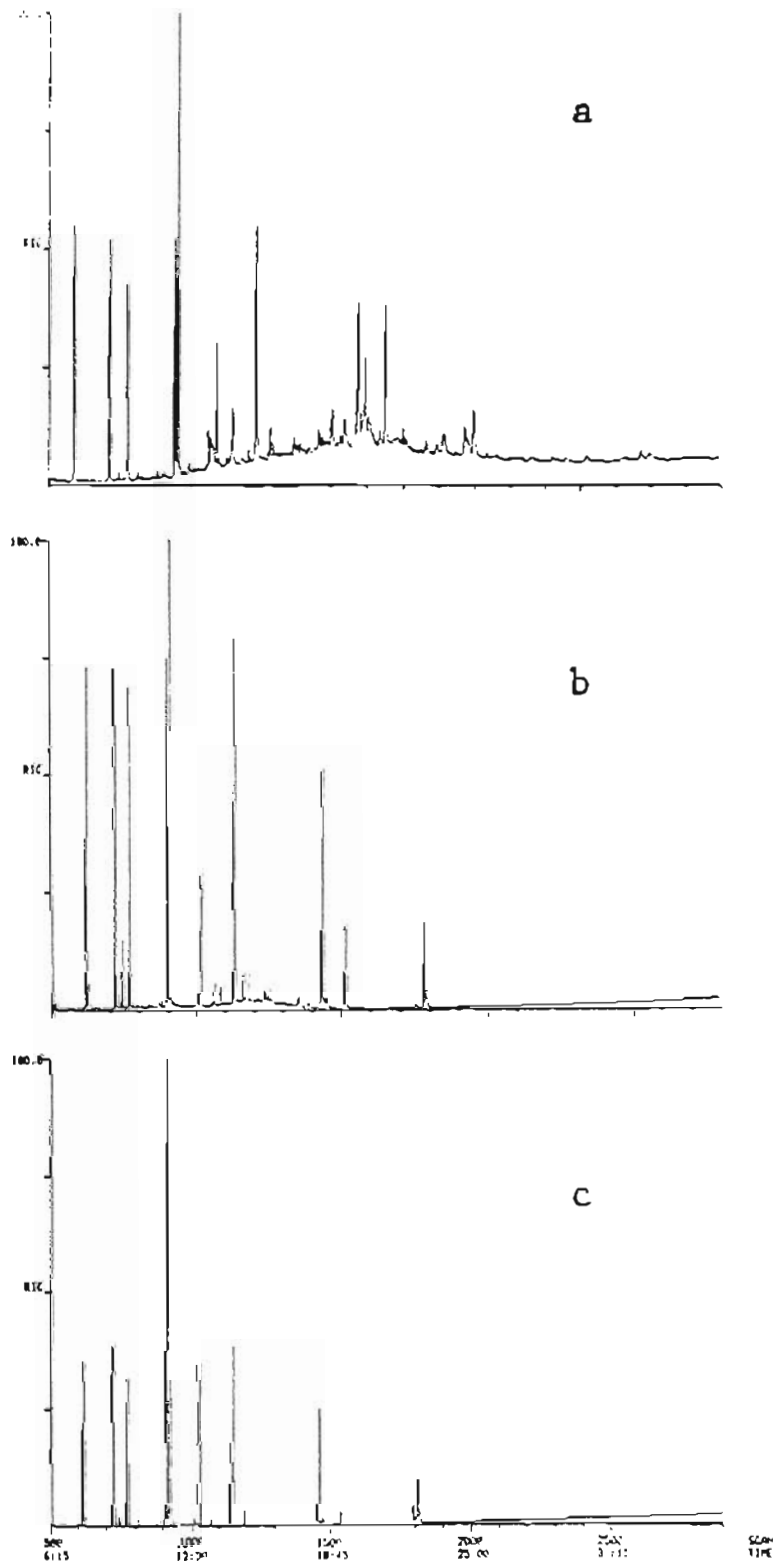
Figure 4.2. Primary (a), backup (b), and blank (c) GFF chromatograms obtained in Portland, Oregon in 1984.

concentration of each target compound found on the backup filters, and the percentage which each is of the corresponding primary filter concentration, are given in Table 4.2. The concentrations on backup filters were quite variable. For one sampling event, no target compounds except chrysene were detected on the backup filters. For another event, 15-40% of the primary filter amounts were found for compounds in the critical vapor pressure range. The other events fell between these two extremes. In a few cases, backup percentages were quite high for individual compounds (e.g. 9-fluorenone on 2/12 and methylphenanthrene on 4/11). In these cases, the amounts on the primary filters were unusually low. The uncertainties in these values are therefore very high. The total concentration of PAHs found on backup filters averaged roughly 3% of the amount found on primary filters. This amount increased to ~20% for fluoranthene and ~30% for the methylphenanthrenes, which have vapor pressures in the range most likely to adsorb. No target compounds more volatile than phenanthrene were found on backup filters. However, due to the extrememly low particulate phase concentrations of these compounds, a vapor adsorption effect of as high as 30% would have been below the detection limit. Vapor adsorption of alkanes and phthalates in the critical vapor pressure range appears to have been even greater than that for PAHs, with backup filter amounts for eicosane averaging 71% of primary filter values.

Table 4.2. Concentrations of Organic Compounds found on GFF Backup Filters and Percentages of Primary Filter Values in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)					
	2/12–2/13	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
9-Fluorenone	0.02 (78)[a]	ND[b]	0.01 (11)	0.06 (39)	ND	ND
Phenanthrene	ND	ND	ND	0.17 (33)	ND	ND
Methylphenanthrenes	0.05 (38)	ND	ND	0.15 (34)	ND	0.09 (85)
9,10-Anthracenedione	0.10 (17)	ND	0.07 (8)	0.31 (33)	ND	ND
Fluoranthene	0.26 (66)	0.06 (12)	ND	0.29 (37)	ND	ND
Pyrene	0.26 (41)	ND	ND	0.26 (28)	ND	ND
Benz[a]anthracene	ND	ND	ND	0.31 (16)	ND	0.04 (8)
Chrysene	0.03 (3)	0.08 (4)	0.08 (7)	0.57 (24)	0.02 (3)	0.12 (16)
Eicosane	0.16 (28)	0.16 (40)	0.13 (68)	2.0 (220)	ND	NA[c]
Heneicosane	0.20 (20)	0.25 (42)	0.22 (59)	3.8 (140)	ND	NA
Docosane	0.34 (32)	ND	0.21 (55)	1.3 (34)	ND	NA
Butylbenzylphthalate	1.4 (41)	ND	0.83 (63)	1.1 (11)	ND	0.91 (52)

[a]Numbers in parentheses are % of front filter concentrations. [b]ND = not detected at a statistically significant level. [c]NA = not available.

4.2.2.2 Side-by-side Comparison of GFFs and TMFs

For four 1985 sampling events, two air samplers were run side-by-side, one equipped with a GFF and one with a TMF. Since the extent of vapor adsorption of organic compounds on Teflon filters is believed to be less than on glass or quartz filters (McDow, 1986), this comparison provided another indication of the importance of vapor adsorption of target compounds on GFFs. However, results from this comparison indicated that there was no difference in the concentrations of most PAHs and oxo-PAHs obtained between the two filters. The GFF/TMF ratios for four sampling events and the significance levels for the deviations of these values from 1.0 are presented in Table 4.3. Only phenanthrene was collected in significantly ($P \leq 0.05$) lower quantities on the GFFs. The methylphenanthrenes appeared to have been present in lower concentrations on the GFFs, but this difference was not statistically significant. Only 7,12-benz[a]anthracenedione and acenaphthylene were present in significantly higher quantities on GFFs. For all of the other compounds studied the GFF/TMF ratios fell between 0.61 and 1.16. This result: 1) differs from the results of a study by Grosjean (1983), who found ratios of 0.25 to 0.76; but 2) agrees with the results of Fitz et al. (1984), who found GFF/TMF ratios of 0.66 to 1.03 for these compounds.

Benzo[a]pyrene is of particular interest in this comparison since it was one of the first carcinogens identified in atmospheric aerosols, and has since been studied extensively. The reactivity of benzo[a]py-

Table 4.3. GFF/TMF Ratios for Particulate PAH and oxo-PAH Compounds in Portland, Oregon in 1985.

Compound	GFF/TMF Ratio					p^a
	2/14	3/3	3/21	3/26	Avg $\pm$ 1s	
Phenanthrene	0.76	0.68	0.55	0.22	0.55 $\pm$ 0.24	.03
Methylphenanthrenes	NA[b]	0.80	0.77	0.18	0.58 $\pm$ 0.35	.18
Fluoranthene	1.12	0.92	1.25	0.60	0.97 $\pm$ 0.28	.86
Pyrene	1.25	1.00	1.28	0.70	1.06 $\pm$ 0.24	.70
Benzo[a]fluorene	0.97	0.94	1.13	0.57	0.90 $\pm$ 0.24	.47
Benzo[b]fluorene	0.93	0.97	1.20	0.63	0.93 $\pm$ 0.23	.63
Benz[a]anthracene	1.37	1.04	1.03	0.79	1.06 $\pm$ 0.24	.66
Chrysene	1.40	1.11	1.21	0.73	1.11 $\pm$ 0.28	.48
Benzo[b+j+k]fluoranthene	1.27	1.13	1.25	0.75	1.10 $\pm$ 0.24	.47
Benzo[e]pyrene	1.21	1.12	1.33	0.80	1.12 $\pm$ 0.23	.39
Benzo[a]pyrene	1.18	0.75	1.05	0.59	0.89 $\pm$ 0.27	.48
Perylene	1.31	1.11	1.08	0.68	1.05 $\pm$ 0.26	.76

Table 4.3. GFF/TMF Ratios for Particulate PAH and oxo-PAH Compounds in Portland, Oregon in 1985.

Compound	GFF/TMF Ratio					
	2/14	3/3	3/21	3/26	Avg $\pm$ 1s	p[a]
Indeno[1,2,3-cd]pyrene	1.13	0.85	1.20	0.76	0.99 $\pm$ 0.21	.90
Dibenz[a,c]anthracene+ Dibenz[a,h]anthracene	1.10	0.83	1.08	0.62	0.91 $\pm$ 0.23	.48
Benzo[ghi]perylene	1.24	1.01	1.17	0.79	1.05 $\pm$ 0.20	.64
Coronene	0.77	0.54	1.40	0.93	0.91 $\pm$ 0.36	.65
9-Fluorenone	0.93	1.00	0.73	0.59	0.81 $\pm$ 0.19	.14
9,10-Anthracenedione	1.29	1.29	0.89	1.17	1.16 $\pm$ 0.19	.19
7-Benz[de]anthracenone	1.22	1.02	1.27	0.86	1.09 $\pm$ 0.19	.40
7,12-Benz[a]anthracenedione	1.14	1.37	1.24	1.31	1.27 $\pm$ 0.10	.01

[a]$P \le 0.05$ means a significant difference of the ratio from 1. [b]NA = not available.

rene collected on filters and exposed to various reactive gases or to ambient urban air has been the subject of several studies (Pitts et al., 1978; Brorstrom et al., 1983; Grosjean et al., 1983). Pitts et al. found some conversion of BaP to various oxygenated and nitrated compounds when milligram quantities were spiked on filters and exposed to ambient air. Brorstrom et al. found losses of up to 40% of BaP in actual ambient samples when 1 ppm NO_2 was added to the airstream. Grosjean et al., however, found no degradation of BaP under similar sampling conditions and NO_2 levels. Although no significant differences in the concentrations of BaP measured on the two types of filters are apparent in Table 4.3, a closer examination of the BaP concentrations is warranted. The ratio of the BaP concentrations to concentrations of benzo[e]pyrene (a less reactive isomer) for each event and each filter are therefore given in Table 4.4. This ratio is much more consistent, and significantly higher ($P = 0.05$), when measured on TMFs. Thus it is possible that slight losses of BaP did occur on the GFFs.

The fact that particulate concentrations of most PAHs were the same whether measured on glass or Teflon filters indicates that, within the uncertainty of the sampling and analytical methods: 1) filter-catalyzed degradation was probably not a significant problem in this study, and 2) vapor adsorption of PAHs of GFFs was not significantly higher than on TMFs.

Table 4.4. BaP/BeP Ratios measured on GFFs and TMFs in Portland, Oregon in 1985.

Date	GFF	TMF
2/14	1.43	1.47
3/3	1.02	1.53
3/21	1.27	1.60
3/26	1.07	1.60
Avg ± 1s	1.20 ± 0.19	1.55 ± 0.06

4.2.3 Breakthrough of Analytes during Sampling

Breakthrough of an analyte on an adsorbent, as described in Section 2.2.1, is a function of the vapor pressure of the compound, the ambient temperature, the sample volume, the adsorbent volume, and the affinity of the analyte for the adsorbent. When backup adsorbent traps are utilized, the amount of material found on the backup trap provides an indication of the efficiency of the trapping process. Breakthrough (B, %) is defined here as

$$B = \frac{\text{amount on backup}}{\text{amount on primary + backup}} \qquad 4.3$$

The B values for intermediate-volatility compounds on the PUFPs are given in Table 4.5. Using the breakthrough curves from Senum (1981) and assuming 7.5 theoretical plates per PUFP (Feng and Bidleman, 1984), for an overall trapping efficiency of 99% on the two-plug system the primary plug must retain at least 75% of the influent material. Thus a B value of < 25% indicates quantitative trapping on the two-plug system. Neutral compounds with volatilities comparable to dibenzofuran were found to be trapped quantitatively by two 7.6 cm x 5.1 cm PUFPs using this criterion. Polar compounds appear to be particularly well retained by PUF. For the sample volumes used here, phenols as volatile as 2,6-dimethylphenol were trapped quantitatively on the two-plug system.

Table 4.5a. Percent Breakthrough[a] (B) of Intermediate-volatility Organic Compounds on PUFPs during Sampling in Portland, Oregon in 1984.

	B (%)						
	Sample Date and Volume (m^3)						
Compound	2/12 230	2/14 53	2/20 150	2/23 200	2/29 50	3/16 200	4/11 140
2,6-Dimethylnaphthalene	NA[b]	18	NA	NA	38	62	58
1,3+1,6-Dimethylnaphthalene	NA	23	NA	NA	43	63	61
1,4+1,5+2,3-Dimethyl naphthalene	NA	16	NA	NA	35	57	55
1,2-Dimethylnaphthalene	NA	13	NA	NA	31	57	51
Hexadecane	44	6	37	27	11	69	48
Acenaphthylene	30	3	39	30	15	55	45
Acenaphthene	35	9	46	14	14	61	47
Dibenzofuran	20	<1	5	5	1	27	14
Fluorene	9	<1	2	3	<1	12	10
Octadecane	3	0	0	0	0	12	17
Hexachlorobenzene	10	0	19	0	0	0	18
9-Fluorenone	0	0	2	0	1	0	1
Phenanthrene	0	0	<1	<1	0	<1	<1

[a]B = [backup]/([primary] + [backup]). [b]NA = not available.

Table 4.5b. Percent Breakthrough (B) of Intermediate-volatility Organic Compounds on PUFPs during Sampling in Portland, Oregon in 1985.

	B (%)								
	Sample Date, Sampler Number, and Sample Volume (m^3)								
	2/14		3/3		3/21		3/26		4/17	4/21
Compound	1 42	2 46	1 82	2 77	1 170	2 170	1 59	2 150	130	350
2,6-Dimethylphenol	12	NA[a]	0	0	NA	8	NA	25	NA	NA
2,4+2,5-Dimethylphenol	0	NA	2	4	2	0	0	0	1	23
4-Ethyl+3,5-dimethyl phenol	0	0	0	1	0	0	0	0	0	0
1-Indanone	5	7	13	11	19	19	10	12	20	52
2,6-Dimethylnaphthalene	35	35	43	43	37	25	43	50	54	58
1,3+1,6-Dimethyl naphthalene	38	38	44	44	37	28	43	52	54	56
1,4+1,5+2,3-Dimethyl naphthalene	30	32	35	37	38	27	34	47	57	57
1,2-Dimethylnaphthalene	16	25	30	32	42	25	25	41	57	57
Acenaphthylene	10	9	20	21	18	12	5	18	32	48
Acenaphthene	11	12	20	20	31	21	9	26	44	57
Dibenzofuran	0	0	1	0	6	5	0	3	6	43
Fluorene	<1	<1	0	0	2	2	<1	<1	2	25

[a]NA = not available.

The temperature effect on breakthrough can be large, due to the strong dependence of vapor pressure on temperature. For example, the vapor pressure of fluorene increases by a factor of 3.6 between 10° and $20^{\circ}C$ (Sonnefeld et al., 1983). The B data for fluorene in Table 4.5 were normalized to $20^{\circ}C$ by multiplying the sample volumes for each event by the ratio of the supercooled liquid vapor pressure at the mean sampling temperature to that at $20^{\circ}C$, as described by Billings and Bidleman (1980). The results are plotted in Figure 4.3. Although a breakthrough volume for fluorene cannot be calculated from this data due to the scatter, there appears to be reasonable agreement with the breakthrough volume of 120 m^3 for 7.6 cm x 7.6 cm PUFPs found for fluorene by Feng and Bidleman (1984).

Under the same sampling conditions, the 5.7 mL Tenax-GC ADC-2s generally retained compounds as volatile as toluene for sampling volumes of 120-670 L (Table 4.6). These results compare favorably with the findings of Krost et al. (1982), who list the breakthrough volumes for toluene and tetrachloroethene as 494 and 361 L, respectively, for 8.0 mL cartridges at $10^{\circ}C$.

4.2.4 Atmospheric Organic Concentrations in Portland, 1984-85

Seven sets of air concentration data were obtained during rain events in Portland during the winter and spring of 1984. Six additional sets were obtained in 1985. Total sample volumes of 40-350 m^3 were obtained over periods of 1-5 days.
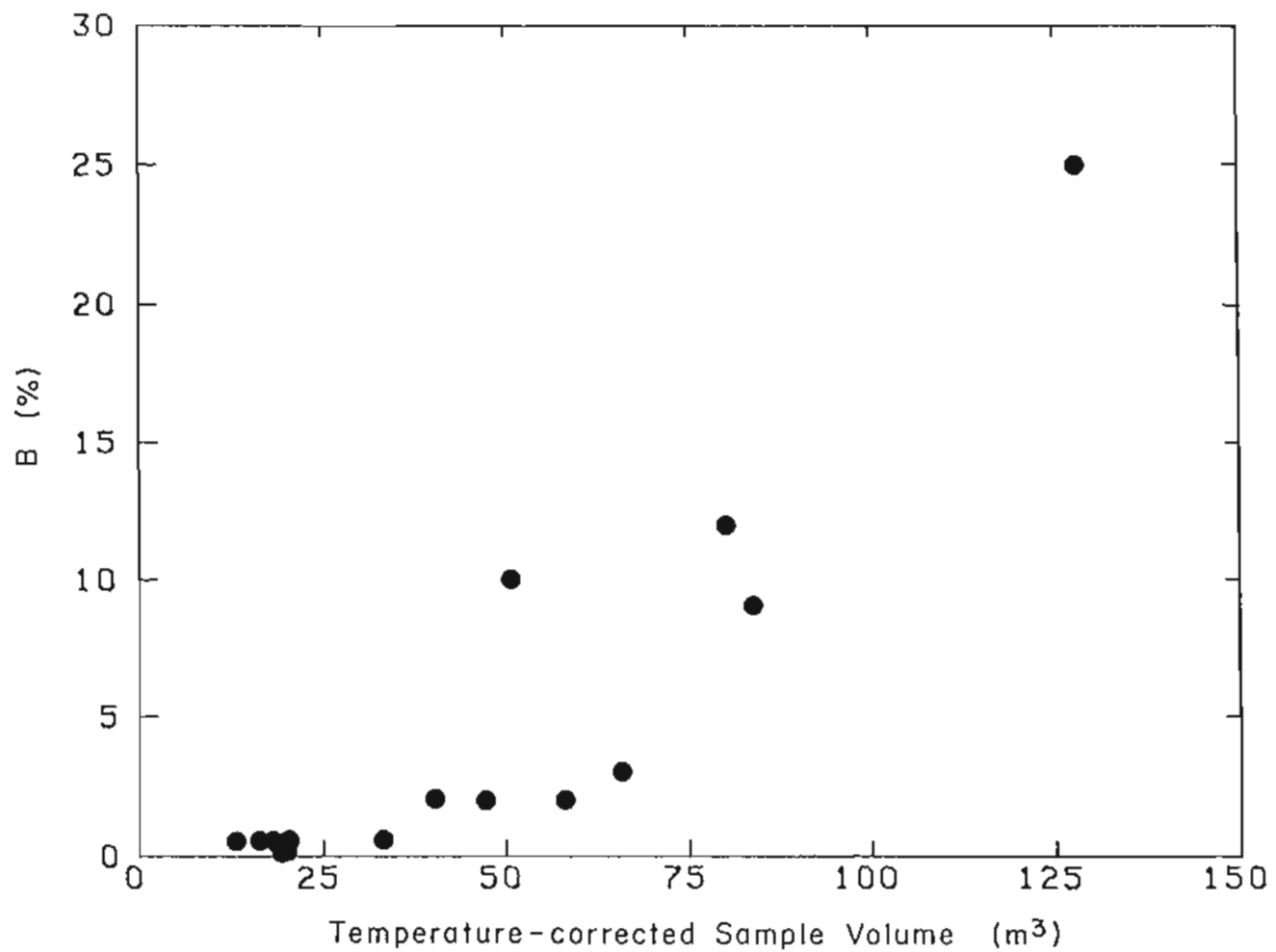
Figure 4.3. Breakthrough B of fluorene on PUFPs as a function of temperature-corrected sample volume.

Table 4.6. Percent Breakthrough[a] (B) of Volatile Organic Compounds on Tenax-GC ADC-2s during Sampling in Portland, Oregon in 1984.

	B (%)						
	Sample Date and Volume (L)						
Compound	2/12 1350	2/14 280	2/20 470	2/23 570	2/29 120	3/16 670	4/11 480
Toluene	NA[b]	2	11	<1	<1	9	<1
Octane	26	2	4	1	<1	1	<1
Dibromochloromethane	32	0	3	0	0	3	0
Tetrachloroethene	22	2	8	1	1	3	<1
Chlorobenzene	21	4	2	0	23	4	0
Ethylbenzene	11	<1	<1	0	<1	0	<1
m+p-Xylene	15	<1	<1	0	<1	0	<1
o-Xylene	19	<1	1	0	<1	0	<1
Bromoform	17	0	0	0	0	0	0
Hexachloroethane	26	0	5	0	0	0	0
Nonane	7	2	<1	0	<1	<1	1
Decane	2	0	0	0	0	0	0
1,4-Dichlorobenzene	1	0	0	0	<1	0	0

[a]B = [backup]/([primary] + [backup]). [b]NA = not available.

Instrument detection limits on the GC/MS were roughly 0.05 ng for the PAHs, phthalates, and alkanes, and up to 0.5 ng for some phenols and pesticides. The 0.05 ng limit translated to atmospheric concentrations of 0.01 to 0.1 ng/m^3 for the PUFP extracts, depending upon the volume of air sampled. The same limit translated to atmospheric concentrations of 0.05 to 0.4 ng/m^3 for the ADC-2 samples and 1 to 5 ng/m^3 for the ADC-1 samples.

4.2.4.1 Vapor Phase Concentrations

Typical primary and blank chromatograms for the PUFPs and the ADC-2s are given in Figures 4.4 and 4.5, respectively. The vertical scale is given at the upper right corner of each chromatogram. The internal standard compounds have been identified on the blank chromatograms. In all concentration determinations, mean blank values were calculated from the mass amounts found on the blanks. The mean blank values for PUFPs and ADCs are given in Table 4.7. The blank values for the phthalates, alkanes, and PAHs were generally lower on the ADCs, due to the smaller amount of sample handling required in those analyses. Toluene, benzaldehyde, and phenol are known Tenax decomposition products and were found in fairly high levels on the ADC blanks.

Primary and backup sample amounts were considered non-zero only if they exceeded the mean blank mass amount at the 95% confidence level. Normalized blank levels for each event were then calculated by dividing the blank mass amounts by the corresponding sample volumes. These normalized blank values were generally less than 5% of the sample levels
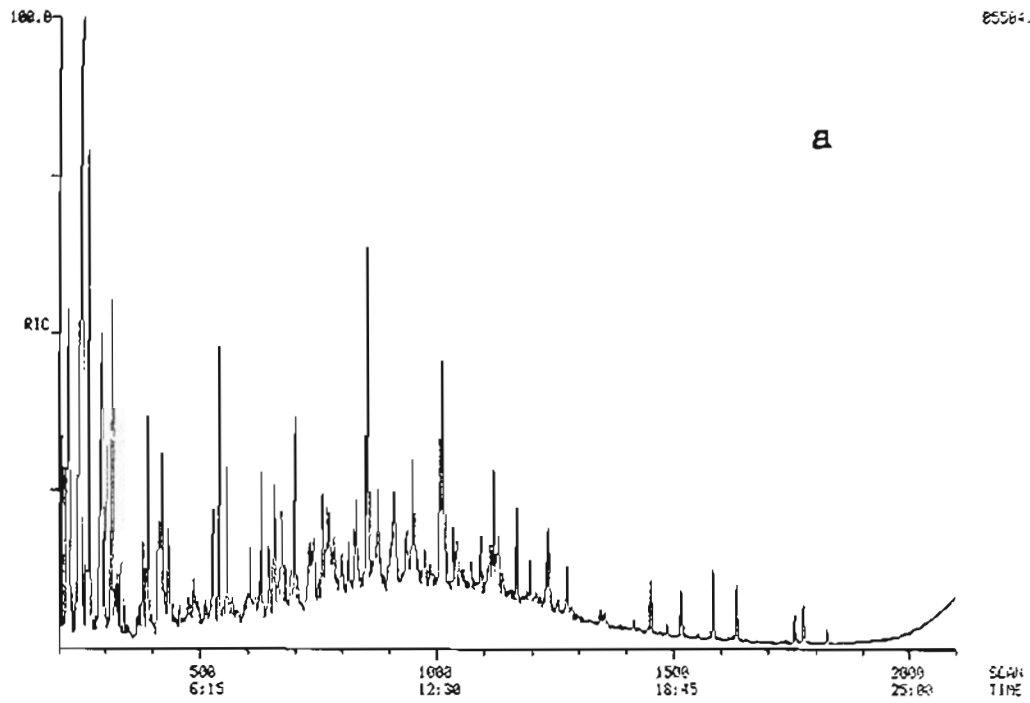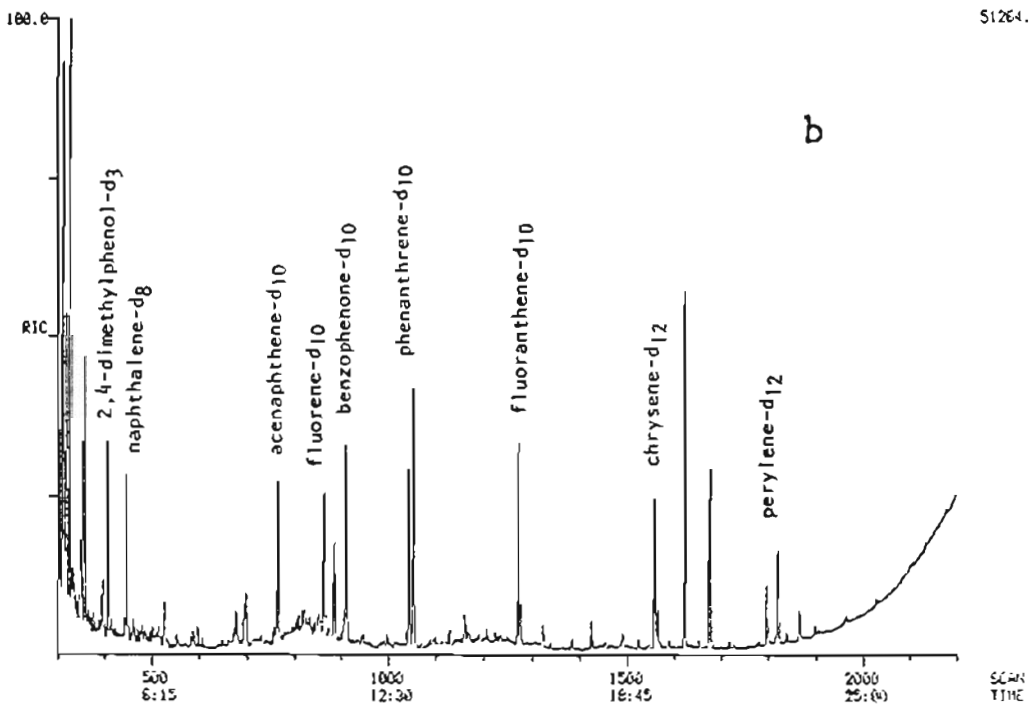
Figure 4.4.   Primary (a) and blank (b) PUFP chromatograms obtained in Portland, Oregon in 1985.
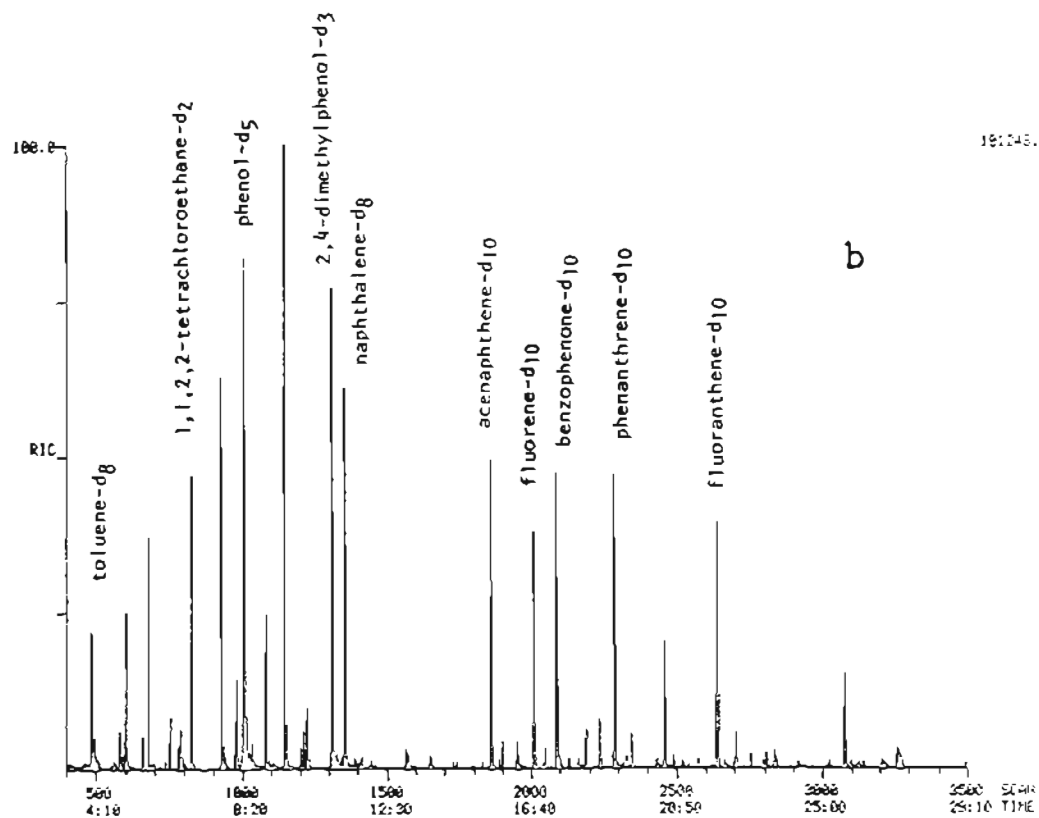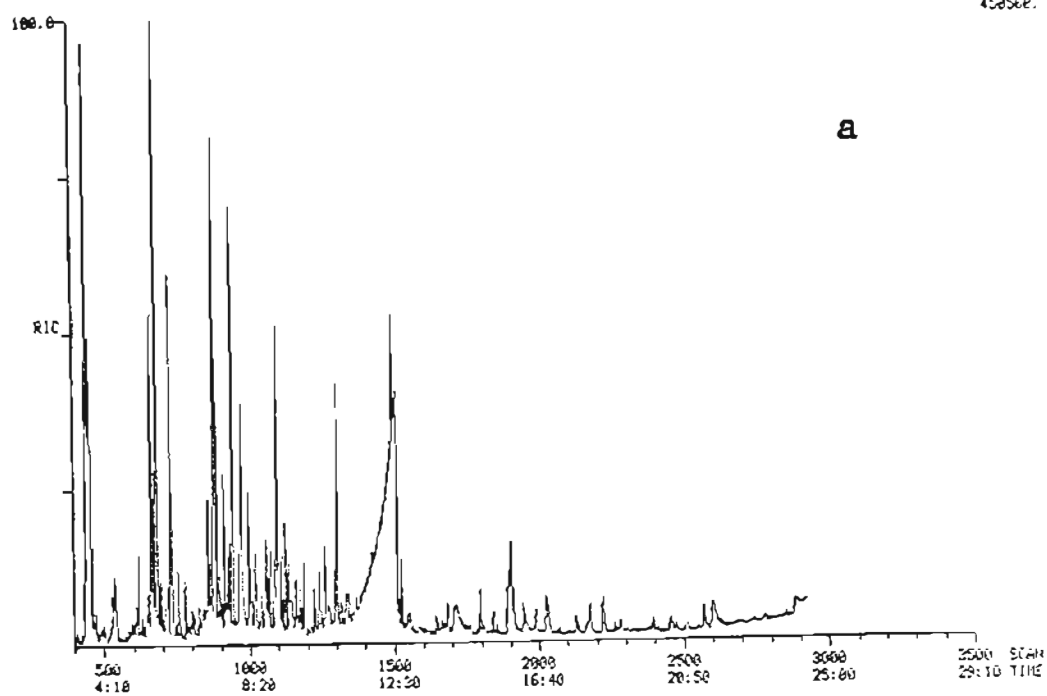
Figure 4.5. Primary (a) and blank (b) ADC chromatograms obtained in Portland, Oregon in 1985.

Table 4.7. Mean Blank Levels (ng) for PUFPs and ADCs.

Compound	PUFPs	ADCs
Toluene	NA[a]	1.9 ± 0.4
Furfural	NA	3.2 ± 2.4
Ethylbenzene	NA	0.13 ± 0.03
2-Heptanone	NA	0.40 ± 0.40
Benzonitrile	NA	6.6 ± 5.1
Phenol	NA	17 ± 7
Salicyclaldehyde	NA	1.4 ± 1.2
3+4-Methylphenol	ND[b]	0.20 ± 0.33
2-Methoxyphenol	ND	0.13 ± 0.17
2,4+2,5-Dimethylphenol	1.00 ± 0.37	2.5 ± 0.2
4-Ethyl+3,5-dimethylphenol	ND	0.20 ± 0.20
Naphthalene	0.75 ± 0.43	0.22 ± 0.12
1-Indanone	ND	0.15 ± 0.07
2-Methylnaphthalene	0.17 ± 0.15	0.041 ± 0.034
1-Methylnaphthalene	0.10 ± 0.10	0.008 ± 0.012
2,6-Dimethylnaphthalene	0.024 ± 0.032	ND
1,3+1,6-Dimethylnaphthalene	0.041 ± 0.050	ND
Dibenzofuran	0.019 ± 0.019	0.019 ± 0.015
Fluorene	0.010 ± 0.015	ND
Diethylphthalate	3.0 ± 1.7	0.27 ± 0.21
9-Fluorenone	ND	0.071 ± 0.057

Table 4.7 (cont'd). Mean Blank Levels (ng) for PUFPs and ADCs.

Compound	PUFPs	ADCs
Phenanthrene	0.048 ± 0.035	0.037 ± 0.027
Anthracene	0.005 ± 0.005	ND
2+3-Methylphenanthrene	0.013 ± 0.019	ND
1+4+9-Methylphenanthrene	0.008 ± 0.014	ND
Dibutylphthalate	41 ± 75	0.40 ± 0.18
Eicosane	0.90 ± 0.51	0.28 ± 0.15
Fluoranthene	0.026 ± 0.021	ND
Heneicosane	1.9 ± 2.3	0.78 ± 0.41
Pyrene	0.11 ± 0.10	ND
Docosane	4.1 ± 5.3	0.19 ± 0.13
Tricosane	6.0 ± 8.5	NA
Butylbenzylphthalate	3.6 ± 2.1	ND
Tetracosane	7.7 ± 10.3	NA
Bis(2-ethylhexyl)phthalate	41 ± 45	NA
Dioctylphthalate	0.51 ± 0.57	NA

[a]NA = not analyzed. [b]ND = not detected.

for the PUFPs and ADC-2s, except in the case of the phthalates. Norma-
lized blank levels were higher for the ADC-1s due to the extremely low
sample volumes collected. For each case when the concentration was
significantly higher than the blank, the normalized blank level was
subtracted from the primary and backup concentrations.

The blank-corrected atmospheric vapor phase concentrations are
given in Table A1.1. The concentrations generally spanned a range of a
factor of 3-5 over the thirteen events, although some compounds such as
α-HCH show virtually no variation in concentration. Volatile vapor
phase compounds which exhibit breakthough on PUF were determined on the
ADCs only. The PUFPs were used for the less volatile compounds. No
ADC data were available for 2/14/85. The cleanup step used for the
PUFP extracts in 1985 (described in Section 4.1.6.2) which was required
in order to keep the chromatography sharp sometimes removed the methoxy
and nitrophenols from the extracts. These compounds were therefore
generally determined on the ADCs alone. Acenaphthylene was lost in the
ADC analyses and was therefore determined on the PUFPs only. This will
be discussed further in Section 4.2.6. For the compounds which were
measured by two or more methods, the results presented in Table A.1.1
are averages of all values. The mean vapor phase concentrations are
presented in Table 4.13.

4.2.4.2 Particulate Phase Concentrations

Table 4.8 gives the blank levels of the normal alkanes, the phtha-
lates and the PAHs on GFFs and TMFs. The blank levels were uniformly

Table 4.8. Comparison of Air Filter Blank Levels (ng) for GFFs and TMFs in 1985.

Compound	TMF (n=9)	GFF (n=4)
Eicosane	0.91 ± 0.60	0.035 ± 0.044
Heneicosane	1.21 ± 1.22	0.020 ± 0.040
Docosane	1.62 ± 2.68	0.029 ± 0.035
Tricosane	2.13 ± 4.22	ND[a]
Tetracosane	2.91 ± 5.15	0.11 ± 0.16
Pentacosane	2.41 ± 4.53	ND
Hexacosane	2.14 ± 4.36	0.062 ± 0.125
Octacosane	1.70 ± 3.53	0.072 ± 0.143
Diethylphthalate	1.04 ± 0.77	0.30 ± 0.14
Dibutylphthalate	2.71 ± 1.13	0.51 ± 0.43
Butylbenzylphthalate	0.59 ± 0.36	0.20 ± 0.20
Bis[2-ethylhexyl]phthalate	9.44 ± 9.18	18.76 ± 14.67
Dioctylphthalate	0.25 ± 0.46	0.026 ± 0.052
Phenanthrene	0.011 ± 0.013	ND
Fluoranthene	0.003 ± 0.007	0.0008 ± 0.0015
Pyrene	0.002 ± 0.005	ND
Chrysene	0.006 ± 0.008	ND

[a]ND = not detected.

higher on the TMFs. This was likely to have been due to the difference in the cleaning procedures used for the two types of filters. Better blanks may be obtained for the TMFs by baking them out at 300°C, just below the melting point of Teflon (McDow, 1986).

The concentration data for particulate-phase organic compounds were subjected to the same significance determination and blank correction described above for the vapor phase data. Because of the high blanks for alkanes and phthalates on the TMFs, these compounds generally did not exhibit ambient concentrations which passed the significance test. The blank-corrected particulate phase concentrations for the thirteen Portland samples are given in Table Al.2. The average concentrations are presented in Table 4.13. Overall, the levels of organic compounds were much lower in the particulate samples than in the vapor phase samples. The concentrations of several of the more volatile compounds were very close to the detection limits. The April 1985 samples were analyzed by MID, as described in Section 4.1.6. The enhanced sensitivity of this method produced a detection limit of 0.005 ng, which translated to atmospheric concentrations of 0.002 to 0.01 ng/m^3 for PAHs.

4.2.4.3 Concentrations of the Various Classes of Target Compounds

In this section the results obtained for each of the major classes of target compounds are examined in greater detail.

4.2.4.3.1 PAHs and Derivatives

In Figure 4.6 the mean concentrations of PAHs in both the vapor and particulate phases are shown. The most striking feature of Figure 4.6 is that by far the bulk of the PAH concentrations are in the vapor phase. The concentrations show a strong vapor pressure effect, with the concentration of naphthalene and the methylnaphthalenes an order of magnitude higher than the concentrations of the other PAHs. The compounds 7,12-benz[a]anthracedione, perylene, indeno[1,2,3-cd]pyrene, dibenz[a,c]anthracene + dibenz[a,h]anthracene, benzo[ghi]perylene, and coronene were not detected for all vapor-phase samples. Naphthalene, the methylnaphthalenes, and the dimethynaphthalenes were not detected in the particulate samples. The compounds 1,2-acenaphthenedione and 9,10-phenanthrenedione were not detected in either phase.

A large data base on the concentrations of particulate PAH compounds exists in the literature. A compilation of particulate PAH concentrations in urban areas is presented in Table 4.9. Portland PAH concentrations are representative of concentrations in the United States, but are much lower than concentrations in many other parts of the world.

4.2.4.3.2 Alkanes

Alkane target compounds ranged from C_8 to C_{28}. Vapor phase concentrations of octane were >100 ng/m^3, decreasing to 1 ng/m^3 for eicosane. No alkanes above C_{22} were detected in the vapor phase at levels
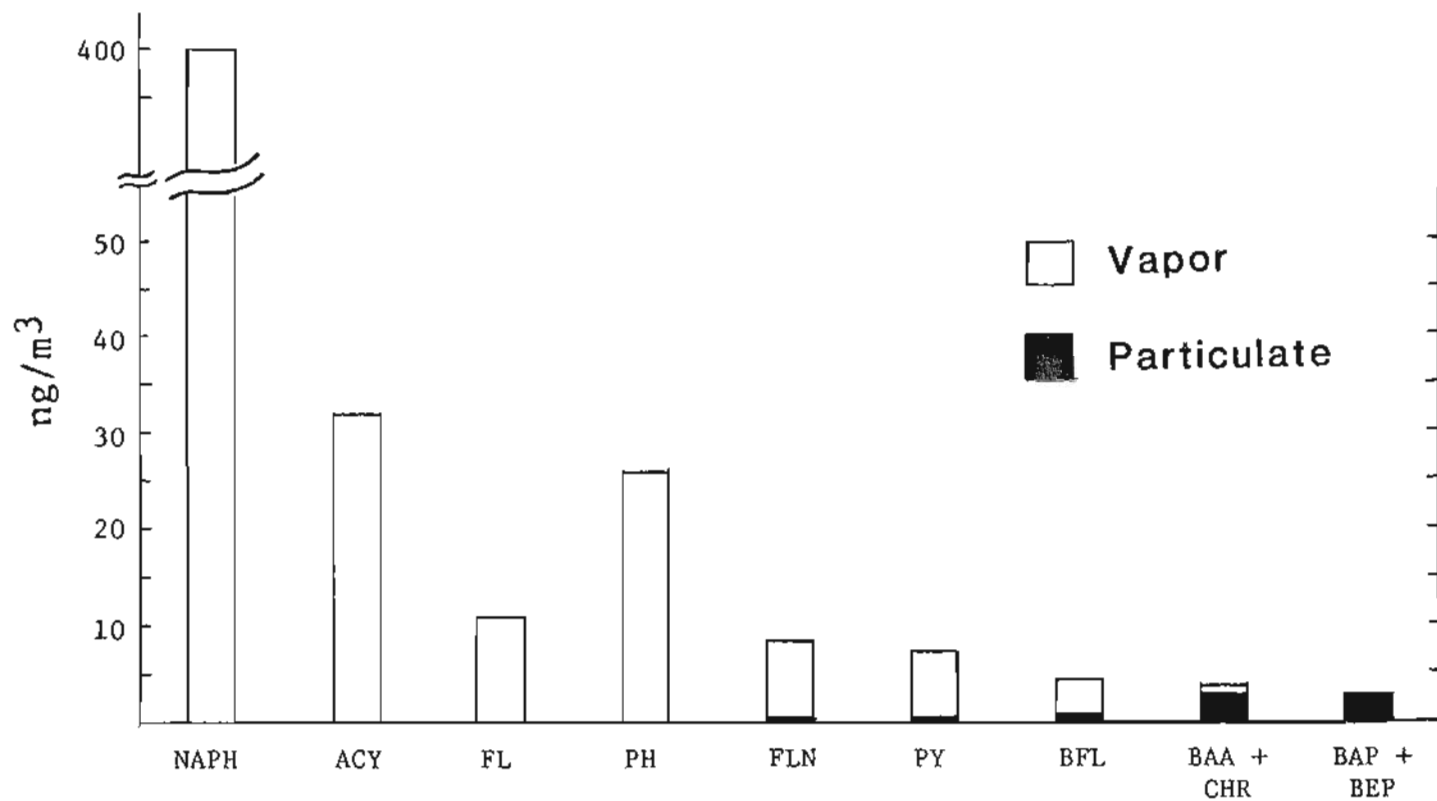
Figure 4.6.   Portland mean vapor and particulate phase PAH concentrations in 1984-85.   NAPH=naphthalene, ACY=acenaphthylene, FL=fluorene, PH=phenanthrene, FLN=fluoranthene, PY=pyrene, BFL-benzo[a+b] fluorenes, BAA + CHR=benz[a]anthracene + chrysene, BAP + BEP = benzo[a]pyrene + benzo[e]pyrene.

Table 4.9. Atmospheric Concentrations of Particulate PAHs in Urban Areas.

Concentration (ng/m^3)

Compound	Portland[a]	New York[b]	Los Angeles[c]	Columbia, SC[d]	Beijing[b]	Toronto[e]	Oslo[f]	London[g]	Antwerp[h]	Christchurch, NZ[i]	Osaka[j]
Fluoranthene	0.53	0.9	0.31	NA	42	NA	NA	NA	1.1	NA	2.8
Pyrene	0.62	0.5	0.45	NA	20	NA	12	NA	0.92	NA	3.1
Benz[a]anthracene	1.2	0.6	0.18	NA	24	NA	NA	NA	7.1*	36	9.4*
Chrysene	1.5	NA	0.60	NA	NA	NA	NA	NA		22	
Benzo[b+j+k] fluoranthene	3.6	1.0	0.91	0.1	30	1.6	NA	NA	15	50	11
Benzo[e]pyrene	1.3	0.9	0.90	NA	19	0.76	NA	0.9	12**	18	10**
Benzo[a]pyrene	1.6	0.5	0.46	0.8	17	1.06	3.0	0.7		35	
Benzo[ghi]perylene	2.4	1.3	3.3	2.2	20	7.0	4.1	1.9	NA	25	6.2

*Benz[a]anthracene + chrysene. **Benzo[e]pyrene + benzo[a]pyrene. [a] This study. [b] Daisey et al., 1983. [c] Gordon, 1976. [d] Keller and Bidleman, 1984. [e] Katz et al., 1978. [f] Moller and Alfheim, 1980. [g] Commins and Hampton, 1976. [h] Cautreels et al., 1977. [i] Cretney et al., 1985. [j] Yamasaki et al., 1982.

above the blanks. Conversely, no alkanes below C_{20} were detected at significant levels in the particulate phase.

4.2.4.3.3 Monocyclic Aromatics

The aromatic compounds benzene, toluene, ethylbenzene, the xylenes, and the trimethylbenzenes were the dominant compounds in the atmospheric vapor phase samples, with levels of 0.5 - 10 $\mu g/m^3$. The aromatic concentrations were also quite variable, due to their reactivity. No aromatics were found in the particulate samples.

4.2.4.3.4 Phenols

Alkylphenol concentrations were fairly high in the vapor phase samples, but were not detected in the particulate phase. Some chlorophenols were detectable in the vapor phase, although present at very low levels. Pentachlorophenol was not measurable in any sample due to its extremely high detection limit.

4.2.4.3.5 Phthalate Esters

Phthalate esters were difficult to measure in the PUFP and filter extracts due to the high blank levels. Vapor phase diethyl and dibutylphthalate were easily quantifiable on the ADCs; the others were not sufficiently volatile to desorb. Diethylphthalate was not detected in the particulate samples.

4.2.4.3.6 Chlorinated Compounds

The chlorinated target compounds ranged from tri- and tetrachloro-ethene, to the chlorinated benzenes and phenols, to the chlorinated pesticides such as α- and γ-HCH, heptachlor, dieldrin and DDT. The concentrations of tri- and tetrachloroethene were very high in the vapor phase samples, exceeded only by the aromatics. By contrast, the compounds dichlorobromomethane, 1,1,2-trichloroethane, 2,4,5,6-tetra-chlorophenol, pentachlorophenol, γ-HCH, heptachlor, aldrin, dieldrin, p,p'-DDD, and p,p'-DDT were not detected in any vapor phase sample. No chlorinated compounds with the exception of p,p'-DDE were detected in any particulate phase sample.

4.2.5 Atmospheric Organic Concentrations at the Oregon Coast, 1985

Three sets of air concentration data were obtained at the coastal site. Total sample volumes ranged from 150 to 250 m^3 and were obtained over periods of 1-3 days. The concentrations of all compounds were subjected to the significance testing and blank correction procedure described above. The blank-corrected vapor and particulate phase con-centrations at the Oregon coast are presented in Table A1.3. The rela-tive magnitude of the concentrations at the Oregon coast and in Port-land are presented in Figure 4.7. The concentrations of the aromatics and alkylphenols were lower by a factor of 4 to 6 than the concentra-tions in the Portland samples. The concentrations of the PAHs were lower by a factor of 2 to 3. The compound α-HCH, a component of the
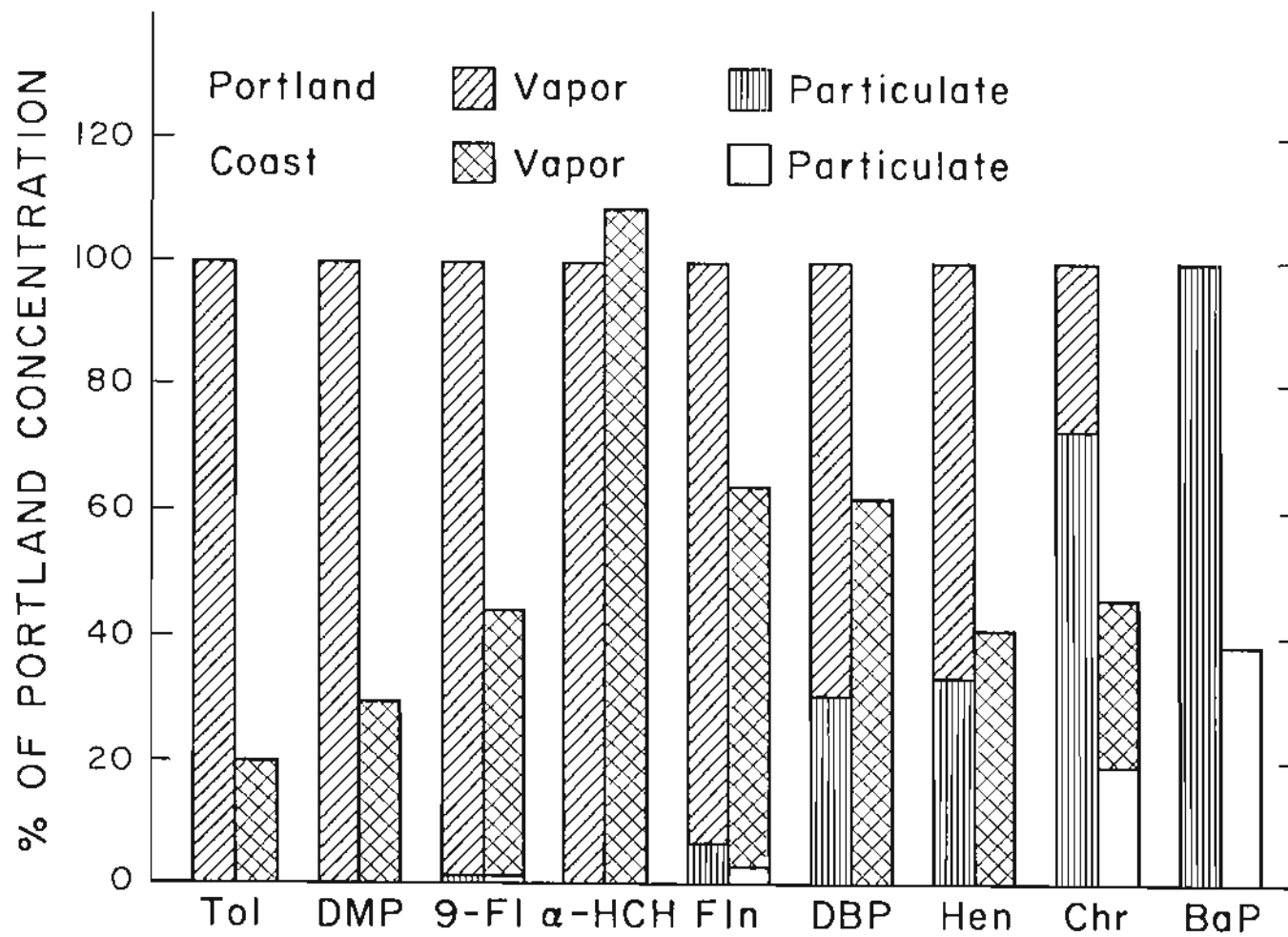
Figure 4.7. Comparison of concentrations of selected compounds at the Oregon coast to those in Portland.

commercial grade of the pesticide lindane, was present at equal levels in Portland and at the coast. The particulate phase concentrations of PAHs were lower by roughly a factor of 4 than those measured in Portland. The alkanes were not measurable in the coastal samples because Teflon filters were used there. As discussed in Section 4.2.4, the high blank levels of alkanes on TMFs precluded their determination at ambient levels. The differences in the particulate phase concentrations between Portland and the Oregon coast are similar to the factor-of-2 differences found between urban and coastal sites in Belgium (Broddin et al., 1980), although the absolute concentrations were much higher in the latter study.

As mentioned in Section 4.1.2, the coastal site was located near a woodstove. While organic emissions from wood burning include PAHs, they are dominated by phenols and furfurals (Hubble et al., 1982). These latter compounds were present at relatively low levels at the coastal site, suggesting that the wood-burning contribution to the vapor phase organic concentrations was low there compared to Portland.

The measured concentrations of α-HCH in Portland and at the Oregon coast, which averaged 0.31 and 0.37 ng/m^3, are comparable to the 0.25 ng/m^3 measured at Enewetok Atoll (Atlas and Giam, 1981). These concentrations are therefore likely to represent global levels of this compound. No other compounds were found at comparable levels at the two Oregon sites. Compounds which were present in much higher concentrations in Portland are likely to be urban pollutants. Assuming that the Portland concentrations are representative of urban areas in general,

the extent of depletion of a compound in the coastal samples can be used as a gauge of the compounds reactivity in the atmosphere. Those compounds which are present in much lower concentrations at the Oregon coast (e.g. toluene) are more reactive, and hence have shorter atmospheric lifetimes, than compounds for which this difference is not as great.

4.2.6 Reproducibility

4.2.6.1 Replicate Analyses

Replicate analyses of air sample extracts generally showed an analytical precision of 10%. This result was true in general even when the analyses were conducted several months apart. (The internal standard compound 2,4-dimethylphenol-d_3 degraded in several of the extracts after prolonged storage.) The comparison of concentrations obtained with the MS in the scan mode to those obtained in the MID mode generally showed good agreement as well, except in cases where the levels were near the scanning MS detection limit. In those cases, the MID analyses generally gave higher values. The MID values were considered to be the correct ones in those cases.

4.2.6.2 Comparison of Results obtained with PUFP and Tenax-GC

As shown in Table 4.5, PUF cannot be used for the determination of neutral compounds more volatile than acenaphthylene for sample volumes > 50 m^3. Conversely, compounds less volatile than pyrene are not de-

sorbed as easily from the large Tenax cartridges used here. (Such compounds have been desorbed successfully from smaller cartridges at temperatures in the 275°-325°C range (Pankow and Kristensen, 1983)). Under the conditions used for the ADC-1 desorptions, concentrations could not be determined for compounds less volatile than phenanthrene. Therefore, concentration data could only be obtained from all three methods for compounds in the range of volatility between acenaphthylene and phenanthrene, as shown in Table 4.10. Concentration data were obtained from both the PUFPs and the ADC-2s for compounds through pyrene. With the exception of acenaphthylene, the agreement was good. As examples, the pooled coefficient of variation (CV) of the concentrations determined by all three methods was 15% for dibenzofuran, and 27% for phenanthrene + anthracene. The average pooled CV was 18%. The pooled CV between the ADC-1s and -2s for all compounds which were not determined on the PUFPs averaged 16%. Larger concentrations of acenaphthylene were found on the ADC-1s than on the ADC-2s, although neither gave concentrations as high as the PUFPs. Since acenaphthylene is known to be reactive (Ligocki and Pankow, 1984), these results suggest that acenaphthylene may be degraded during sampling with Tenax-GC. A likely degradation product of acenaphthylene is 1,2-acenaphthenedione. The latter compound was included in the list of target compounds during the 1985 sampling in order to determine whether it had formed from acenaphthylene, either in the atmosphere or as a sampling artifact. However, it was not found in any sample.

Table 4.10. Atmospheric Vapor Phase Organic Concentrations Obtained in Portland, Oregon in 1984 with PUFP and Tenax (ADC-1 and -2) and Pooled Coefficient of Variation (CV) among Methods.

Compound	Method	Concentrations (ng/m^3)							
		Sample Date							Pooled CV
		2/12	2/14	2/20	2/23	2/29	3/16	4/11	
Acenaphthylene	PUFP	>15	35	>27	>15	47	>11	>14	139
	ADC-1	9.4	4.9	3.4	1.7	9.3	1.9	0.9	
	ADC-2	6.1	1.3	2.1	0.82	3.1	NA[a]	NA	
Acenaphthene	PUFP	>3.5	5.3	>5.9	>7.2	9.3	>4.2	>3.3	16
	ADC-1	3.6	3.3	5.3	5.4	7.7	5.9	2.8	
	ADC-2	3.9	4.4	6.4	6.7	9.9	NA	NA	
Dibenzofuran	PUFP	12	21	22	13	22	10	14	15
	ADC-1	17	22	29	15	25	16	16	
	ADC-2	NA	22	25	13	26	NA	NA	
Fluorene	PUFP	8.8	12	15	8.6	16	7.8	7.1	17
	ADC-1	7.4	8.5	9.2	6.7	15	9.4	7.6	
	ADC-2	6.5	9.8	10	8.0	12	NA	NA	
α-HCH	PUFP	0.36	0.35	0.30	0.29	0.33	0.33	0.44	13
	ADC-1	ND[b]	ND	ND	ND	ND	ND	ND	
	ADC-2	0.33	0.32	ND	ND	0.43	ND	ND	

Table 4.10 (cont'd). Atmospheric Vapor Phase Organic Concentrations Obtained in Portland, Oregon in 1984 with PUFP and Tenax-GC (ADC-1 and -2) and Pooled Coefficient of Variation (CV) among Methods.

| Compound | Method | Concentration (ng/m^3) | | | | | | | Pooled CV |
| | | Sample Date | | | | | | | |
		2/12	2/14	2/20	2/23	2/29	3/16	4/11	
Hexachlorobenzene	PUFP	0.09	0.05	0.11	0.07	0.07	0.08	0.06	
	ADC-1	ND	ND	ND	ND	ND	ND		
	ADC-2	0.09	ND	0.07	ND	NA	ND	ND	
9-Fluorenone	PUFP	3.9	7.4	6.7	4.6	7.6	4.0	4.2	36
	ADC-1	2.8	ND	6.4	6.1	7.4	15	6.9	
	ADC-2	5.7	10	10	6.6	NA	6.4	7.6	
Dibenzothiophene	PUFP	1.1	1.2	2.2	1.2	1.6	1.8	1.2	26
	ADC-1	0.6	ND	2.3	0.7	1.4	2.4	1.0	
	ADC-2	1.4	1.4	2.7	1.4	NA	2.4	1.2	
Phenanthrene + Anthracene	PUFP	19	39	29	20	35	20	21	27
	ADC-1	ND	ND	37	30	ND	54	26	
	ADC-2	26	39	41	27	NA	30	22	
Methylphenanthrenes	PUFP	12	14	17	11	18	10	9.2	19
	ADC-2	8.3	11	15	7.6	NA	7.7	9.9	

Table 4.10 (cont'd). Atmospheric Vapor Phase Organic Concentrations Obtained in Portland, Oregon in 1984 with PUFP and Tenax-GC (ADC-1 and -2) and Pooled Coefficient of Variation (CV) among Methods.

| Compound | Method | Concentration (ng/m^3) | | | | | | | Pooled CV |
| | | Sample Date | | | | | | | |
		2/12	2/14	2/20	2/23	2/29	3/16	4/11	
9,10-Anthracenedione	PUFP	2.2	3.0	3.8	2.6	3.3	1.7	1.5	14
	ADC-2	1.5	3.0	3.3	2.7	NA	NA	NA	
Eicosane	PUFP	2.9	2.1	6.6	3.6	5.4	3.9	2.8	9
	ADC-2	3.2	2.3	6.8	3.9	NA	3.9	3.7	
Fluoranthene	PUFP	6.0	9.5	9.2	6.8	10	7.1	5.3	9
	ADC-2	5.4	9.2	11	6.7	NA	NA	6.5	
Pyrene	PUFP	5.4	8.4	8.5	6.5	10	5.8	4.7	17
	ADC-2	4.1	6.7	8.6	4.8	NA	NA	6.1	

[a]NA = not available.   [b]ND = not detected at a statistically significant level.

4.2.6.3 Comparison of Side-by-Side Samplers

As described earlier, four events in 1985 were sampled with side-by-side air samplers. The samplers were not exact duplicates because of the use of different filter types. Because no differences were found in the concentrations measured on the two types of filters, as discussed in Section 4.2.2 and Table 4.3, the comparison of the vapor phase concentrations should not be affected by the difference in filters. The comparison of the concentrations obtained for vapor phase compounds on the two samplers is presented in Table 4.11. The agreement between samplers is quite good, with coefficients of variation averaging 7-18% for the four events. This degree of uncertainty is comparable to the uncertainty due to analytical methods. During the 3/26/85 sampling period, a power failure occurred which affected one sampler only. Consequently, the samples for this date were not exact duplicates since the sample volumes were not identical for the two samples. This may explain the higher coefficient of variation observed for this date. Overall, however, the reproducibility in the air sampling system was quite good.

4.2.6.4 Degradation of Tenax and Artifact Formation during Ambient Sampling

Although Tenax-GC possesses a high thermal stability, a few degradation products such as benzaldehyde and acetophenone are well-known (Pellizzari et al., 1984). Artifact formation during sampling has also

Table 4.11. Comparison of Vapor Phase Organic Concentrations (ng/m^3) from Duplicate Samplers in Portland, Oregon in 1985 and Coefficient of Variation (CV) between Samplers.

Compound	2/14			3/3			3/21			3/26		
	1	2	CV	1	2	CV	1	2	CV	1	2	CV
Toluene	NA[a]	NA	—	2900	2500	11	1900	1900	2	4300	1600	65
Tetrachloroethene	NA	NA	—	390	410	5	400	470	11	1100	910	15
Furfural	NA	NA	—	530	630	11	200	250	16	440	290	30
Ethylbenzene	NA	NA	—	830	1050	17	780	880	9	2500	1200	48
Methylfurfurals	NA	NA	—	94	170	39	61	69	9	170	72	57
Salicylaldehyde	NA	NA	—	300	390	19	480	620	19	270	230	11
2-Methylphenol	180	>110	—	88	101	10	65	72	8	83	68	14
3+4-Methylphenol	300	340	11	150	180	16	110	110	3	130	110	16
2-Methoxyphenol	NA	NA	—	160	210	16	120	120	1	170	120	22
2,6-Dimethylphenol	28	NA	—	NA	7.2	—	7.9	7.5	4	22	13	36
2-Nitrophenol	NA	NA	—	58	60	2	33	30	6	55	45	14
2-Ethylphenol	20	NA	—	12	8.9	22	6.0	6.0	0	9.1	6.0	29
2,4+2,5-Dimethyl phenol	83	NA	—	65	55	11	45	38	12	65	44	26
2,4-Dichlorophenol	ND[b]	ND	—	ND	ND	—	0.50	0.59	12	0.22	0.09	59

Table 4.11 (cont'd). Comparison of Vapor Phase Organic Concentrations (ng/m^3) from Duplicate Samplers in Portland, Oregon in 1985 and Coefficient of Variation (CV) between Samplers.

Compound	2/14			3/3			3/21			3/26		
	1	2	CV	1	2	CV	1	2	CV	1	2	CV
Naphthalene	NA	NA	—	360	340	3	300	300	0	570	370	31
4-Ethyl+3,5-Dimethylphenol	90	NA	—	68	49	22	44	40	8	64	41	32
2,4-Dimethyl benzaldehyde	NA	NA	—	37	34	6	34	31	7	68	54	16
3,4-Dimethylphenol	32	NA	—	23	11	49	6.4	7.6	12	8.7	8.3	3
2-Methoxy-4-methyl phenol	79	NA	—	150	84	39	61	42	26	104	61	36
4-Methyl-2-nitro phenol	NA	NA	—	17	33	46	15	14	6	17	20	11
1-Indanone	42	28	29	22	17	17	16	18	7	29	29	2
2-Methylnapthalene	NA	NA	—	190	190	2	180	170	2	340	270	17
1-Methylnaphthalene	NA	NA	—	95	100	3	92	89	3	170	140	17
2,6-Dimethyl naphthalene	60	67	8	24	27	7	22	18	14	36	35	3
1,3+1,6-Dimethyl naphthalene	106	118	8	48	54	7	41	36	9	58	49	12
Coumarin	13	9.0	24	7.7	7.8	1	14	14	1	8.9	8.8	1

Table 4.11 (cont'd). Comparison of Vapor Phase Organic Concentrations (ng/m^3) from Duplicate Samplers in Portland, Oregon in 1985 and Coefficient of Variation (CV) between Samplers.

Compound	2/14			3/3			3/21			3/26		
	1	2	CV	1	2	CV	1	2	CV	1	2	CV
1,4+1,5+2,3-Dimethyl naphthalene	38	38	0	14	15	5	12	10	11	20	20	0
1,2-Dimethyl naphthalene	18	18	2	5.6	6.1	6	3.8	3.5	6	7.1	7.2	1
Acenaphthylene	89	87	1	26	24	4	19	17	6	28	22	18
Acenaphthene	15	14	7	4.6	4.7	1	3.2	3.0	5	4.5	4.2	6
Dibenzofuran	46	42	6	21	22	4	15	14	5	19	16	13
1+2-Naphthol	27	9.5	67	6.9	5.5	16	3.2	4.5	24	4.0	3.4	11
Fluorene	34	32	5	11	10	4	8.7	8.0	6	11.9	9.7	14
Diethylphthalate	108	NA	—	10.3	9.5	6	6.1	6.1	0	ND	3.4	—
9-Fluorenone	15	11	19	7.1	6.4	7	5.1	5.1	0	8.1	6.1	20
Dibenzothiophene	4.9	4.8	1	1.6	1.9	10	1.2	1.1	6	1.8	1.4	18
Phenanthrene	50	51	2	25	24	0	19	18	2	27	24	7
Anthracene	10.9	9.3	11	3.9	3.4	11	2.8	2.1	18	4.1	3.8	4
Xanthone	2.5	3.2	17	1.3	1.6	17	1.3	1.2	7	1.8	1.0	39
2+3-Methylphenanthrene	18	18	1	5.3	5.9	8	4.1	4.0	2	7.2	5.9	13

Table 4.11 (cont'd). Comparison of Vapor Phase Organic Concentrations (ng/m^3) from Duplicate Samplers in Portland, Oregon in 1985 and Coefficient of Variation (CV) between Samplers.

Compound	2/14			3/3			3/21			3/26		
	1	2	CV	1	2	CV	1	2	CV	1	2	CV
1+4+9-Methyl phenanthrene	14	13	5	4.4	4.4	0	3.8	3.5	5	6.7	5.4	15
Dibutylphthalate	ND	ND	—	15	11	17	2.8	ND	—	5.0	6.3	16
9,10-Anthracenedione	4.1	5.2	16	2.3	2.0	9	1.9	2.0	2	2.8	2.0	24
Eicosane	13	8.5	31	2.4	3.1	17	3.6	3.0	13	4.3	4.9	10
Fluoranthene	16	16	4	7.5	7.3	2	6.1	5.9	1	8.8	8.3	4
Heneicosane	ND	ND	—	ND	ND	—	3.1	4.4	24	ND	ND	—
Pyrene	14	12	8	5.9	5.7	2	4.9	5.0	1	7.5	6.9	6
Benzo[a]fluorene	2.9	3.2	6	1.7	1.7	1	1.1	1.2	4	1.8	1.5	10
Benzo[b]fluorene	2.5	2.9	9	1.5	1.5	1	1.0	1.1	3	1.5	1.4	6
Benz[a]anthracene	0.42	0.35	14	0.31	0.14	52	0.19	0.21	7	0.28	ND	—
Chrysene	0.44	0.44	1	0.37	0.41	7	0.39	0.27	26	0.49	ND	—
Average CV			11			12			7			18

[a]NA = not available. [b]ND = not detected at a statistically significant level.

been attributed to the interaction of the sorbent and sorbed analytes with reactive gases such as ozone (Bunch and Pellizzari, 1979), and has been reported when sampling was conducted in the presence of water vapor (Pellizzari et al., 1984).

If degradation occurs due to thermal decomposition or the sorbent during analysis, the effects upon blank, backup, and primary cartridges would all be similar. If degradation is due to the interaction during sampling of the sorbent with some non-sorbing gas, the effect upon backup sorbent cartridges would be similar to that on primary cartridges. If, however, the interaction is between a sorbed compound and a non-sorbing gas, then a distinction between primary and backup cartridges would be observed. Table 4.12 presents the levels of benzaldehyde and acetophenone on the blank, backup and primary ADC-2s. Ambient NO_x levels measured at the same site by ODEQ and summed concentrations of 74 neutral organic contaminants are presented in the footnote for Table 4.12. Ambient ozone levels were not measured, but were probably negligible during rainstorms.

The levels of benzaldehyde and acetophenone found on the backup cartridges were not statistically different (90% confidence level) from those found on the field blanks. The levels of both compounds found on the primary cartridges were significantly (99% confidence level) higher than the backup levels using a t-test in which the variances were not assumed to be equal. Two possible explanations for the observed occurrences of benzaldehyde and acetophenone are that they represent: 1) the actual atmospheric concentrations; and 2) degradation products

Table 4.12. Levels of Benzaldehyde and Acetophenone Found on Blank, Backup, and Primary Tenax-GC ADC-2s in 1984 in Portland, Oregon[a].

Sample	Date	Benzaldehyde (ng/g Tenax-GC)	Acetophenone (ng/g Tenax-GC)
Laboratory blank		2.2	4.1
Field blank	2/14	94	430
Field blank	2/23	60	160
Field blank	3/16	52	95
Field blank	4/11	66	120
Average field blank		68 $\pm$ 18	200 $\pm$ 150
Backup	2/12	290	180
Backup	2/14	160	290
Backup	2/20	120	79
Backup	2/23	93	120
Backup	2/29	39	47
Backup	4/11	81	130
Average backup		130 $\pm$ 88	140 $\pm$ 86
Primary	2/12	2400	870
Primary	2/14	1000	610
Primary	2/20	1300	520
Primary	2/23	1100	500
Primary	2/29	730	130
Primary	3/16	1600	1400
Primary	4/11	670	640
Average primary		1300 $\pm$ 600	670 $\pm$ 390

[a]The levels of NO_x measured by ODEQ at the sampling site were "not available", 24, 32, 22, 33, 34, and 20 ppb for 2/12, 2/14, 2/20, 2/23, 2/29, 3/16 and 4/11, respectively. The summed concentrations for 74 neutral organic compounds were 10, 16, 18, 9.4, 33, 11, and 11 $\mu g/m^3$ for the same dates, respectively.

formed in sampling. Indeed, benzaldehyde has been observed to form from the degradation of styrene during ambient sampling (Pellizzari and Krost, 1984), although elevated levels of Cl_2 were used in that study. The observed degradation of acenaphthylene during sampling in this study (Section 4.2.6) demonstrates that significant losses of some sorbed compounds can occur even without elevated levels of reactive gases.

When expressed in units of $ng/g-m^3$, neither the benzaldehyde levels, nor those of acetophenone, nor the losses of acenaphthylene correlated well with the ambient NO_x concentrations during sampling. The levels of benzaldehyde, but not acetophenone, did correlate well with the overall concentration of organic pollutants. While acetophenone is almost certainly an artifact product, the measured benzaldehyde levels may represent actual atmospheric concentrations.

Another approach to this problem has been described by Walling (1984) and applied to the benzaldehyde and acetophenone problem by Walling et al. (1986). The approach, called distributed air volume sampling, involves the comparison of samples obtained at varying flow rates. It is reasoned that artifacts will show up as inconsistencies in the apparent concentrations. In those studies, benzaldehyde and acetophenone were found to give inconsistent concentrations. In this study, benzaldehyde concentrations measured on the ADC-1s and ADC-2s agreed within 20% for two events, disagreed for two events, and were not significantly higher than the blank values on the ADC-1s for the remaining events. Due to this contradictory information, benzaldehyde

concentrations were not reported here.

4.2.7 Determination of the Vapor/Particle Distribution

From Equation 3.1 it can be seen that the determination of ϕ is critical to the prediction of overall scavenging ratios, as well as to the determination of the dominant scavenging mechanism. These topics will be discussed further in Section 6.3. In this section, ϕ values are calculated and analyzed in the context of Equation 2.1. Possible corrections to the ϕ values due to artifacts are presented.

The mean blank-corrected vapor and particulate phase concentrations measured in Portland in 1984-85 are given in Table 4.13. The resulting mean ϕ values are also presented. The mean ϕ values range from < 0.1 for the three-ring PAHs, to 0.06 to 0.8 for four-ring PAHs, and are essentially 1.0 for five-ring PAHs. These results are in good agreement with previously reported ϕ values (Cautreels and Van Cauwenberghe, 1977; Thrane and Mikalson, 1981; Yamasaki et al., 1982). For the alkanes, compounds smaller than C_{22} were found predominantly in the vapor phase, while those larger than C_{22} were found predominantly in the particulate phase. The large vapor adsorption artifact observed for the alkanes, however, makes their ϕ values questionable.

To correct for the vapor adsorption artifact, the concentrations in Table 4.13 were recalculated using the backup filter information from Table 4.2 as follows

$$[air,vapor]_{corr} = [air,vapor]_{meas} + 2[air,backup]_{meas} \qquad 4.4$$

Table 4.13. Mean Vapor and Particulate Phase Concentrations and Resulting ϕ Values in Portland, Oregon in 1984-85.

	Concentrations (ng/m^3)		ϕ
Compound	Vapor	Particulate	
Acenaphthylene	32 ± 24	0.021 ± 0.011	0.0010 ± 0.0005
Dibenzofuran	19 ± 9	0.10 ± 0.11	0.0024 ± 0.0025
1+2-Naphthol	6.8 ± 5.6	0.25 ± 0.20	0.055 ± 0.054
Fluorene	11 ± 7	0.067 ± 0.076	0.0062 ± 0.0075
9-Fluorenone	7.0 ± 2.5 (7.0 ± 2.5)[a]	0.14 ± 0.14 (0.12 ± 0.14)	0.018 ± 0.014 (0.016 ± 0.013)
Dibenzothiophene	1.8 ± 1.0	0.039 ± 0.041	0.023 ± 0.025
Phenanthrene	26 ± 10 (26 ± 10)	0.28 ± 0.25 (0.27 ± 0.23)	0.010 ± 0.007 (0.010 ± 0.006)
Anthracene	3.4 ± 2.2	0.035 ± 0.020	0.009 ± 0.004
Xanthone	1.5 ± 0.7	0.060 ± 0.035	0.039 ± 0.021
2+3-Methylphenanthrene	7.2 ± 3.8 (7.2 ± 3.8)	0.19 ± 0.13 (0.15 ± 0.09)	0.025 ± 0.013 (0.020 ± 0.009)
1+4+9-Methylphenanthrene	5.7 ± 2.8 (5.8 ± 2.8)	0.16 ± 0.10 (0.12 ± 0.08)	0.027 ± 0.013 (0.020 ± 0.011)
9,10-Anthracenedione	2.5 ± 1.0 (2.5 ± 1.0)	0.59 ± 0.22 (0.52 ± 0.18)	0.19 ± 0.04 (0.17 ± 0.04)
Eicosane	4.8 ± 2.6 (5.4 ± 3.0)	0.88 ± 0.63 (0.30 ± 0.17)	0.15 ± 0.07 (0.059 ± 0.025)
Fluoranthene	7.9 ± 3.1 (8.0 ± 3.1)	0.53 ± 0.31 (0.42 ± 0.25)	0.061 ± 0.027 (0.049 ± 0.023)
Heneicosane	2.6 ± 1.3 (3.4 ± 2.5)	1.1 ± 1.1 (0.69 ± 0.53)	0.33 ± 0.14 (0.19 ± 0.09)

Table 4.13 (cont'd). Mean Vapor and Particulate Phase Concentrations and Resulting ϕ Values in Portland, Oregon in 1984-85.

	Concentrations (ng/m³)		ϕ
Compound	Vapor	Particulate	
Pyrene	6.7 ± 2.7 (6.8 ± 2.7)	0.62 ± 0.37 (0.53 ± 0.31)	0.083 ± 0.038 (0.071 ± 0.032)
Benzo[a]fluorene	1.6 ± 0.8	0.43 ± 0.30	0.19 ± 0.09
Benzo[b]fluorene	1.5 ± 0.7	0.45 ± 0.32	0.22 ± 0.10
Docosane	1.4 ± 0.4 (1.9 ± 1.0)	2.9 ± 2.6 (2.1 ± 1.8)	0.47 ± 0.21 (0.31 ± 0.17)
Benz[a]anthracene	0.32 ± 0.14 (0.37 ± 0.21)	1.2 ± 0.8 (1.2 ± 0.8)	0.76 ± 0.10 (0.73 ± 0.11)
Chrysene	0.49 ± 0.17 (0.66 ± 0.30)	1.5 ± 0.9 (1.4 ± 0.9)	0.72 ± 0.11 (0.65 ± 0.12)
7-Benz[de]anthracenone	0.067 ± 0.029	1.7 ± 1.2	0.97 ± 0.02
Dioctylphthalate	0.39 ± 0.39	0.48 ± 0.25	0.56 ± 0.30
Benzo[b+j+k]fluoranthene	0.11 ± 0.12	3.6 ± 1.9	0.96 ± 0.04

[a] Values in parentheses are corrected for vapor adsorption using backup filter data from Table 4.2.

$$[air, particulate]_{corr} = [air, particulate]_{meas} - [air, backup]_{meas} \qquad 4.5$$

These "corrected" values appear in Table 4.13 in parentheses. The factor of 2 in Equation 4.4 arises from the fact that both the backup filter concentration and an equal amount due to the assumed vapor contribution to the primary filter concentration must be added to the vapor concentration. In the calculation of the adsorption-corrected vapor and particulate phase concentrations for 1985, the average backup filter percentage for each compound from the 1984 samples was assumed. Because contributions of the volatilization artifact were not measured in this study, these "corrected" values should not be considered as necessarily more correct than the measured values. They are useful primarily as indicators of the uncertainties in the measured values.

The mean ϕ values measured at the Oregon coast are compared to the Portland ϕ values in Table 4.14. By re-arranging Equation 2.1 as follows,

$$\frac{1 - \phi}{\phi} = \frac{[air, vapor]}{[air, particulate]} = \frac{P}{c\Theta} \qquad 4.6$$

the mean Θ values at Portland and at the Oregon coast can be compared, assuming the value of c for each compound to be the same at both sites. Table 4.14 indicates that the mean value of Θ at the coastal site is roughly a factor of 2-3 lower than at the Portland site.

No corrections were made in Tables 4.13 and 4.14 for sample-to-sample variations in ambient temperatures. However, ϕ is a function of

Table 4.14. Comparison of the Mean ϕ Values at Portland and the Oregon Coast, and the Ratios of the Resulting Mean θ Values[a].

Compound	$\phi_{Portland}$	ϕ_{Coast}	$\theta_{Portland}/\theta_{Coast}$
Dibenzofuran	0.002	0.002	1.0
Fluorene	0.006	0.002	4.0
9-Fluorenone	0.018	0.010	1.8
Phenanthrene	0.010	0.006	1.7
Anthracene	0.009	0.013	0.7
Xanthone	0.041	0.029	1.4
3+2-Methylphenanthrene	0.025	0.023	1.1
1+4+9-Methylphenanthrene	0.027	0.027	1.0
9,10-Anthracenedione	0.19	0.073	3.0
Fluoranthene	0.061	0.047	1.3
Pyrene	0.083	0.075	1.1
Benzo[a]fluorene	0.19	0.13	1.6
Benzo[b]fluorene	0.22	0.14	1.8
Butylbenzylphthalate	0.42	0.11	5.9
Benz[a]anthracene	0.76	0.47	3.6
Chrysene	0.72	0.42	3.6
7-Benz[de]anthracenone	0.97	0.79	8.6

[a] From Equation 4.6, $\theta_{Portland}/\theta_{Coast} = \{(1-\phi)/\phi\}_{Coast}/\{(1-\phi/\phi)\}_{Portland}$

[b] NA = not available.

temperature. For subsequent analysis the $(1-\phi)/\phi$ values for each event were normalized to 20°C by the following formula

$$\left(\frac{1-\phi}{\phi}\right)_{20} = \left(\frac{P}{c\Theta}\right)_{20} = \left(\frac{1-\phi}{\phi}\right)_{T} \frac{(P)_{20}}{(P)_{T}} \qquad 4.7$$

where the subscripts T and 20 refer to those parameters evaluated at the mean sampling temperature and 20°C, respectively. For those PAHs for which the temperature dependence of the vapor pressures was not known, a relation analogous to the other PAHs was assumed.

In Figure 4.8 the mean temperature-corrected $(1-\phi)/\phi$ values are plotted against solid vapor pressures for several PAHs for the Portland data. Assuming that Equation 2.1 holds, and that Θ values were constant over the thirteen sampling events, and using $c = 0.13$, the resulting value for the particle surface area concentration Θ is 7×10^{-7} cm²/cm³. By contrast, a Θ value of 4×10^{-6} can be calulated from the average Portland TSP concentration of 30 $\mu g/m^3$ and assuming the particle size distribution reported by Whitby et al. (1972). This difference may be due to uncertainty in the value of c.

It has been suggested that the supercooled liquid vapor pressure is a more appropriate parameter than the solid vapor pressure for modeling adsorption onto particles (Bidleman and Keller, 1984; Yamasaki et al., 1984; Bidleman et al., 1986), since this phase corresponds more closely to the adsorbed state. The Portland $(1-\phi)/\phi$ data are therefore plotted in Figure 4.9 against supercooled liquid vapor pressures. These data appear to curve over quite clearly for the higher vapor
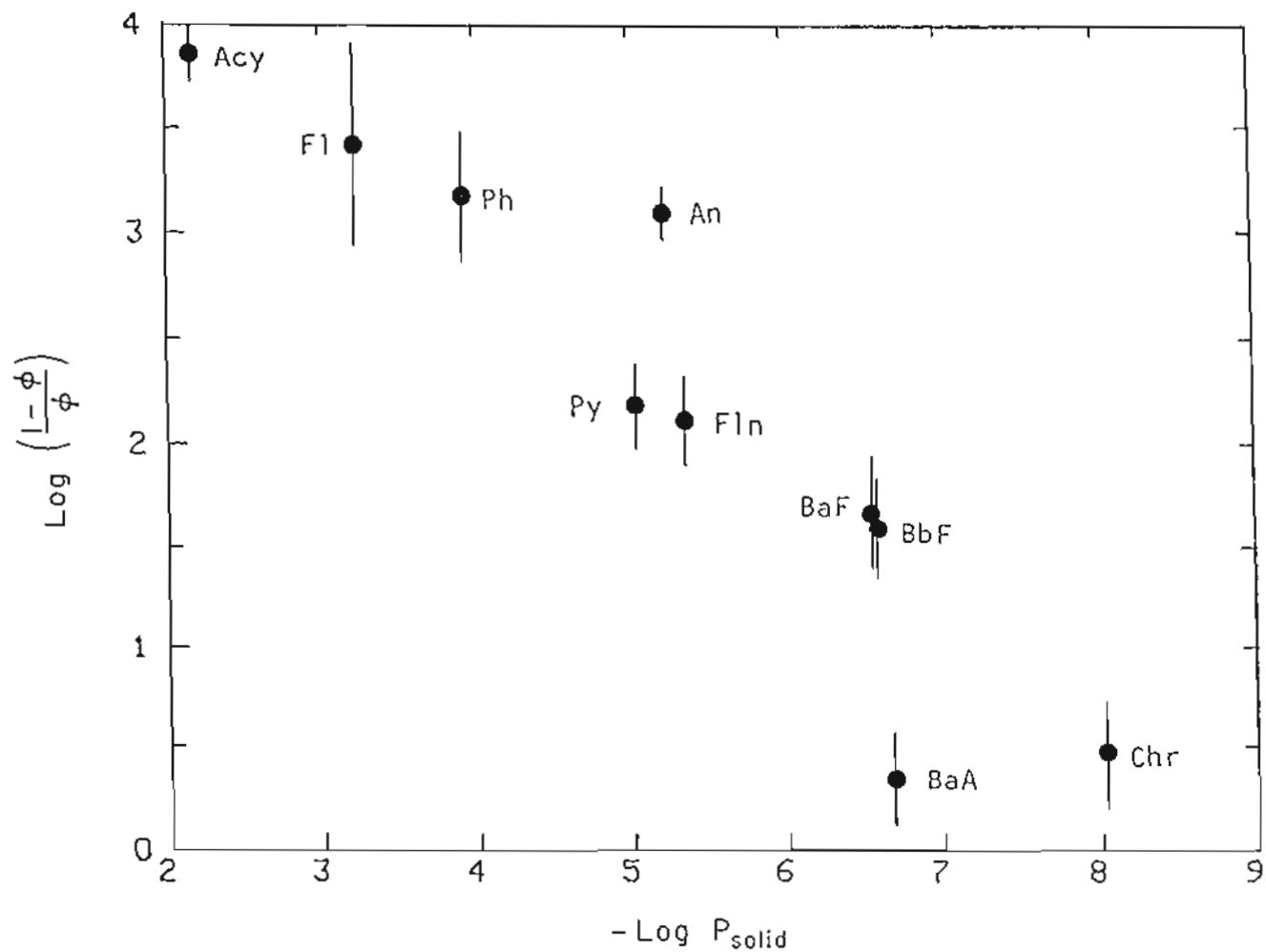
Figure 4.8. Mean vapor/particle distribution of PAHs as a function of solid vapor pressure in Portland, Oregon in 1984-85. Acy = acenaphthylene, Fl = fluorene, Ph = phenanthrene, An = anthracene, Fln = fluoranthene, Py = pyrene, BaF = benzo[a]fluorene, BbF = benzo[b]fluorene, BaA = benz[a]anthracene, Chr = chrysene.
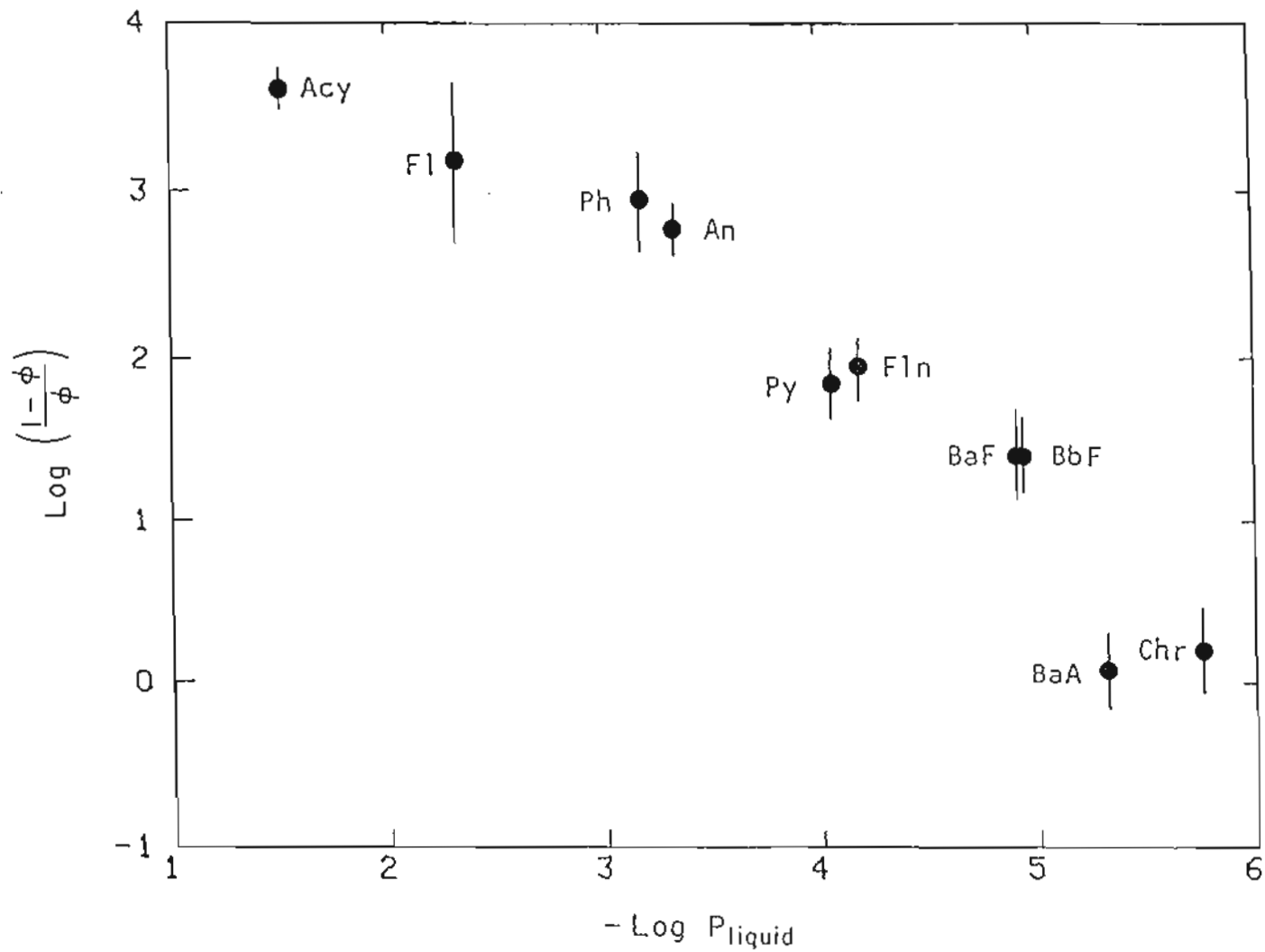
Figure 4.9. Mean vapor/particle distribution of PAHs as a function of supercooled liquid vapor pressure in Portland, Oregon in 1984-85. Abbreviations are as given in Figure 4.8.

pressure region, indicating that adsorption of volatile PAHs on parti-
cles is greater than that predicted by Equation 2.1. The analogous
plot for the coastal data is given in Figure 4.10. This plot shows the
same curvature, but the entire curve is shifted down by roughly a fac-
tor of 3. This factor of 3 difference, seen in Table 4.14 as well,
indicates that while the Oregon coastal site is cleaner than the Port-
land site, it is not a remote site such as Siskiwit Lake (McVeety,
1986).

Although the slopes in Figures 4.8-4.10 were used above to esti-
mate a mean θ value, this parameter was probably not constant for the
events sampled. Some of the scatter in Figures 4.8-4.10 may therefore
be attributable to variations in θ. If θ data were available, the
degree of agreement of the PAH data to Equation 2.1 would be more ap-
parent by plotting the mean value of the quantity $(1-\phi)\theta/\phi$ vs. P. In
the absence of θ data, another particle loading parameter can be used.
Yamasaki et al. (1982) and Bidleman and Keller (1984) successfully used
the parameter

$$\frac{[air,vapor]\ TSP}{[air,particulate]} = \frac{(1-\phi)\ TSP}{\phi} \qquad 4.8$$

where TSP is total suspended particulate mass, to correlate vapor/par-
ticle distributions of single compounds at varying temperatures.
Bidleman et al. (1986) found a linear relationship between this parame-
ter and the supercooled liquid vapor pressures for a limited number of
organic compounds with volatilities between those of phenanthrene and
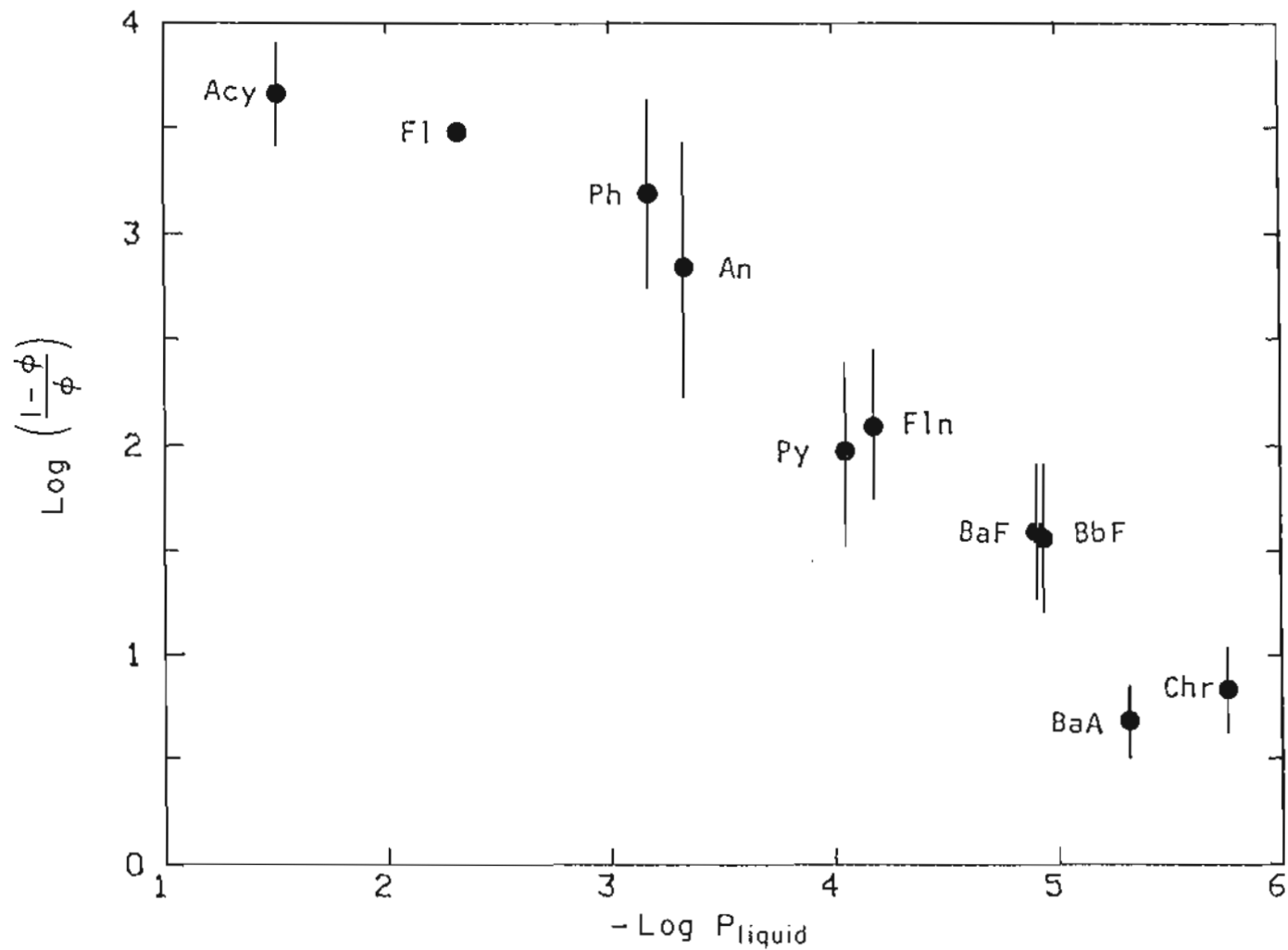
Figure 4.10. Mean vapor/particle distribution of PAHs as a function of supercooled liquid vapor pressure at Ft. Stevens, Oregon in 1985. Abbreviations are as given in Figure 4.8.

benzo[a]pyrene. In the present study, however, TSP was not measured directly. Some TSP data is available at the Portland site during some of the sampling events, but the sampling periods used by ODEQ to obtain the TSP data did not coincide exactly with those used in this study. However, total particulate carbon (TPC) concentrations were measured in this study for several events. TPC may be a better choice than TSP for correlating vapor/particle distributions to vapor pressure, since organic compounds may associate most strongly with carbonaceous particles. TPC levels in Portland ranged from 7 to 27 $\mu g/m^3$. By comparison, TSP concentrations measured by the Oregon Dept. of Environmental Quality (ODEQ) at the same site ranged from 20 to 72 $\mu g/m^3$. In Figure 4.11, the quantity

$$\left(\frac{[air,vapor]_{meas} \; TPC}{[air,particulate]_{meas}} \right)_{20} = \left(\frac{(1-\phi) \; TPC}{\phi} \right)_{20} \qquad 4.9$$

is plotted versus supercooled liquid vapor pressure for PAHs in Portland. The resulting curve has the same shape as the curves in Figures 4.8-4.10. The values which have been corrected for vapor adsorption are also shown in Figure 4.11. The vapor adsorption correction does not make the curve more linear. Even if a 30% adsorption is assumed for the volatile PAHs, the curve would not become linear. The existence of a volatilization artifact in the sampling would cause measured particulate concentrations to be too low for the volatile compounds, and would therefore increase the non-linearity. Thus, the nonlinearity does not appear to be due to artifacts. Instead, it may be due to the
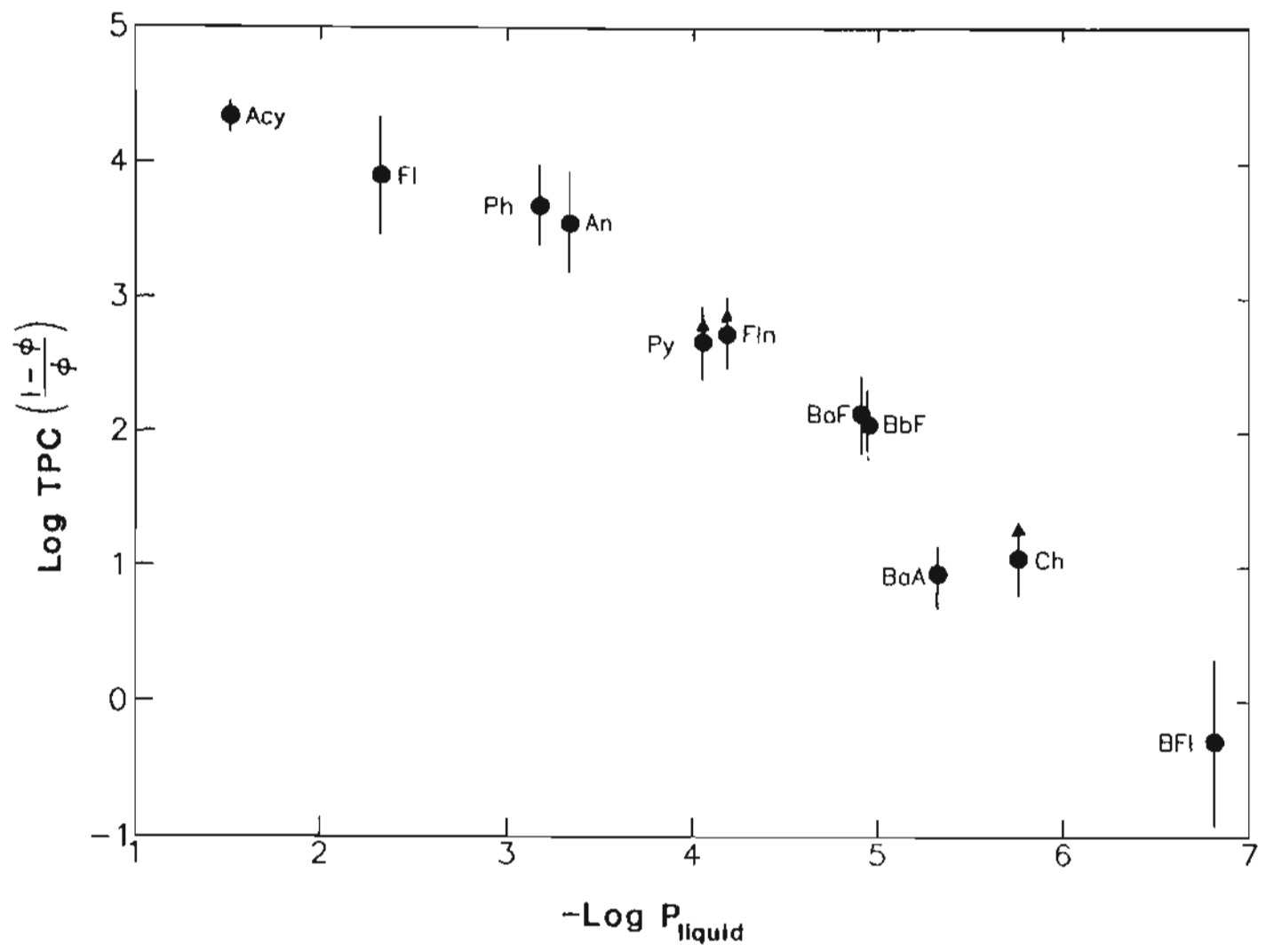
Figure 4.11. Mean TPC-weighted vapor/particle distributions of PAHs as a function of supercooled liquid vapor pressure in Portland, Oregon in 1984-85.
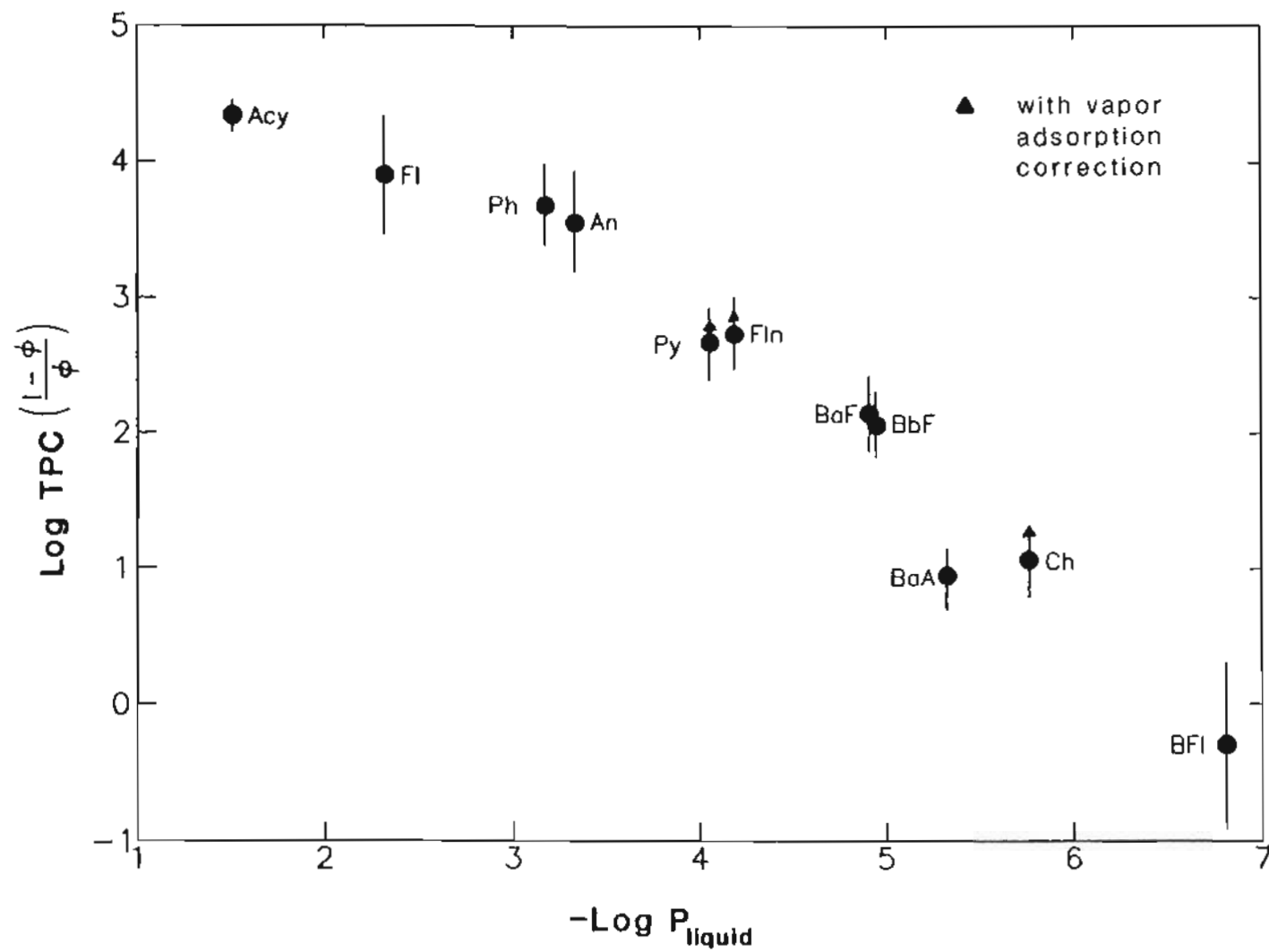
Figure 4.11. Mean TPC-weighted vapor/particle distributions of PAHs as a function of supercooled liquid vapor pressure in Portland, Oregon in 1984-85.

presence of a portion these compounds in a bound form within the particles where rapid exchange with the vapor phase does not occur.

CHAPTER 5   RAIN SAMPLING FOR ORGANIC COMPOUNDS

In this chapter the details of the rain sampler design and opera-
tion are presented.   The analytical procedures, where they differ from
those presented in Chapter 4, are described, and the results from two
years of rain sampling are presented.   The discussion of scavenging
ratios is left for Chapter 6.

5.1   Experimental Procedure

5.1.1   Sampling Apparatus

The rain sampler employed in this study was a modified version of
the rain sampler developed by Pankow et al. (1984).   It was designed to
collect and process rainwater automatically in the field.   The rain
sampler (Figure 5.1) utilized a 0.89 m^2 Teflon collection surface moun-
ted in an aluminum box.   The lid of this box opened automatically at
the onset of precipitation to expose the Teflon surface, and closed
after the cessation of rainfall to prevent contamination of the collec-
tion surface.   Collected rainwater was channelled into an organic sam-
pling train.   Figure 5.1 shows the organic sampling train configuration
used in this study.   This configuration was modified from the design
described by Pankow et al. (1984).   The original system used a peri-
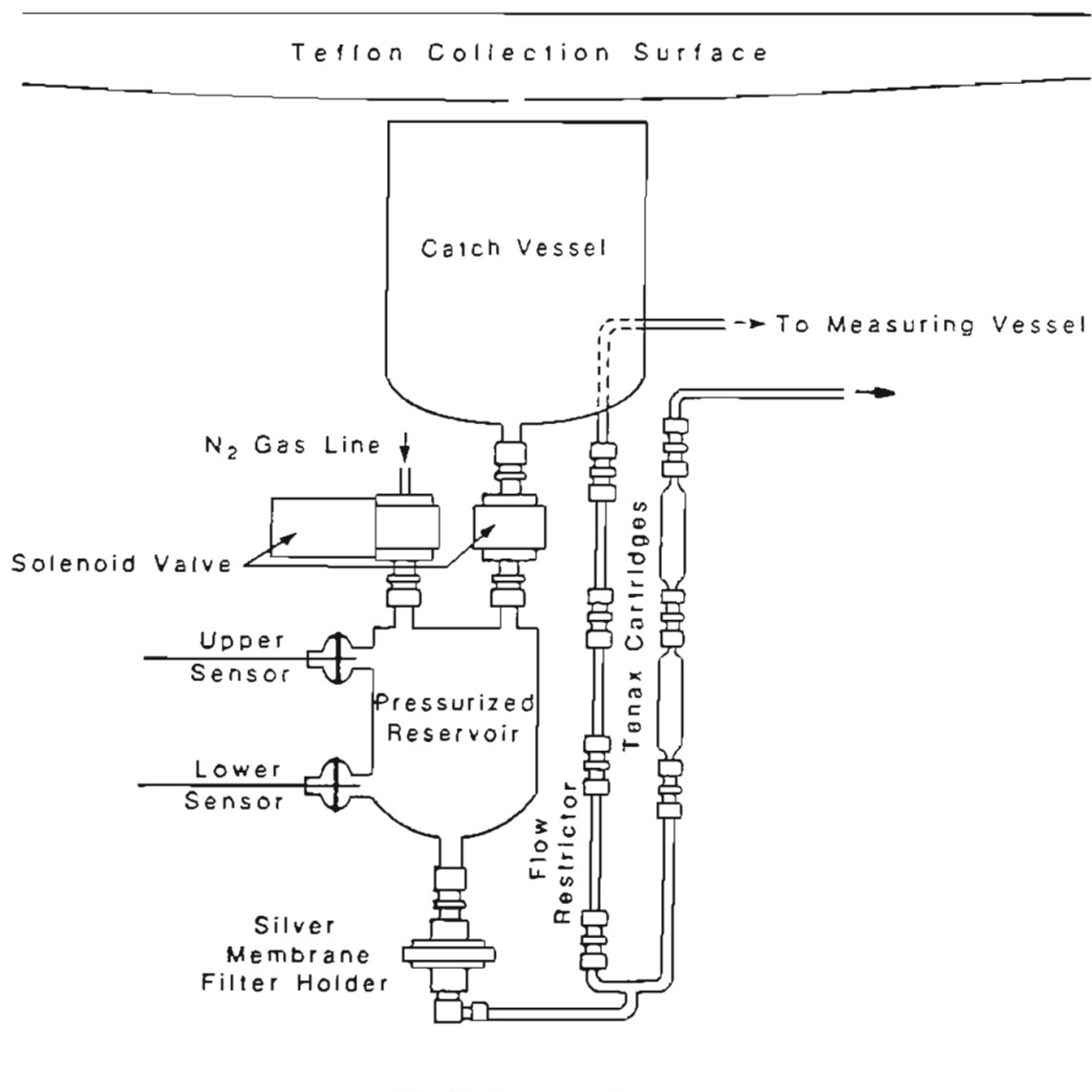
Figure 5.1. Filtration and organic sampling system for the rain sampler.

staltic pump to pump the rainwater through a glass fiber filter and the organic sampling train. After preliminary studies suggested that glass fiber filters may not be appropriate for rain sampling, silver membrane filters of pore size 0.2 μm were substituted. The change to a pressurized system was necessary for this conversion because the greater flow resistance of the silver membrane filters required a driving force of greater than one atmosphere. By using a 0.2 μm membrane filter instead of a glass fiber filter, the sampler was capable of collecting much smaller particles and thus providing a more accurate determination of the particulate concentrations in rain.

The pressurizable vessel was constructed of medium-wall Pyrex glass. The flows of rainwater and purified nitrogen were controlled by the two Teflon solenoid valves (Mace Models 800-1244-7-0 and 800-1344-7-0) . All fittings were stainless steel Swagelok fittings with Teflon ferrules (Crawford Fitting Co., Solon, OH). The level sensors consisted of two stainless steel electrodes spot-welded to tungsten rods which were either fused into Uranium glass (Corning 3320) or press-fit into machined Teflon blocks. Viton O-rings provided the seal between the vessel and the level sensors. The glass-to-glass joints provided a better seal than the glass-to-Teflon joints, but were extremely susceptible to breakage.

During a rain event, rainwater which fell on the Teflon collection surface flowed into the collection vessel and continued through the inlet valve into the pressurizable vessel. During this process, the flow resistance of the 0.2 μm pores in the filter prevented any flow of

rainwater through the filter. When the level of the collected rain-water reached the upper level sensor, the inlet valve closed. At the same time, the 3-way valve opened to the pressurized nitrogen supply, allowing the system to pressurize slowly through a needle valve to 20 psi. This pressure was sufficient to force the rainwater through the filters and on through the remainder of the organic sampling train at a rate of 60 mL/min. During the filtration cycle, freshly fallen rain-water accumulated in the collection vessel. When the water level in the pressurizable vessel dropped below the lower level sensor, the 3-way valve immediately opened to the atmosphere, venting the vessel. After a delay of 2 s, the inlet valve reopened and the cycle was repeated. A schematic diagram of the rain sampler valve electronics is given in Appendix 2.

The organic sampling train on the rain sampler consisted of a Teflon prefilter (10 μm pore size) and the 0.2 μm silver membrane filter, followed by two sets of cartridges packed with 60/80 mesh Tenax-GC or Tenax-TA. In the second year of sampling (1985) a third set of cartridges was added which were packed with cyclohexyl bonded phase (CBP) material. The flows were adjusted such that 50 mL/min was passed through the larger "rain extraction Tenax cartridges" (RECs). Approximately 10-20% of this amount was passed through the smaller "rain desorption Tenax cartridges" (RDCs). The CBP cartridges received approximately 2% of the total flow. The rainwater which passed through each channel of the organic sampling train was collected for sample

volume determination. As the filter became loaded, the overall flow rate often decreased from 50 mL/min to 20 mL/min or less. The Teflon collection sheets on the rain samplers were cleaned prior to each sampling event with acetone and clean water. The internal glassware was cleaned in the laboratory with Chromerge (American Scientific, Portland, OR).

Two rain samplers were used in the 1985 sampling. For two rain events the samplers were run side-by-side at the Portland site. One of the samplers was then moved to the coastal site at Ft. Stevens State Park, which is described in Section 4.1.2. Two rain events were sampled simultaneously in Portland and at the coast. A third event was sampled at the coast; however, that front did not reach Portland.

5.1.2 Materials

The Teflon pre-filters were purchased from Millipore (Bedford, MA). The 47 mm silver membrane filters were obtained from Selas (Huntingdon Valley, PA). The Teflon solenoid valves and the Teflon filter holder (Model 930-1244-1) were from Mace (South El Monte, CA). Tenax-GC and Tenax-TA (60/80 mesh) was purchased from Alltech Assoc. (Deerfield, IL). Cyclohexyl bonded phase material was obtained from Analytichem International (Harbor City, CA) in mesh size 300 (40 μm).

5.1.3 Preparation of Sampling Materials

5.1.3.1 Filter Preparation

The Teflon pre-filters were pre-cleaned by sonic extraction for 24 h in acetone and were air dried. The silver membrane filters were baked in a muffle furnace for 1 h at 375°C or sonicated in 60:40 acetone:hexane immediately prior to sampling. The rain filters were then assembled into a 47 mm Teflon filter holder in the laboratory. The entire filter assembly then was placed in a clean screw-capped glass jar fitted with a Teflon capliner for transport to the site. Identical units were prepared as field blanks, and were transported to and from the site along with the samples.

5.1.3.2 Adsorbent Material Preparation

All cartridges were packed prior to cleaning of the sorbent, and the sorbent was secured in place with glass wool plugs. The filled RECs were cleaned by extraction with 60:40 acetone:hexane in a special cycling extraction device, then conditioned by heating at 275°C under a flow of 100 mL/min of ultrapure helium for 3 hours. Filled RDCs and CBPs were cleaned by pumping approximately 1 L of 60:40 acetone:hexane solvent through a series of six cartridges. The RDCs and CBPs were then dried, either by vacuum or under a stream of ultrapure helium, and then conditioned as with the RECs. All cartridges were capped with pre-cleaned brass Swagelok fittings equipped with Teflon ferrules. The Teflon ferrules and the brass fittings were cleaned by sonication in

60:40 acetone:hexane, air dried, and then degassed under vacuum at 150°C prior to assembly. The capped cartridges were stored and transported in clean Pyrex culture tubes.

5.1.4 Recovery Studies

Recovery studies were not conducted for the RECs and RDCs because such studies were available (Leuenberger and Pankow, 1984; Pankow et al., 1987). In those studies selected analytes of interest were added to a stream of water which was then passed through the cartridges. Thus the trapping efficiencies, as well as the recoveries from the analytical procedures, were available.

5.1.5 Analysis of Samples

The analyses of all rain filters and RECs from the 1984 sampling period were conducted by Christian Leuenberger and the results are presented in Leuenberger et al. (1985) and Ligocki et al. (1985a,b). The analytical procedure was generally the same for the 1985 samples and is therefore presented here in detail.

5.1.5.1 Filters

The rain filter samples and field blanks were stored at 5°C prior to extraction. In the 1984 samples, each rain filter and pre-filter pair was analyzed as a unit. In the 1985 samples the filter and pre-filter were analyzed individually. Each unit was spiked with 50 μL of

the same internal standard solution used for the air GFFs. The spiked filters were Soxhlet extracted and concentrated as described for the air samples in Section 4.1.6. The rain filter extracts were not fractionated. Some of the 1985 extracts were cleaned up on silica gel, as described for the air filters. External standard addition and GC/MS/DS analysis proceeded as with the air filter extracts. All 1984 rain filters were re-extracted for 4 h with 75:25 toluene:methanol. These extracts were prepared in the same manner as the acetone:methylene chloride extracts. Several of the 1985 rain extracts were also analyzed with the GC/MS in the MID mode for enhanced sensitivity, as described for the air filters in Section 4.1.6.

5.1.5.2 RECs

The RECs were dried after sampling by centrifugation followed by vacuum drying for 20 min. Studies in this laboratory have shown that adsorbed compounds as volatile as toluene are retained by Tenax during this procedure (Pankow et al., 1987). RECs were spiked with 50 μL of the internal standard solution in acetone and were extracted for 3 h with 15 mL of 60:40 acetone:hexane. The extracts were concentrated to 1 mL in a miniature Kuderna-Danish (K-D) apparatus. The 1985 extracts were cleaned up on silica gel. 10 μL of the external standard solution was added to all REC extracts just before analysis. GC/MS/DS analysis proceeded as described for the rain filter extracts.

5.1.5.3 RDCs

The RDCs were analyzed by thermal desorption and capillary GC/MS/DS. The RDCs were dried as described above for the RECs. A 2 μL aliquot of the ADC internal standard solution in methanol was injected into each RDC immediately prior to analysis, as described for the ADCs in Section 4.1.6.

All the RDC analyses utilized the HP 5790A GC and the Finnigan MS/DS. For analysis, a cartridge was placed in the desorption apparatus and purged for 10 min. The RDCs were desorbed at 250°C for 10 min under a pressure of 30 psi. The oven temperature was held at -80°C during the desorption step, then programmed to 250°C at 10°C/min. Other conditions were the same as previously described.

5.1.5.4 CBPs

The CBP cartridges were dried as described for the RECs. An initial attempt was made to analyze the CBP cartridges by direct thermal desorption. As will be discussed in Section 5.2.2, this method of analysis was found to be unsatisfactory. The following procedure was then adopted for the analysis of the CBPs. A 10 μL aliquot of the RDC internal standard solution was added to each cartridge. The cartridge was then extracted by passing 10 mL of methylene chloride through it at a flow rate of 2 mL/min. The solvent volume was reduced to 2 mL in a miniature K-D apparatus, then 0.5 mL of methanol was added and the methylene chloride evaporated. A 0.1 mL aliquot of the methanol ex-

tract was applied to a clean Tenax-TA cartridge which was then purged with ultrapure helium for 30 min at a flow rate of 20 mL/min to remove the methanol. A 2 μL aliquot of the RDC external standard solution was then added to the cartridge, which was thermally desorbed as previously described for the RDCs. The overall procedure was termed ASERTD, for adsorption, solvent extraction, re-adsorption and thermal desorption.

5.2 Concentrations of Organic Compounds in Rain

In this section, the results from the rain sampling episodes in Portland and at the coast are presented, along with comparisons to other available rain data. Also presented are discussions of problems encountered with the sampling and analytical methods.

5.2.1 Breakthrough

As discussed in Section 3.2, breakthrough of organic compounds in aqueous sampling may have several causes. Sample volume and temperature may not be as important as they are in air sampling. The breakthrough B of organic compounds on the RECs, RDCs and CBPs is given in Table 5.1 for the 1985 Portland sampling. B is defined as in Section 4.2.3. The difference in breakthrough observed for non-polar and polar compounds was very distinct. Breakthrough of non-polar organic compounds averaged 5% and 2% for Tenax and CBP, which was quite adequate to ensure quantitative trapping of the analytes on a two-cartridge system. The breakthrough increased with the polarity of the compound, to an average of 47% and 40% for the methylphenols on Tenax and CBP.

Table 5.1. Percent Breakthrough (B)[a] of Dissolved Organic Compounds in Rain on Tenax and CBP Cartridges in Portland, Oregon in 1985.

Compound	Method	B							
		2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21

Nonpolar Neutral Compounds

Compound	Method	2/14	3/3	3/21 1	3/21 2	3/26 1	3/26 2	4/17	4/21
Naphthalene	REC	11	12	6	9	6	0	0	2
	RDC	7	1	1	4	NA	3	2	2
	CBP	0	0	0	0	0	0	0	0
2-Methylnaphthalene	REC	7	14	2	8	3	11	0	2
	RDC	6	3	2	4	NA	3	2	3
	CBP	0	0	0	5	0	0	0	0
1-Methylnaphthalene	REC	10	13	4	9	6	8	0	2
	RDC	7	3	3	4	NA	4	3	2
	CBP	0	0	0	11	0	0	0	0
2,6-Dimethylnaphthalene	REC	0	0	0	0	0	0	0	2
	RDC	19	0	8	NA	NA	7	8	0
	CBP	0	0	0	12	0	NA	0	0
Acenaphthylene	REC	9	13	35	12	9	10	0	0
	RDC	14	6	5	NA	NA	6	9	2
	CBP	0	0	15	0	0	0	0	0
Acenaphthene	REC	20	0	0	0	0	9	0	0
	RDC	6	0	27	NA	NA	0	0	33
	CBP	0	0	0	0	0	0	NA	0
Dibenzofuran	REC	5	0	3	6	3	0	0	13
	RDC	9	8	6	NA	NA	5	0	0
	CBP	0	0	22	10	0	0	22	1
Phenanthrene	REC	8	11	4	9	6	9	0	4
	RDC	7	1	1	NA	NA	5	2	0
	CBP	0	0	0	11	0	0	0	0
Fluoranthene	REC	5	10	4	8	4	5	0	3
	RDC	5	0	0	NA	NA	0	0	NA
	CBP	0	0	0	9	0	0	0	0

Table 5.1 (cont'd). Percent Breakthrough (B)[a] of Dissolved Organic Compounds in Rain on Tenax and CBP Cartridges in Portland, Oregon in 1985.

Compound	Method	B							
		2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
Pyrene	REC	4	7	4	9	4	0	0	4
	RDC	4	0	0	NA	NA	0	0	NA
	CBP	0	0	0	0	0	0	0	0
Polar Neutral Compounds									
2+3-Tolualdehyde	REC	27	27	16	25	27	19	11	3
	RDC	21	8	8	25	NA	17	26	13
	CBP	0	0	0	0	0	0	0	3
4-Tolualdehyde	REC	25	25	17	18	22	14	11	4
	RDC	0	6	7	28	NA	15	0	9
	CBP	0	0	0	0	0	0	0	0
2,4-Dimethyl benzaldehyde	REC	14	21	12	15	16	14	5	14
	RDC	13	9	6	8	NA	8	6	8
	CBP	0	0	0	0	0	0	0	0
1-Indanone	REC	32	36	37	32	47	26	25	47
	RDC	27	37	21	23	NA	29	3	19
	CBP	0	0	0	4	0	0	0	0
Coumarin	REC	33	37	36	34	34	17	34	28
	RDC	35	43		NA	NA	26	8	20
	CBP	0	4	0	4	NA	NA	0	0
Diethylphthalate	REC	32	NA	0	0	NA	NA	NA	0
	RDC	15	0	20	NA	NA	20	5	14
	CBP	0	NA	0	NA	NA	NA	NA	0
9-Fluorenone	REC	16	26	12	20	18	13	4	10
	RDC	9	4	4	NA	NA	8	3	5
	CBP	0	0	3	4	0	0	0	0

Table 5.1 (cont'd). Percent Breakthrough (B)[a] of Dissolved Organic Compounds in Rain on Tenax and CBP Cartridges in Portland, Oregon in 1985.

Compound	Method	B							
		2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
Xanthone	REC	10	18	0	15	19	0	5	13
	RDC	7	5	3	NA	NA	9	0	4
	CBP	0	0	4	31	0	0	0	0
9,10-Anthracenedione	REC	10	24	9	20	20	0	7	13
	RDC	7	8	NA	NA	NA	0	7	NA
	CBP	0	0	0	1	0	0	0	0
Phenols									
2-Methylphenol	REC	50	50	61	44	57	36	50	33
	RDC	58	46	48	49	NA	59	27	45
	CBP	30	53	52	36	41	41	8	58
3+4-Methylphenol	REC	48	46	63	42	58	36	51	40
	RDC	53	44	50	36	NA	57	28	47
	CBP	26	56	54	36	44	40	5	64
2-Methoxyphenol	REC	43	62	52	45	30	NA	26	33
	RDC	52	43	38	41	NA	54	14	38
	CBP	36	60	66	34	47	21	0	65
2,6-Dimethylphenol	REC	39	48	32	45	30	25	0	25
	RDC	60	39	25	45	NA	30	7	24
	CBP	0	26	8	35	8	26	0	20
2-Nitrophenol	REC	4	38	17	22	0	NA	11	15
	RDC	22	6	6	73	NA	9	0	9
	CBP	0	48	10	34	0	0	0	NA
2-Ethylphenol	REC	40	36	52	NA	47	22	46	24
	RDC	49	NA	NA	NA	NA	38	17	NA
	CBP	0	27	14	34	16	0	0	22

Table 5.1 (cont'd). Percent Breakthrough (B)[a] of Dissolved Organic Compounds in Rain on Tenax and CBP Cartridges in Portland, Oregon in 1985.

Compound	Method	B							
		2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
2,4+2,5-Dimethylphenol	REC	39	37	50	36	49	28	37	37
	RDC	60	36	33	44	NA	35	12	37
	CBP	0	20	0	33	5	0	0	8
4-Ethyl+3,5-dimethyl phenol	REC	45	38	53	35	58	27	42	36
	RDC	63	48	40	NA	NA	37	14	36
	CBP	0	17	3	21	0	NA	0	5
4-Methyl-2-methoxy phenol	REC	38	60	39	44	19	NA	10	32
	RDC	65	41	31	44	NA	36	9	32
	CBP	0	0	4	26	0	0	0	14
3,4-Dimethylphenol	REC	60	33	NA	NA	43	28	NA	0
	RDC	NA	NA	NA	NA	NA	47	24	ND
	CBP	0	38	12	38	0	0	0	26
4-Methyl-2-nitrophenol	REC	14	38	29	29	11	NA	15	15
	RDC	21	20	30	16	NA	20	29	35
	CBP	0	9	0	0	0	0	0	0
1+2-Naphthol	REC	38	5	NA	49	30	28	18	83
	RDC	7	43	NA	NA	NA	31	16	38
	CBP	0	0	NA	0	NA	NA	0	0
Pentachlorophenol	REC	NA	NA	NA	26	NA	NA	0	NA
	RDC	16	14	10	NA	NA	7	0	9
	CBP	NA	NA	NA	0	NA	NA	NA	0

[a]B = [backup]/{[primary]+[backup]}. [b]Sampler number. [c]NA = not available.

At B levels of >20%, the two-cartridge system provided a poor estimate of the total concentration. For B levels between 20% and about 45%, the total concentration C may be estimated from the primary (P) and backup (S) concentrations with the following formula (Leuenberger et al., 1985):

$$C = \frac{P}{1 - S/P} \qquad 5.1$$

Breakthrough is also a function of sampling flow rate. For the first four samples obtained in 1984, REC sample flow rates were approximately 100 mL/min. The breakthrough of slightly polar compounds such as 9-fluorenone and 9,10-anthracenedione averaged 31% for those events. Subsequently the flow rate was decreased to $\leq$ 50 mL/min. The breakthrough of 9-fluorenone and 9,10-anthracenedione decreased to 10%, and the breakthrough of the other non-polar and slightly polar compounds decreased to the levels shown in Table 5.1

5.2.2 Assessment of CBP Cartridges

An attempt was made to analyze the CBP cartridges by direct thermal desorption, as with the Tenax RDCs. Initial desorptions of blank cartridges showed no problems with the thermal desorption of the CBPs or various other bonded phase cartridges other than high blank levels in specific regions of the chromatogram. However, the analysis of the first field blank CBP cartridge showed an unusual problem: several of the deuterated internal standard compounds (2,4-dimethylphenol-d$_3$,

phenol-d_5 and acenaphthene-d_{10}) degraded during desorption through the mechanism of hydrogen exchange. This was in contrast to the perfect stability of these compounds during desorptions from Tenax cartridges. Figure 5.2a shows the mass spectrum for 2,4-dimethylphenol-d_3 after desorption from a Tenax cartridge. Figure 5.2b shows the mass spectrum for the same peak after desorption from a CBP cartridge. The latter spectrum is shifted down one mass unit, with peaks formerly at m/e 125 and 110 appearing at 124 and 109, respectively. This indicates that the compound was transformed into 2,4-dimethylphenol-d_2. As discussed in Section 4.2.6, 2,4-dimethylphenol-d_3 also degrades in solution during prolonged storage. Since phenol-d_5 and 2,4-dimethylphenol-d_3 were the internal standards for the alkylphenols, and the CBP cartridges were to be used specifically for the determination of the alkylphenols, this degradation was not acceptable.

The hybrid solvent extraction/thermal desorption method (ASERTD) described in Section 5.1.5 worked quite well for the phenols. Table 5.2 gives the absolute recoveries of the internal standard compounds for this procedure. The recoveries were good, even for the relatively volatile compounds. The ASERTD procedure had the additional advantage of allowing replicate analyses to be performed, an option which is not available with direct thermal desorption. Table 5.3 gives the results of replicate analyses of one CBP primary sample. The reproducibility was excellent, with coefficients of variation for the phenols ranged from 2% to 14%.
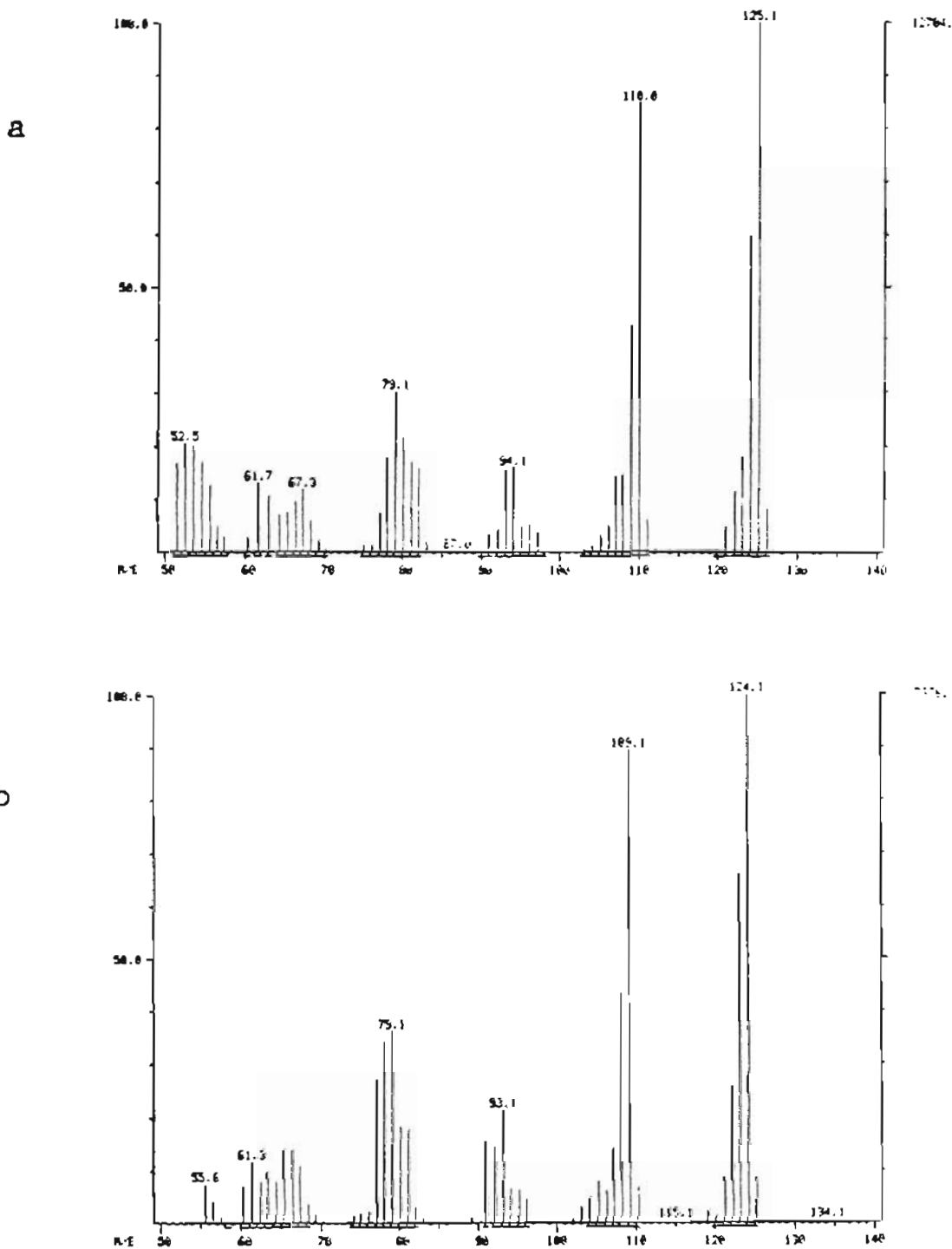
Figure 5.2. a) Mass spectrum of 2,4-dimethylphenol-d$_3$. b) Mass spectrum of product formed from 2,4-dimethylphenol-d$_3$ during desorption from a CBP cartridge.

Table 5.2. Average Absolute Recoveries of the Internal Standard
Compounds from the CBP Cartridges during the ASERTD Procedure, and
Recoveries Relative to that of Fluoranthene-d_{10}.

Compound	Absolute Recovery	Relative Recovery
Tetrachloroethane-d_2	47 ± 22	61 ± 29
Phenol-d_5	64 ± 17	82 ± 21
2,4-Dimethylphenol-d_3	61 ± 16	78 ± 19
Naphthalene-d_8	59 ± 16	75 ± 23
2,4-Dibromophenol	60 ± 16	76 ± 15
Acenaphthene-d_{10}	69 ± 16	89 ± 16
Fluorene-d_{10}	71 ± 13	93 ± 9
2,4,6-Tribromophenol	57 ± 26	73 ± 27
Phenanthrene-d_{10}	73 ± 13	95 ± 6
Fluoranthene-d_{10}	78 ± 13	100

Table 5.3. Results from Replicate Analyses of the CBP Primary Extract from 3/26/85 by ASERTD.

Compound	Concentration (ng/L)			
	Rep 1	Rep 2	Rep 3	Avg $\pm$ 1 s (CV)
Phenols				
Phenol	300	260	280	280 $\pm$ 20 (6.8)
2-Methylphenol	250	260	260	260 $\pm$ 8 (3.0)
3+4-Methylphenol	450	480	480	470 $\pm$ 13 (2.8)
2-Methoxyphenol	390	460	400	420 $\pm$ 36 (8.7)
2,6-Dimethylphenol	73	87	78	79 $\pm$ 7 (9.3)
2-Ethylphenol	73	57	67	65 $\pm$ 8 (12)
2,4+2,5-Dimethylphenol	560	540	550	550 $\pm$ 11 (1.9)
4-Ethyl+3,5-dimethylphenol	640	570	600	600 $\pm$ 37 (6.1)
2-Methoxy-4-methylphenol	1300	1300	1200	1300 $\pm$ 46 (3.6)
3,4-Dimethylphenol	100	110	90	100 $\pm$ 14 (14)
4-Methyl-2-nitrophenol	44	51	47	47 $\pm$ 3 (7.3)
2,6-Dimethoxyphenol	500	670	620	590 $\pm$ 88 (15)
Aldehydes				
Salicylaldehyde	240	250	220	240 $\pm$ 16 (6.6)
2+3-Tolualdehyde	340	400	330	360 $\pm$ 41 (11)
2,4-Dimethylbenzaldehyde	41	48	54	47 $\pm$ 7 (14)

Table 5.3 (cont'd). Results from Replicate Analyses of the CBP Primary Extract from 3/26/85 by ASERTD.

Compound	Concentration (ng/L)			
	Rep 1	Rep 2	Rep 3	Avg ± 1 s (CV)
PAHs and Derivatives				
Naphthalene	73	75	75	74 ± 1 (1.1)
1-Indanone	170	140	180	160 ± 19 (12)
2-Methylnaphthalene	41	43	46	43 ± 2 (5.6)
1-Methylnaphthalene	23	24	26	24 ± 1 (6.1)
2,6-Dimethylnaphthalene	4.5	4.3	3.8	4.2 ± 0.3 (7.8)
1,3+1,6-Dimethylnaphthalene	11	9.0	8.6	9.5 ± 1.2 (13)
1,4+1,5+2,3-Dimethyl napthalene	5.4	3.6	4.1	4.4 ± 0.9 (21)
Acenaphthylene	26	26	27	26 ± 1 (2.8)
1,2-Dimethylnaphthalene	3.2	2.5	2.7	2.8 ± 0.4 (15)
Acenaphthene	3.9	2.4	2.6	3.0 ± 0.8 (27)
Dibenzofuran	9.7	11	12	11 ± 1 (9.8)
Fluorene	11	12	13	12 ± 1 (7.3)
9-Fluorenone	47	41	45	44 ± 3 (6.9)
Phenanthrene	51	52	54	52 ± 1 (2.7)
Anthracene	3.6	3.1	3.5	3.4 ± 0.3 (7.4)
Xanthone	11	8.4	10	9.9 ± 1.4 (14)
3+2-Methylphenanthrene	9.1	8.6	7.4	8.4 ± 0.9 (10)

Table 5.3 (cont'd). Results from Replicate Analyses of the CBP Primary Extract from 3/26/85 by ASERTD.

	Concentration (ng/L)			
Compound	Rep 1	Rep 2	Rep 3	Avg ± 1 s (CV)
1+4+9-Methylphenanthrene	8.5	7.2	6.7	7.5 ± 0.9 (13)
9,10-Anthracenedione	53	39	45	45 ± 7 (16)
Fluoranthene	28	30	29	29 ± 1 (2.3)
Pyrene	33	31	31	32 ± 1 (3.8)
Phthalates				
Diethylphthalate	18	21	19	19 ± 2 (8.9)
Dibutylphthalate	64	120	140	110 ± 39 (36)
Butylbenzylphthalate	58	39	52	49 ± 10 (20)

5.2.3 Concentrations in Portland, 1984-85

During the 1984 sampling period, seven events were sampled at the Portland site. In 1985, six events were sampled there. For two of the 1985 events, two samplers were run side by side. Rain sample volumes of 2-27 L were collected over periods of 1-5 days. The temperature during sampling ranged from 0-16°C and averaged 7°C. The thirteen events included six cold fronts, one warm front, one frontal cyclone and four poorly defined rain events. Winds were generally from the S or SE during sampling. These meteorological and sampling parameters are summarized in Appendix 2.

The GC/MS scanning detection limits were the same as described for the air samples. Depending upon the sample volume, the 0.05 ng limit translated to rain concentrations of 0.2 - 2 ng/L for the RECs, 0.01 - 0.3 ng/L for the RDCs, and 0.3 - 3 ng/L for the CBPs.

5.2.3.1 Dissolved Phase Concentrations

In all of the rain concentration determinations, primary and back-up sample amounts were considered non-zero only if they exceeded the mean blank value at the 95% confidence level, as described for the air samples in Section 4.2.4. The mean blank levels for the RECs, RDCs and CBPs are summarized in Table 5.4. The RDCs generally exhibited the lowest blank levels because they received the smallest amount of sample handling. Typical primary and blank chromatograms for the RECs, RDCs and CBPs are presented in Figures 5.3-5.5.

Table 5.4. Mean Blank Levels (ng) for RECs, RDCs and CBPs.

Compound	REC	RDC	CBP
Methylisobutyl ketone	NA[a]	ND[b]	20 ± 5
Toluene	NA	1.2 ± 0.1	8.7 ± 1.9
Tetrachloroethene	NA	0.63 ± 0.08	45 ± 7
Furfural	NA	0.68 ± 0.57	2.3 ± 2.9
Ethylbenzene	NA	0.07 ± 0.01	8.2 ± 3.1
Benzaldehyde	NA	34 ± 18	7.1 ± 2.1
Methylfurfural	NA	ND	0.27 ± 0.36
Benzonitrile	NA	1.4 ± 0.6	0.31 ± 0.29
Phenol	NA	9.8 ± 5.2	8.9 ± 1.9
Salicylaldehyde	NA	0.22 ± 0.23	1.1 ± 1.8
Acetophenone	ND	27 ± 16	3.1 ± 1.5
3+4-Methylphenol	ND	0.07 ± 0.05	0.20 ± 0.30
2,4+2,5-Dimethylphenol	0.85 ± 0.27	1.9 ± 0.8	3.1 ± 0.2
Naphthalene	0.18 ± 0.33	0.04 ± 0.02	0.38 ± 0.13
1-Indanone	ND	ND	0.26 ± 0.45
2-Methylnaphthalene	ND	ND	0.13 ± 0.15
1-Methylnaphthalene	ND	ND	0.06 ± 0.07
Diethylphthalate	0.76 ± 0.63	0.29 ± 0.08	1.8 ± 1.2
9-Fluorenone	ND	0.007 ± 0.011	0.004 ± 0.010
Phenanthrene	0.008 ± 0.020	0.006 ± 0.007	0.15 ± 0.11
Dibutylphthalate	19 ± 35	0.28 ± 0.14	14 ± 23
Fluoranthene	ND	ND	0.026 ± 0.041
Pyrene	ND	ND	0.052 ± 0.047
Butylbenzylphthalate	0.62 ± 0.66	ND	12 ± 17
Bis(2-ethylhexyl)phthalate	9.5 ± 18	NA	NA

[a]NA = not analyzed. [b]ND = not detected.
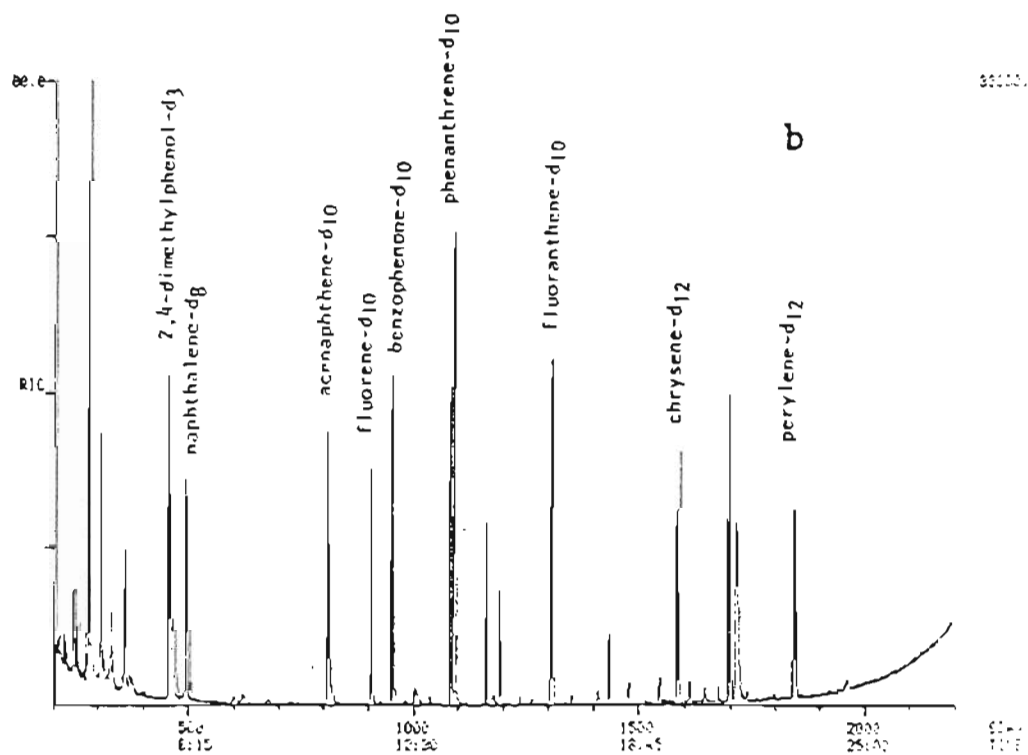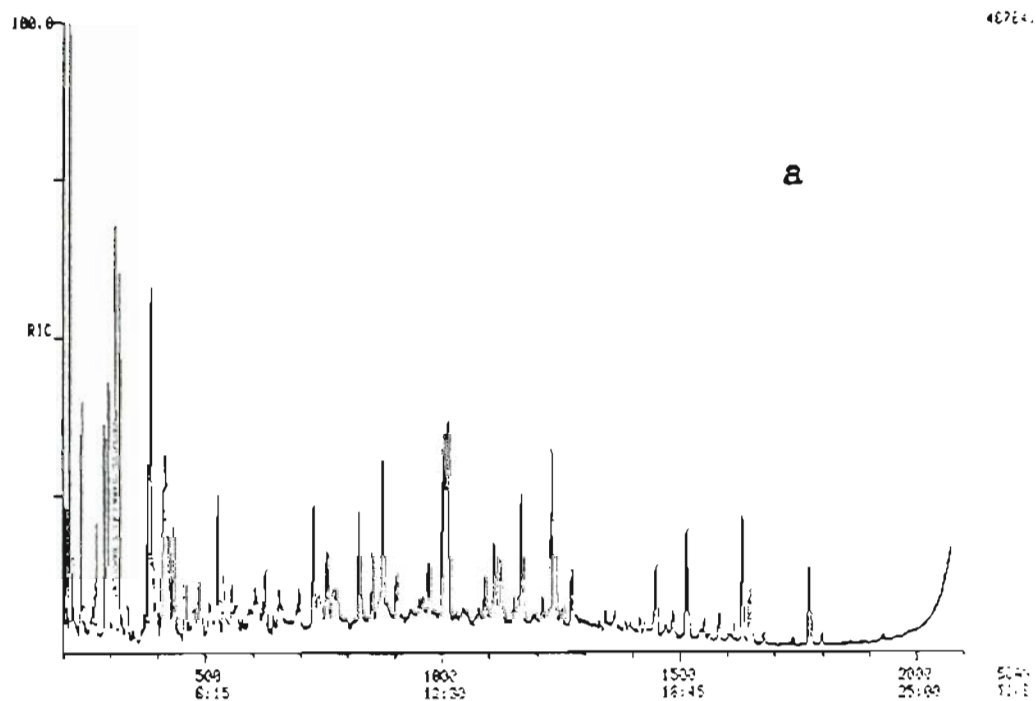
Figure 5.3.   Primary (a) and blank (b) REC chromatograms obtained in Portland, Oregon in 1985.
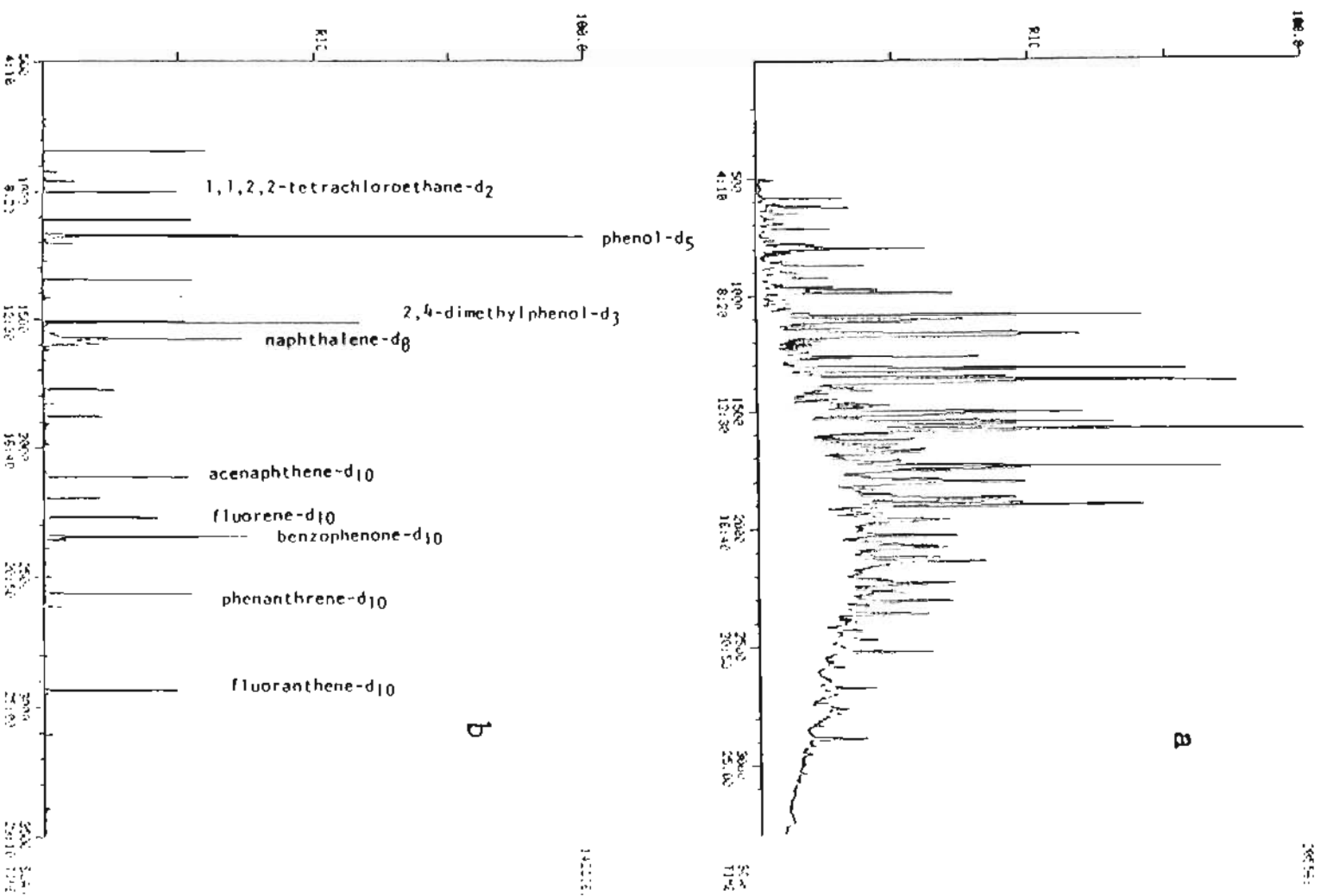
Figure 5.4. Primary (a) and blank (b) RDC chromatograms obtained in Portland, Oregon in 1985.

1,1,2,2-tetrachloroethane-d₂

phenol-d₅

2,4-dimethylphenol-d₃

naphthalene-d₈

acenaphthene-d₁₀

fluorene-d₁₀

benzophenone-d₁₀

phenanthrene-d₁₀

fluoranthene-d₁₀

b

a
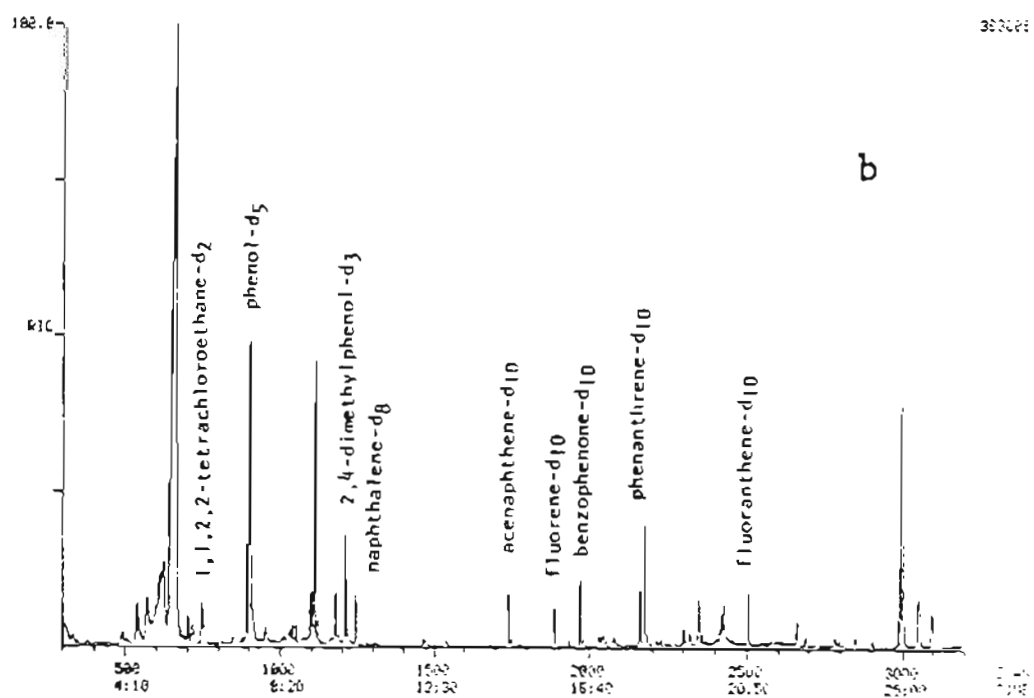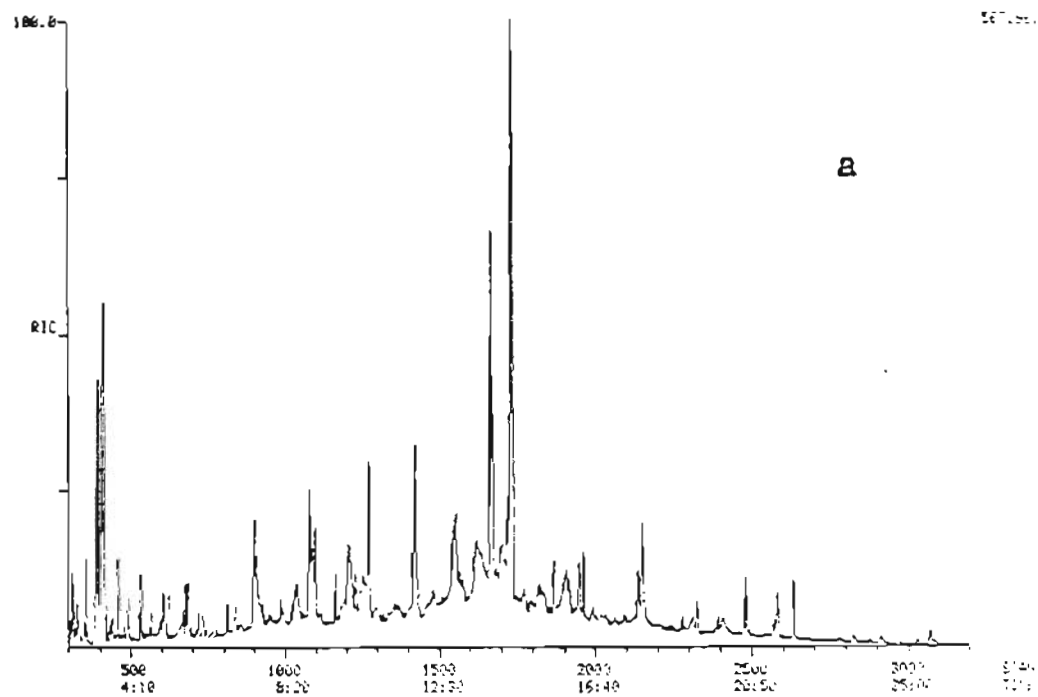
Figure 5.5.   Primary (a) and blank (b) CBP chromatograms obtained in
               Portland, Oregon in 1985.

The three methods demonstrated different advantages and disadvantages. The sensitivity obtained in the thermal desorption analyses of the RDCs was generally greater than that obtained with the RECs or CBPs. Also, the most volatile compounds could only be determined with the RDCs. The CBPs generally showed the least breakthrough (Table 5.1). During the course of some of the RDC analyses, problems with the chromatography due to column overloading and premature heating of the carrier gas were observed. These problems were apparently due to the migration of a portion of the trapped analytes ahead of the main peak. Figure 5.6 shows a typical peak during a run in which this phenomenon was observed. The assumption was made that the presence of the large number of chemically similar internal standard compounds allowed accurate quantification to be performed on these samples despite the problems with the chromatography.

For these reasons, the concentration of a given compound obtained by one method was sometimes selected over that obtained by the other methods. For many compounds, however, the concentration data was of comparable quality for two or three methods. In those cases the number presented here is the average of both determinations. The blank-corrected dissolved rain concentrations for all thirteen Portland rain events are given in Appendix 2. Concentrations of phenols were generally in the μg/L range, while concentrations of other compounds were generally in the 10-100 ng/L range. The concentration ranges for individual compounds over the thirteen events were generally a factor of 2 to 5. For the phenols the ranges were a factor of 10 to 20. The
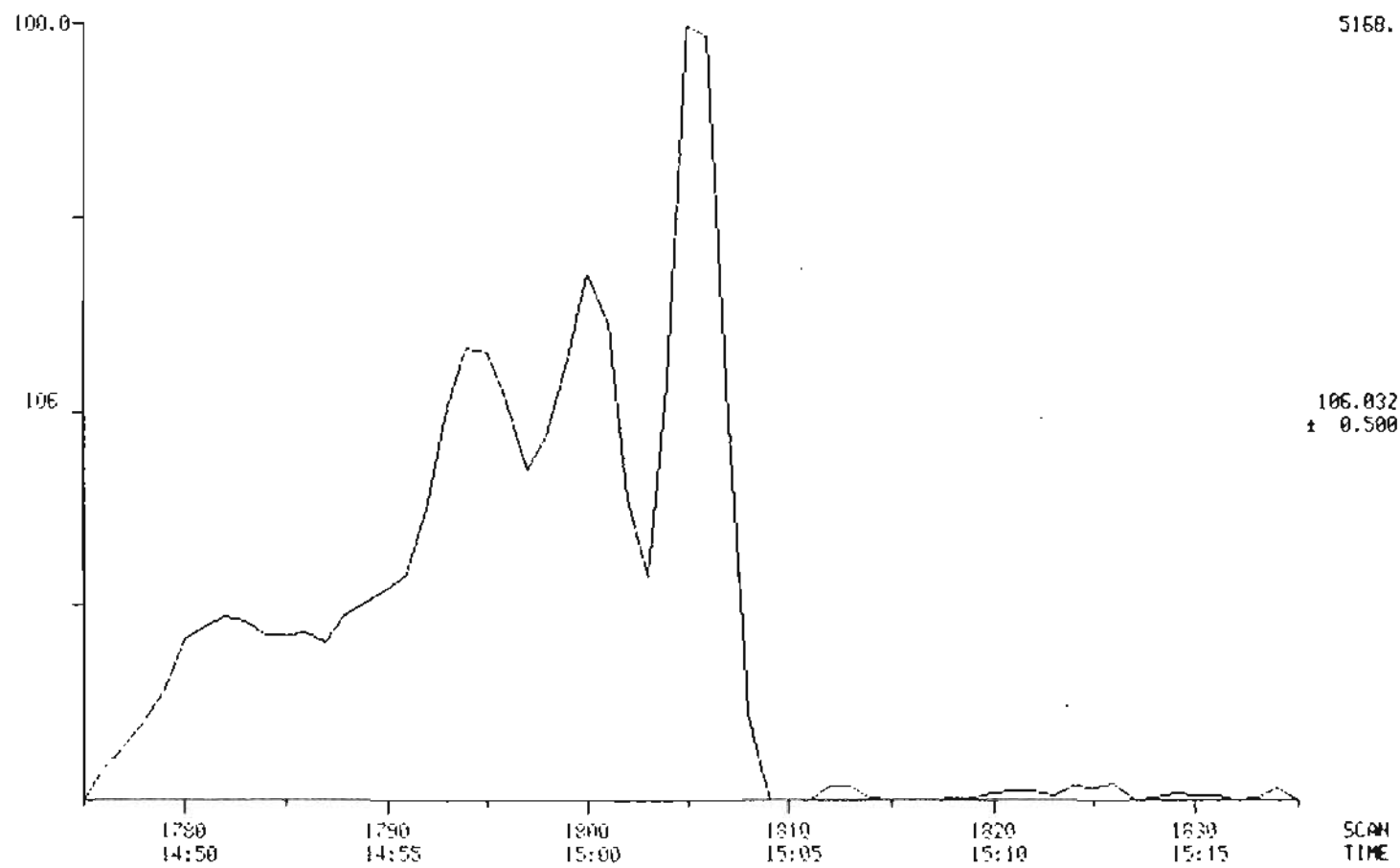
Figure 5.6. Typical peak from a chromatogram of a primary RDC in which overloading was observed.

average concentrations are presented in Table 6.1.

5.2.3.2 Particulate Phase Concentrations

Typical primary and blank chromatograms for the rain TMFs are given in Figure 5.7. The blank-corrected particulate phase concentrations are presented in Appendix 2. The 1985 particulate rain samples were analyzed by scanning and by MID, as described in Section 4.1.6. The MID detection limit of 0.005 ng translated to concentrations of 0.02 to 0.2 ng/L. No compounds more volatile than acenaphthylene were detected in any rain filter sample. No pesticides except p,p'-DDT were detected. No phenols except pentachlorophenol were detected. The concentrations of several of the compounds were very close to the detection limit. The average particulate phase concentrations are given in Table 6.5.

5.2.3.3 Size Distribution of Collected Particulate Material

For the 1985 sampling, some information about the particle size distribution in rain was available, since the pre-filters and filters were analyzed separately. Surprisingly, most of the organic compounds were found on the pre-filter, indicating that -- at the time of collection -- they were present on particles larger than 10 μm. The percentages of organic compounds which passed through the pre-filter and were trapped by the 0.2 μm filter are given in Table 5.5, and averaged about 8%. The presence of the majority of the organic compounds on the pre-filter may indicate that only large particles are scavenged efficient-
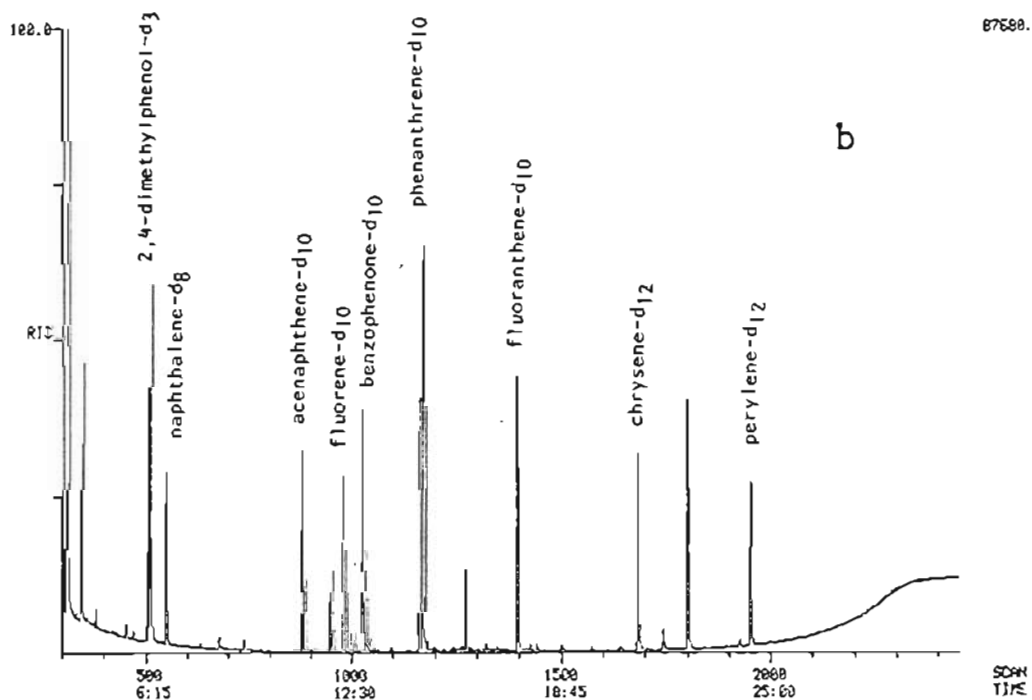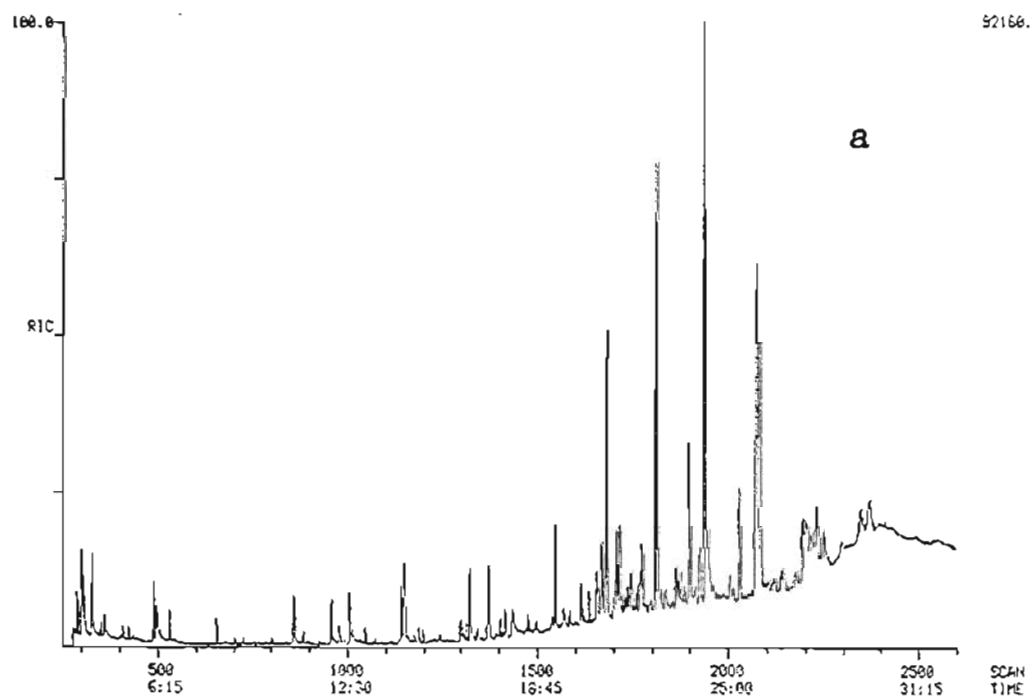
Figure 5.7. Primary (a) and blank (b) rain TMF chromatograms obtained in Portland, Oregon in 1985.

Table 5.5. Percentage of Particulate Organic Compounds in Rain which passed through the 10 μm Pre-filter during Sampling in Portland, Oregon in 1985.

Compound	2/14	3/3	3/21	3/26	4/17	4/21	Avg
Dibenzofuran	ND[a]	13	22	0	9	16	10
Fluorene	16	0	NA	0	0	24	8
9-Fluorenone	ND	7	18	0	0	15	7
Phenanthrene	0	0	26	0	0	17	8
Anthracene	0	0	25	0	0	21	8
2+3-Methylphenanthrene	3	0	20	0	0	16	7
1+4+9-Methylphenanthrene	0	0	23	0	0	18	7
9,10-Anthracenedione	4	3	7	0	0	41	9
Fluoranthene	2	0	18	0	2	14	6
Pyrene	3	0	17	0	3	18	7
Benzo[a]fluorene	7	0	23	0	0	13	7
Benzo[b]fluorene	0	0	6	0	0	17	4
Benz[a]anthracene	0	7	18	0	5	15	7
Chrysene	0	7	14	0	3	12	6
7-Benz[de]anthracenone	0	0	12	0	0	13	4
Benzo[b+j+k]fluoranthene	14	6	17	4	1	11	9
Benzo[e]pyrene	0	0	6	3	0	12	4
Benzo[a]pyrene	0	0	8	3	0	10	4
Indeno[1,2,3-cd]pyrene	0	0	14	0	0	6	4
Benzo[ghi]perylene	0	0	12	0	0.5	6	3
Coronene	0	ND	2	0	0.4	0	0.5

[a]ND = not detected on the pre-filter at a statistically significant level.

ly. This would be the case if all organic compounds resided on hydro-phobic carbonaceous particles which did not act as condensation nuclei. In this case particle scavenging would be the result of below-cloud scavenging only. Below-cloud scavenging is much more efficient for larger particles. Alternatively, smaller particles may be scavenged but then coagulate into larger particles during the course of the rain-drop's fall from the cloud, due to velocity gradients within the drop. In this case, no conclusions about the scavenging mechanism or the size of the scavenged particles may be drawn. In either case, this result indicates that the use of a 0.2 μm filter, and hence a pressurized filtration system, may not be required. A much simpler system in which water is drawn through a 1 or 2 μm pore size filter by a pump may be equally effective in retaining suspended particulate material in rain. However, the pressurized system may be more desirable regardless of the pore size of the filter because with it there is no possibility of a partial vacuum existing inside the sampling train if the filter becomes heavily loaded.

5.2.3.4 Particulate Losses in the Rain Sampler

Some particulate material was visible on the Teflon collection surface and inside the pressurizable vessel at the conclusion of the rain sampling events. After the Tenax cartridges were removed from the sampling train, the Teflon surface was rinsed with distilled water which was then flushed through the filter. No studies were made of the losses of particulate material on the collection surface and in the

pressurizable vessel; such a study would be useful to future work.

5.2.3.5 Rain Concentrations of the Various Classes of Compounds

5.2.3.5.1 PAHs and Derivatives

The mean PAH concentrations in the dissolved and particulate phases are shown in Figure 5.8. Unlike the air samples, the concentrations of all PAHs fall within an order of magnitude and show no vapor pressure effect. PAHs beyond benzo[a]pyrene and 7,12-benz[a]anthracenedione were not detected in the dissolved samples; while naphthalene and the methylnaphthalenes were not detected in the particulate samples. The compounds 1,2-acenaphthenedione and 9,10-phenanthrenedione were not detected in any rain samples.

Mean total rain concentrations (dissolved + particulate) of PAHs are presented in Table 5.6 and are compared to concentrations obtained in rain in other urban areas. Concentrations in Portland are low compared to concentrations in the European cities for which data are available.

5.1.2.5.2 Alkanes

No alkanes were found in the dissolved samples. This is not surprising considering their low water solubilities. The normal alkanes were found in the particulate samples in fairly high concentrations.
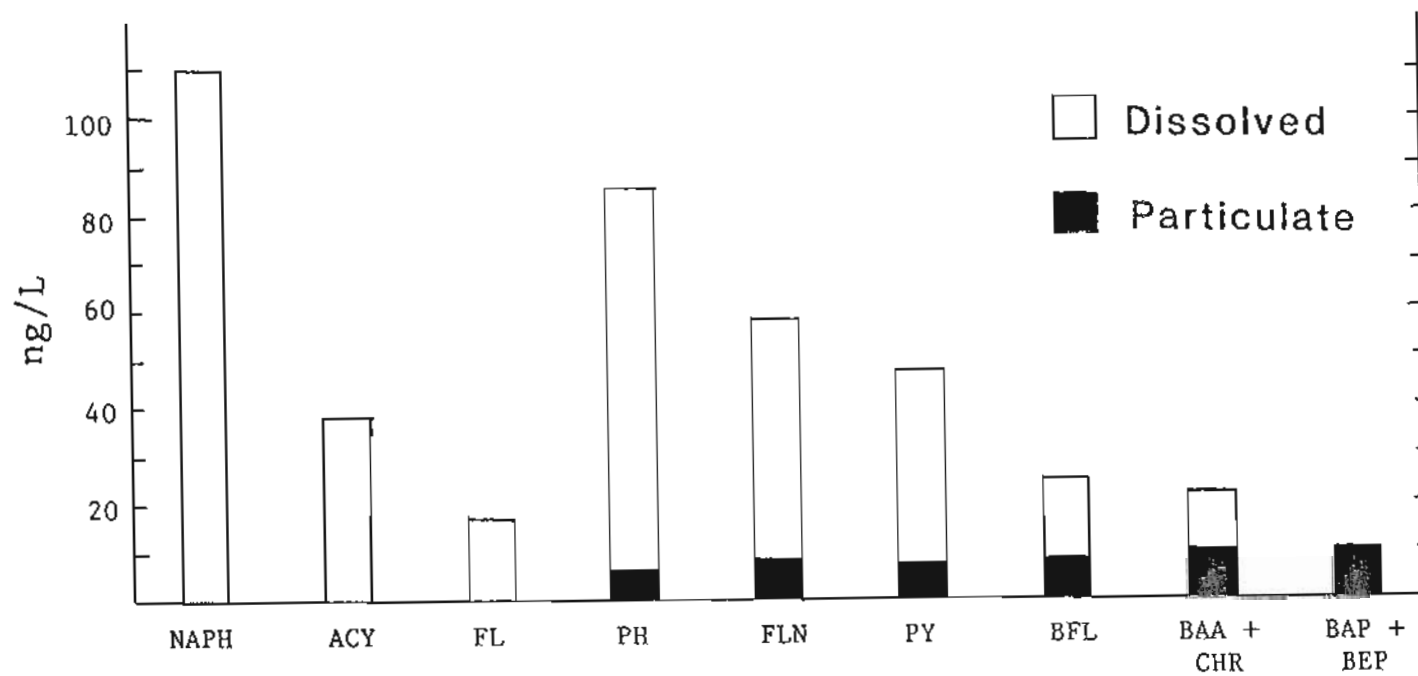
Figure 5.8   Portland mean dissolved and particulate phase PAH concentrations in rain in 1984-85.   NAPH=naphthalene, ACY=acenaphthylene, FL=fluorene, PH=phenanthrene, FLN=fluoranthene, PY=pyrene, BFL=benzofluorenes, BAA + CHR=benz[a]pyrene + benzo[e]pyrene.

Table 5.6. Concentrations of PAHs in Rain in Urban Areas.

Compound	Concentration (ng/L)			
	Portland[a]	The Hague[b]	Brussels[c]	Frankfurt[d]
Fluoranthene	59	290	100	600
Pyrene	48	390	NA	300
Benz[a]anthracene	5.5	38	NA	NA
Chrysene	15	NA	NA	200
Benzo[b+k]fluoranthene	16	120	28	NA
Benzo[a]pyrene	5.4	69	9.1	NA
Indeno[1,2,3-cd]pyrene	13	32	15	NA
Benzo[ghi]perylene	11	NA	NA	80

[a] This study. [b] van Noort and Wondergem, 1985. [c] Quaghebeur et al., 1983. [d] Georgii and Schmitt, 1983.

5.2.3.5.3 Aromatics

Unlike the vapor phase samples, the aromatics were not dominant components of the rain sample chromatograms. Due to high blank levels of toluene on the Tenax cartridges, the concentration of toluene was actually below the detection limit in several samples.

5.2.3.5.4 Phenols

The phenols are somewhat of a special case due to their degree of breakthrough on Tenax cartridges, as demonstrated by Table 5.1. The phenols were of great interest in this study since the alkylphenols were the dominant compounds overall in the rain dissolved phase sam- ples, and pentachlorophenol was the dominant chlorinated compound. The breakthrough correction, as described in Section 5.2.1, was applied to all phenol concentrations in Table A.2.2 as well as to several of the other polar and slightly polar compounds which exhibited break- through of >20%. No phenols except pentachlorophenol were detected in the rain particulate phase samples.

5.2.3.5.5 Phthalate Esters

As with the air samples, the determination of phthalate concentra- tions was hindered by the high blank levels. Phthalate concentrations in the rain, however, were high enough to be quantifiable above the blank levels in most cases.

5.2.3.5.6 Chlorinated Compounds

Concentrations of chlorinated compounds were generally low in the rain samples. Among the pesticides, only α- and γ-HCH were consistently found in the dissolved phase. No pesticides except p,p'-DDT were found in the particulate phase. The compounds 1,2-dichloropropane, dichlorobromomethane, 1,1,2-trichloroethane, dibromochloromethane, chlorobenzene, hexachloroethane, hexachlorobutadiene, hexachlorobenzene, heptachlor, aldrin, dieldrin, p,p'-DDE, p,p'-DDD, and p,p'-DDT were not detected in any of the rain dissolved samples.

5.2.4 Concentrations at the Oregon Coast, 1985

Three storm events were sampled at the coastal site in 1985. Sample volumes of 6-17 L were collected over periods of 1-3 days. The average temperature during sampling was $7^{\circ}C$. The concentrations were subjected to the significance testing and blank correction process described in Section 4.2.4. The blank-corrected dissolved and particulate rain concentrations are presented in Table A2.4. The mean concentrations are given in Tables 6.2 and 6.5. The mean concentrations of several of the compounds at the coastal site are expressed as percentages of the Portland concentrations in Figure 5.9. The dissolved concentrations of alkylphenols and aromatics were generally a factor of 4-7 lower than those measured in Portland. The PAHs and oxo-PAHs were generally a factor of 2-3 lower than in Portland, the phthalates were variable but roughly a factor of 2 lower, and the chlorophenols were
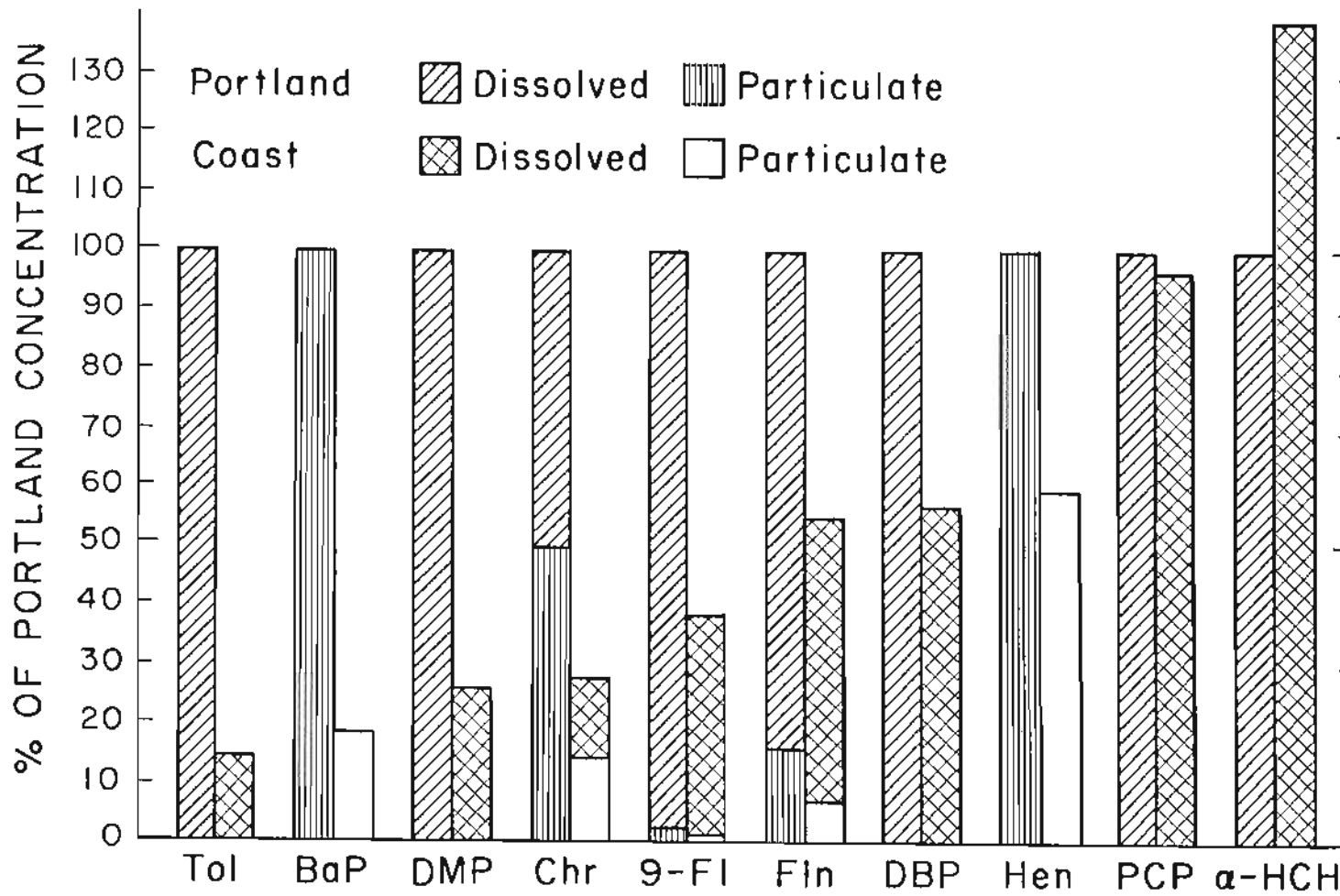
Figure 5.9. Comparison of dissolved and particulate phase concentrations of selected compounds at the Oregon coast to those from Portland.

less than a factor of 2 lower than in Portland. These differences can be interpreted in terms of the varying reactivities and atmospheric lifetimes of the various classes of compounds, as discussed in Section 4.2.5.

The particulate PAH and oxo-PAH concentrations were also generally a factor of 4 lower than those measured in Portland. The alkane concentrations, however, were very similar at the two sites. The percentages of the particulate concentrations which were associated with particles that passed through the pre-filter are given in Table 5.7, and are similar to the percentages found in Portland.

5.2.5 Reproducibility

The comparison of the concentrations found for the dissolved phase in Portland in 1985 by the three analytical methods is presented in Table 5.8. The mean coefficients of variation among methods ranged from 21% to 46% and were generally much higher than the 18% found for the inter-method comparison of the atmospheric vapor phase samples (Section 4.2.6). While the use of the breakthrough correction in the determination of the concentrations of the more polar compounds introduced additional error, the coefficients of variation were quite high even for many non-polar neutral compounds which did not require any breakthrough correction.

The results from the comparison of the results from the duplicate samplers were more encouraging. Duplicate samplers were run for two storm events. Varying amounts of leakage and filter plugging (two

Table 5.7. Percentage of Particulate Organic Compounds in Rain which passed through the 10 μm Pre-filter during Sampling at the Oregon Coast in 1985.

Compound	4/17	4/21	4/25	Avg
Dibenzofuran	17	4	11	11
Fluorene	ND[a]	20	13	17
9-Fluorenone	27	15	11	18
Phenanthrene	0	7	6	5
Anthracene	0	ND	10	5
2+3-Methylphenanthrene	15	39	8	21
1+4+9-Methylphenanthrene	16	46	10	24
9,10-Anthracenedione	0	0	0	0
Fluoranthene	15	9	11	12
Pyrene	6	22	16	15
Benzo[a]fluorene	0	0	0	0
Benzo[b]fluorene	0	0	0	0
Benz[a]anthracene	16	10	24	17
Chrysene	16	11	30	19
7-Benz[de]anthrecenone	0	0	65	22
Benzo[b+j+k]fluoranthene	9	7	28	15
Benzo[e]pyrene	5	3	19	6
Benzo[a]pyrene	6	0	19	8
Indeno[1,2,3-cd]pyrene	0	0	0	0
Benzo[ghi]perylene	0	0	0	0
Coronene	0	ND	0	0

[a]ND = not detected on the pre-filter at a statistically significant level.

Table 5.8. Coefficients of Variation (CV) for the Concentrations of Dissolved Organic Compounds in Rain Analyzed by Three Methods[a] for 1985 Portland Sampling.

Compound	CV							
	2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
Nonpolar Compounds								
Naphthalene	4	24	48	27	43	14	33	34
2-Methylnaphthalene	28	35	35	31	43	31	8	32
1-Methylnaphthalene	24	27	45	31	48	23	6	32
2,6-Dimethylnaphthalene	41	58	9	31	66	34	30	35
1,3+1,6-Dimethyl naphthalene	41	45	32	27	52	28	42	31
1,4+1,5+2,3-Dimethyl naphthalene	54	60	14	21	61	38	10	67
Acenaphthylene	17	20	14	41	53	18	67	83
1,2-Dimethylnaphthalene	29	16	16	19	21	51	49	40
Acenaphthene	37	14	60	20	47	21	18	70
Dibenzofuran	4	20	37	24	48	16	75	34
Fluorene	6	32	35	21	64	25	74	28
Dibenzothiophene	17	29	10	36	43	44	17	47
Phenanthrene	9	28	38	15	38	17	47	32
Anthracene	9	21	NA	NA	NA	14	NA	8
2+3-Methylphenanthrene	11	29	49	44	37	17	54	53
1+4+9-Methylphenanthrene	13	28	41	36	32	23	61	46
Fluoranthene	3	15	47	26	NA	24	NA	59

Table 5.8 (cont'd). Coefficients of Variation (CV) for the Concentrations of Dissolved Organic Compounds in Rain Analyzed by Three Methods[a] for 1985 Portland Sampling.

	CV							
Compound	2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
Pyrene	10	24	13	24	NA	25	NA	42
Benzo[a]fluorene	46	NA	25	NA	NA	23	50	NA
Benzo[b]fluorene	23	NA	30	NA	NA	42	29	NA
Polar Compounds								
Salicylaldehyde*	88	34	4	NA	62	11	NA	49
2-Methylphenol*	NA	NA	NA	20	NA	21	NA	89
2+3-Tolualdehyde*	38	27	37	36	40	34	71	32
4-Tolualdehyde*	17	19	36	3	29	37	89	28
3+4-Methylphenol*	28	14	NA	47	NA	13	NA	NA
2-Methoxyphenol*	51	NA	NA	54	50	NA	3	59
2,6-Dimethylphenol*	20	16	31	16	50	66	73	31
2-Nitrophenol*	44	24	37	12	8	5	50	43
2-Ethylphenol*	17	30	NA	NA	NA	31	NA	6
2,4+2,5-Dimethylphenol*	33	31	11	29	18	6	26	47
2,4-Dichlorophenol	NA	96	43	24	NA	NA	6	17
4-Ethyl+3,5-dimethyl phenol*	10	37	8	3	10	36	73	19
2,4-Dimethylbenzaldehyde	24	20						

Table 5.8 (cont'd). Coefficients of Variation (CV) for the Concentrations of Dissolved Organic Compounds in Rain Analyzed by Three Methods[a] for 1985 Portland Sampling.

	CV							
Compound	2/14	3/3	3/21 1[b]	3/21 2	3/26 1	3/26 2	4/17	4/21
4-Methyl-2-methoxyphenol[*]	63	15	36	33	20	8	NA	46
3,4-Dimethylphenol[*]	NA	73	NA	NA	65	40	NA	NA
4-Methyl-2-nitrophenol[*]	23	38	35	14	33	33	26	59
1-Indanone[*]	26	30	42	24	28	8	7	33
Coumarin[*]	54	15	44	7	17	16	35	24
1+2-Naphthol[*]	71	64	NA	NA	22	17	64	92
Diethylphthalate[*]	26	NA	60	NA	NA	NA	78	11
9-Fluorenone[*]	7	22	33	26	50	13	31	40
Xanthone	20	27	57	46	6	30	37	52
Dibutylphthalate	13	NA	NA	NA	NA	NA	NA	NA
9,10-Anthracenedione	20	17	NA	NA	NA	11	14	65
Butylbenzylphthalate	8	NA	42	NA	NA	NA	43	NA
Average Nonpolar	21	29	31	28	46	26	38	43
Average Polar	32	32	35	25	32	23	39	42

[*]Indicates that the breakthrough correction was applied to the concentration. [a] ASE/Tenax, ATD/Tenax and ASERTD/CBP. [b] Sampler number. [c]NA = not available, because concentration could be determined by only one method.

persistent problems with the rain sampler) led to differences in the sample volumes collected by the two samplers. If the concentrations in the rain were changing substantially during the course of the rain events, the samplers therefore might not have responded to those changes equally. The dissolved concentrations obtained with the two samplers are given in Table 5.9, along with the coefficients of variation between samplers. The dissolved concentrations were averaged over the three analytical methods as described in Section 5.2.4. Coefficients of variation averaged 22% and 23% for the two sets of samples. The good agreement between the samplers suggests that the sampling difficulties did not bias the concentration determinations. This result indicates that the major uncertainty in the concentration determinations was due to the analytical procedures rather than the sampling procedures. The same result was found for the air samples in Section 4.2.6.

The particulate rain concentrations obtained with the duplicate samplers and coefficients of variation between samplers for the two events are presented in Table 5.10. The mean coefficients of variation were 18% and 23% for the two events. The good agreement between the two samplers suggests that there were no large sampling losses for particles in either of the samplers, despite the fact that some particulate material often remained on the Teflon collection surfaces and in the glass collection vessels after rain events, as discussed in Section 5.2.3.4.

Table 5.9. Comparison of Dissolved Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

	3/21			3/26		
	Conc (ng/L)		CV	Conc (ng/L)		CV
Compound	1	2		1	2	
Toluene	9.0	NA[a]	—	83	60	23
Ethylbenzene		NA	—	41	21	46
2-Heptanone*	24	NA	—	50	62	14
Heptanal*	37	NA	—	70	77	6
Benzaldehyde	540	500	5	1600	1900	10
Methylfurfural*	1300	1200	3	3800	6300	35
Benzonitrile*	32	70	53	71	80	8
Salicylaldehyde*	170	NA	—	610	910	28
2-Methylphenol*	1900	830	54	800	3500	88
2+3-Tolualdehyde*	180	240	18	670	880	19
4-Tolualdehyde*	120	150	15	450	610	20
3+4-Methylphenol*	NA	960	—	2200	6100	67
2-Methoxyphenol*	770	1200	33	2600	3300	17
2,6-Dimethylphenol*	60	110	43	120	170	24
2-Nitrophenol*	43	42	2	66	58	9
2-Ethylphenol*	51	75	27	81	200	61
2,4+2,5-Dimethylphenol*	340	460	20	620	1030	35
2,4-Dichlorophenol	7.5	5.4	23	3.7	2.7	21

Table 5.9 (cont'd). Comparison of Dissolved Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

	3/21			3/26		
	Conc (ng/L)		CV	Conc (ng/L)		CV
Compound	1	2		1	2	
Naphthalene	46	68	28	150	130	9
4-Ethyl+3,5-dimethyl phenol[*]	470	460	2	650	1200	42
2,4-Dimethylbenzaldehyde	20	29	24	93	74	16
4-Methyl-2-methoxyphenol[*]	830	920	8	1500	2200	25
3,4-Dimethylphenol[*]	80	130	36	190	280	26
4-Methyl-2-nitrophenol[*]	91	76	13	77	92	13
1-Indanone[*]	160	150	4	230	300	16
2-Methylnaphthalene	25	36	25	77	71	6
1-Methylnaphthalene	16	24	28	49	46	6
2,6-Dimethylnaphthalene	2.8	4.5	33	8.2	6.9	12
1,3+1,6-Dimethylnaphthalene	6.7	9.1	21	19	17	9
1,4+1,5+2,3-Dimethyl naphthalene	2.5	3.7	28	6.2	6.6	5
Coumarin[*]	60	62	2	120	110	7
Acenaphthylene	13	21	37	65	52	16
1,2-Dimethylnaphthalene	1.1	2.1	44	3.6	3.2	6
Acenaphthene	2.5	2.8	7	6.5	7.6	11
Dibenzofuran	9.9	13	18	24	21	9

Table 5.9 (cont'd). Comparison of Dissolved Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

| Compound | 3/21 | | | 3/26 | | |
| | Conc (ng/L) | | CV | Conc (ng/L) | | CV |
	1	2		1	2	
1+2-Naphthol[*]	NA	31	—	230	190	14
2,3,4,6-Tetrachlorophenol	7.0	7.2	3	9.7	7.3	20
Fluorene	9.5	13	19	23	26	8
Diethylphthalate	19	19	0	23	34	27
α-HCH	5.3	2.1	60	6.6	6.3	3
9-Fluorenone	47	53	9	130	110	7
Dibenzothiophene	3.3	2.9	8	5.3	5.1	2
Pentachlorophenol	62	32	45	36	17	51
Phenanthrene	38	47	15	87	89	1
Anthracene	2.5	2.0	16	11	NA	—
Xanthone	13	16	16	36	29	14
2+3-Methylphenanthrene	9.6	11.3	12	27	25	6
1+4+9-Methylphenanthrene	8.5	9.7	9	26	24	6
Dibutylphthalate	27	NA	—	40	15	65
9,10-Anthracenedione	51	41	15	95	72	20
Fluoranthene	21	27	18	82	59	24
Pyrene	13	22	38	69	45	29
Benzo[a]fluorene	3.2	4.0	16	16	9.6	37

Table 5.9 (cont'd). Comparison of Dissolved Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

Compound	3/21 Conc (ng/L) 1	3/21 Conc (ng/L) 2	CV	3/26 Conc (ng/L) 1	3/26 Conc (ng/L) 2	CV
Benzo[b]fluorene	3.1	4.7	29	17	9.5	40
Butylbenzylphthalate	31	50	33	120	NA	—
Benz[a]anthracene	1.2	1.5	20	5.4	3.6	28
Chrysene	3.5	4.6	20	10.9	9.1	13
7-Benz[de]anthracenone	4.0	8.5	52	37	11	78
Average			22			23

*Indicates that breakthrough correction was applied to estimate the concentration. ^{a}NA = not available.

Table 5.10. Comparison of Particulate Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

Compound	3/21 Conc (ng/L) 1	2	CV^a	3/26 Conc (ng/L) 1	2	CV
Acenaphthylene	0.69	0.53	19	0.25	0.35	24
Dibenzofuran	0.68	0.54	16	0.35	0.51	26
Fluorene	0.18	0.25	22	0.14	0.22	31
9-Fluorenone	1.12	0.96	11	0.52	0.70	21
Dibenzothiophene	0.14	0.24	37	0.07	0.08	9
Phenanthrene	5.8	4.8	13	2.2	3.3	28
Anthracene	0.62	ND^b	—	0.39	0.21	42
3+2-Methylphenanthrene	3.1	5.6	41	1.4	2.3	34
1+4+9-Methylphenanthrene	2.5	3.8	29	1.1	1.8	34
9,10-Anthracenedione	1.8	3.7	49	1.1	2.2	47
Eicosane	6.5	8.5	19	ND	ND	—
Fluoranthene	9.7	10.2	4	5.5	8.1	27
Heneicosane	38	30	17	ND	ND	—
Pyrene	8.6	7.8	7	5.2	7.2	23
Docosane	29	21	23	ND	ND	—
Benzo[a+b]fluorene	4.1	6.3	30	4.3	5.7	20
Butylbenzylphthalate	ND	ND	—	99	123	15
Benz[a]anthracene	2.4	2.0	13	3.2	2.9	7

Table 5.10 (cont'd). Comparison of Particulate Rain Concentrations of Organic Compounds Measured with Duplicate Samplers in Portland, Oregon in 1985.

	3/21			3/26		
	Conc (ng/L)			Conc (ng/L)		
Compound	1	2	CV	1	2	CV
Chrysene	6.7	6.6	1	5.0	8.1	33
Pentacosane	150	190	17	32	48	28
7-Benz[de]anthracenone	2.0	2.7	21	2.5	3.7	27
7,12-Benz[a]anthracenedione	ND	ND	—	0.59	0.42	24
Dioctylphthalate	22	15	27	7.4	7.9	5
Benzo[b+j+k]fluoranthene	9.3	7.8	12	9.5	9.9	3
Benzo[e]pyrene	3.5	2.9	13	3.4	4.1	13
Benzo[a]pyrene	3.3	3.6	6	3.5	2.2	32
Octacosane	64	66	2	ND	ND	—
Indeno[1,2,3-cd]pyrene	4.2	3.7	9	4.6	4.2	6
Benzo[ghi]perylene	6.5	5.9	7	6.5	5.9	7
Coronene	3.4	2.8	14	2.6	1.7	30
Average CV			18			23

[a]Coefficient of variation between samplers. [b]Not detected at a statistically significant level.

CHAPTER 6   SCAVENGING RATIOS FOR ORGANIC COMPOUNDS

In this chapter, the concentration data presented in Chapters 4 and 5 are combined to yield gas, particle, and overall scavenging ratios. Gas scavenging ratios are examined in the context of equilibrium scavenging. Scavenging ratios which have been weighted by precipitation amount are discussed in Chapter 8 in conjunction with the calculation of wet depositional fluxes.

6.1 Gas Scavenging Ratios

Gas scavenging ratios (W_g) were obtained from the measured atmospheric vapor phase concentrations in Tables A1.1 and A1.3 and the rain dissolved phase concentrations in Tables A2.2 and A2.4 by use of the following equation:

$$W_g = (1000 \text{ L/m}^3) \ \frac{[\text{rain, dissolved}](\text{ng/L})}{[\text{air,vapor}](\text{ng/m}^3)} \qquad 6.1$$

As discussed in Section 3.1.1, for equilibrium gas scavenging,

$$W_g = \alpha = RT/H \cong RTS/P \qquad 6.2$$

where S is the solubility of the pure compound in some reference state, and P is its vapor pressure in the same state. The following sections

will examine the comparability of the W_g values obtained in this study and α values obtained from the literature.

6.1.1 Gas Scavenging Ratios in Portland

The average measured W_g values ($\overline{W_g}$), along with the corresponding α values from Table 3.1 are given for a number of compounds in Table 6.1. Measured values of W_g were averaged over all storm events despite the fact that the average temperature varied from 3 to $10^\circ C$ over the 13 events. $\overline{W_g}$ values ranged from ~3 for tetrachloroethene to ~10^5 for 7-benz[de]anthracenone. The measured $\overline{W_g}$ values for several of the phenols may be underestimates, due to breakthrough of these compounds as discussed in Section 5.2.2.

Several trends are apparent in Table 6.1. For example, volatile chlorinated compounds such as tri- and tetrachloroethene have low gas scavenging ratios. For the PAHs, W_g increases with increasing molecular weight. Addition of alkyl substituents has little effect on W_g values, while addition of oxo substituents greatly increases W_g values, as shown in Figure 6.1.

Nearly all of the measured $\overline{W_g}$ values in Table 6.1 are a factor of 3-6 higher than the corresponding α values calculated for $25^\circ C$. Fortunately, α values could be calculated for several of the PAHs at the actual average ambient temperatures during sampling from temperature-dependent solubility (May et al., 1978) and vapor pressure (Sonnefeld et al., 1983) data. The comparison between the measured W_g values and

Table 6.1. Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

| Compound | Mean Concentrations | | Correlation | $\overline{W_g}$ (meas) | a(lit) |
	Rain (ng/L ± 1s)	Air (ng/m^3 ± 1s)	(r)	3-10°C[a]	25°C[b]
Tetrachloroethene	4.7 ± 4.2 (10)	970 ± 610 (12)	0.96	3.2 ± 1.2 (9)	1.6
Trichloroethene	5.6 ± 5.6 (7)	1500 ± 1300 (7)	0.90	3.7 ± 1.3 (7)	2.6
Mesitylene	5.1 ± 2.5 (7)	430 ± 220 (7)	0.91	12 ± 3 (7)	4.5
Toluene	79 ± 71 (10)	3300 ± 1900 (12)	0.96	19 ± 8 (10)	3.7
Durene	2.9 ± 1.3 (7)	120 ± 70 (7)	0.85	26 ± 9 (7)	1.0
1,2,4-Trimethylbenzene	30 ± 14 (7)	1300 ± 800 (7)	0.57	27 ± 9 (7)	4.2
Ethylbenzene	31 ± 20 (12)	1300 ± 600 (12)	0.82	26 ± 18 (11)	3.0
m+p-Xylene	110 ± 73 (7)	3400 ± 2000 (7)	0.83	33 ± 17 (7)	3.5
o-Xylene	45 ± 31 (7)	1300 ± 690 (7)	0.89	35 ± 15 (7)	4.8
1,4-Dichlorobenzene	4.8 ± 1.2 (6)	120 ± 32 (7)	0.46	39 ± 10 (6)	8.2
1,2-Dichlorobenzene	0.26 ± 0.20 (5)	5.8 ± 2.3 (7)	0.95	46 ± 13 (5)	11
1,2,4-Trichlorobenzene	0.25 ± 0.17 (3)	3.8 ± 0.4 (7)	--[c]	66 ± 51 (3)	11
2,6-Dimethylnaphthalene	5.6 ± 3.6	29 ± 14	0.92	190 ± 40	160

Table 6.1 (cont'd). Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

Compound	Mean Concentrations Rain (ng/L ± 1s)	Air (ng/m^3 ± 1s)	Correlation (r)	$\overline{W_g}$ (meas) 3-10°C[a]	α(lit) 25°C[b]
1,6+1,3-Dimethyl naphthalene	12 ± 8	52 ± 23	0.91	220 ± 60	
Naphthalene	110 ± 60	400 ± 190 (12)	0.64	240 ± 60 (12)	59
2-Methylnaphthalene	54 ± 33	220 ± 100	0.80	240 ± 60 (12)	48
1-Methylnaphthalene	34 ± 20	110 ± 50	0.85	270 ± 100 (12)	56
1,4+1,5+2,3-Dimethyl naphthalene	4.9 ± 3.4	16 ± 8	0.95	300 ± 60	170
Biphenyl	6.9 ± 2.6 (7)	21 ± 7 (7)	0.00	350 ± 160 (7)	
1,2-Dimethylnaphthalene	2.2 ± 1.3	6.1 ± 4.0	0.96	370 ± 60	
Benzonitrile*	74 ± 52 (5)	110 ± 26 (5)	---	440 ± 680 (4)	
2-Heptanone*	49 ± 37 (5)	61 ± 60 (4)	---	900 ± 690 (3)	500
Dibenzofuran	19 ± 10	19 ± 9	0.95	950 ± 180	410
2,4-Dimethylbenzaldehyde	66 ± 42 (6)	43 ± 16 (5)	0.91	1200 ± 300 (5)	
Acenaphthene	6.0 ± 2.9	5.5 ± 3.2	0.77	1200 ± 500	250

Table 6.1 (cont'd). Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

| Compound | Mean Concentrations | | Correlation | $\overline{W_g}$ (meas) | α(lit) |
	Rain (ng/L $\pm$ 1s)	Air (ng/m^3 $\pm$ 1s)	(r)	3-10°C[a]	25°C[b]
Acenaphthylene	39 $\pm$ 25	32 $\pm$ 24 (9)	0.90	1400 $\pm$ 600 (9)	72
Fluorene	17 $\pm$ 9	11 $\pm$ 7	0.91	1600 $\pm$ 400	350
Salicylaldehyde*	670 $\pm$ 520 (6)	320 $\pm$ 140 (5)	0.03	1700 $\pm$ 1200 (5)	
Anthracene	6.4 $\pm$ 3.6	3.4 $\pm$ 2.2	0.81	2000 $\pm$ 700	680
2-Nitrophenol*	78 $\pm$ 58	34 $\pm$ 19 (12)	0.44	2200 $\pm$ 1000 (12)	1600
Dibenzothiophene	4.4 $\pm$ 2.3	1.8 $\pm$ 1.0	0.85	2600 $\pm$ 800	
3+2-Methylphenanthrene	18 $\pm$ 7	6.9 $\pm$ 3.8	0.78	2700 $\pm$ 800	
1+4+9-Methylphenanthrene	16 $\pm$ 7	5.5 $\pm$ 2.8	0.79	3100 $\pm$ 900	400
Phenanthrene	80 $\pm$ 38	26 $\pm$ 10	0.92	3100 $\pm$ 500	1100
Methylisobutyl ketone*	390 $\pm$ 210 (2)	42 $\pm$ 28 (4)	--	3500 (1)	510
Benzo[a]fluorene	8.1 $\pm$ 4.6 (6)	1.6 $\pm$ 0.8 (6)	0.49	5100 $\pm$ 2400 (6)	14000
Benzo[b]fluorene	8.1 $\pm$ 5.3 (6)	1.5 $\pm$ 0.7 (6)	0.71	5400 $\pm$ 2800 (6)	
Benzo[e]pyrene	0.37 $\pm$ 0.20 (2)	0.03 $\pm$ 0.01 (5)	--	5800 (1)	80000

Table 6.1 (cont'd). Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

| Compound | Mean Concentrations | | Correlation | $\overline{W_g}$ (meas) | α(lit) |
	Rain (ng/L ± 1s)	Air (ng/m^3 ± 1s)	(r)	3-10°C[a]	25°C[b]
Pyrene	40 ± 17	6.7 ± 2.7	0.70	6100 ± 2000	2900
Fluoranthene	50 ± 21	7.9 ± 3.1	0.75	6300 ± 1800	2400
4-Methyl-2-nitrophenol*	140 ± 71 (6)	17 ± 8 (5)	0.00	6400 ± 3300 (5)	
2,4-Dichlorophenol	8.8 ± 5.9	1.2 ± 0.7 (10)	0.00	9400 ± 9600 (10)	5700
Benzo[b+j+k]fluoranthene	2.3 ± 1.5 (5)	0.11 ± 0.12 (6)	--	10000 ± 5000 (3)	
Benz[a]anthracene	3.2 ± 1.4 (12)	0.29 ± 0.08	0.39	11000 ± 5000 (12)	4300
Benzothiazole	100 ± 57 (7)	9.8 ± 2.5 (5)	0.38	12000 ± 7000 (5)	
2,6-Dimethylphenol*	160 ± 120	14 ± 7	0.48	12000 ± 6000	5000
Butylbenzylphthalate	69 ± 34	5.0 ± 0.8 (3)	--	14000 ± 11000 (3)	20000
9-Fluorenone*	110 ± 70	7.0 ± 2.5	0.81	16000 ± 5000	
2-Ethylphenol*	190 ± 160 (6)	12 ± 7 (6)	0.59	16000 ± 8000 (6)	
Chrysene	8.2 ± 3.5 (12)	0.44 ± 0.07	0.41	19000 ± 8000 (12)	16000
2-Methylphenol*	2600 ± 3400 (7)	82 ± 39	0.86	19000 ± 14000 (7)	15000

Table 6.1 (cont'd). Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

| Compound | Mean Concentrations | | Correlation | W_g (meas) | α(lit) |
	Rain (ng/L ± 1s)	Air (ng/m^3 ± 1s)	(r)	$3\text{-}10^{\circ}C^a$	$25^{\circ}C^b$
2,6-Dichlorophenol	1.4 ± 0.7 (6)	0.14 ± 0.09 (6)	0.75	20000 ± 24000 (5)	
Dioctylphthalate	4.0 ± 3.7 (7)	0.39 ± 0.39 (5)	—	20000 ± 20000 (4)	
1-Indanone*	460 ± 300 (6)	22 ± 8 (6)	0.66	21000 ± 9000 (6)	
Xanthone	34 ± 18 (6)	1.5 ± 0.7 (6)	0.92	22000 ± 7000 (6)	
Coumarin*	200 ± 150 (6)	9.6 ± 3.2 (6)	0.01	22000 ± 14000 (6)	
3+4-Methylphenol*	5400 ± 8400 (7)	140 ± 64	0.73	22000 ± 17000 (7)	27000
Diethylphthalate*	95 ± 76 (11)	4.5 ± 2.9 (9)	0.15	24000 ± 19000 (7)	31000
2,4,5+2,4,6-Trichloro phenol	2.3 ± 1.0 (5)	0.15 ± 0.12 (6)	0.00	25000 ± 24000 (5)	5100
3,4-Dimethylphenol*	220 ± 220	15 ± 15 (8)	0.87	25000 ± 12000 (8)	29000
2-Methoxyphenol*	3800 ± 5400 (12)	150 ± 57 (12)	0.39	27000 ± 37000 (8)	18000
2,4+2,5-Dimethylphenol*	1100 ± 960	46 ± 24	0.71	27000 ± 16000	9600
1+2-Naphthol*	180 ± 140 (6)	6.8 ± 5.6 (6)	0.90	28000 ± 15000 (6)	

Table 6.1 (cont'd). Mean Dissolved Rain Concentrations, Mean Vapor Phase Concentrations, Correlations between Rain and Air Data, and Gas Scavenging Ratios in Portland, Oregon in 1984-85.

| Compound | Mean Concentrations | | Correlation | $\overline{W_g}$ (meas) | α (lit) |
	Rain (ng/L $\pm$ 1s)	Air (ng/m^3 $\pm$ 1s)	(r)	$3-10^{\circ}C^a$	$25^{\circ}C^b$
4-Ethyl+3,5-dimethyl phenol[*]	1100 $\pm$ 1400	39 $\pm$ 26	0.96	29000 $\pm$ 19000	21000
4-Methyl-2-methoxyphenol[*]	2400 $\pm$ 2300 (6)	91 $\pm$ 38 (6)	-0.13	30000 $\pm$ 29000 (6)	
Methylfurfurals[*]	3500 $\pm$ 2900 (4)	83 $\pm$ 52 (4)	--	31000 $\pm$ 16000 (2)	
9,10-Anthracenedione	82 $\pm$ 27	2.5 $\pm$ 1.0	0.61	36000 $\pm$ 14000	
Dibutylphthalate	88 $\pm$ 80	4.8 $\pm$ 4.9 (5)	0.87	38000 $\pm$ 43000 (5)	74000
α-HCH[*]	10.5 $\pm$ 3.5	0.31 $\pm$ 0.09 (9)	0.40	42000 $\pm$ 18000 (9)	4200
7-Benz[de]anthracenone	17 $\pm$ 7	0.07 $\pm$ 0.03 (3)	--	180000 $\pm$ 80000 (2)	

[*]Indicates that breakthrough correction was applied to the rain concentration. [a]Temperature range during sampling. [b]25°C α literature values are from Table 3.1. [c]Correlation not computed for n < 5.

fluorene
$W_g = 1600$

9-fluorenone
$W_g = 16,000$

anthracene
$W_g = 2000$

9,10-anthracenedione
$W_g = 36,000$

toluene
$W_g = 19$

2-methylphenol
$W_g > 19,000$
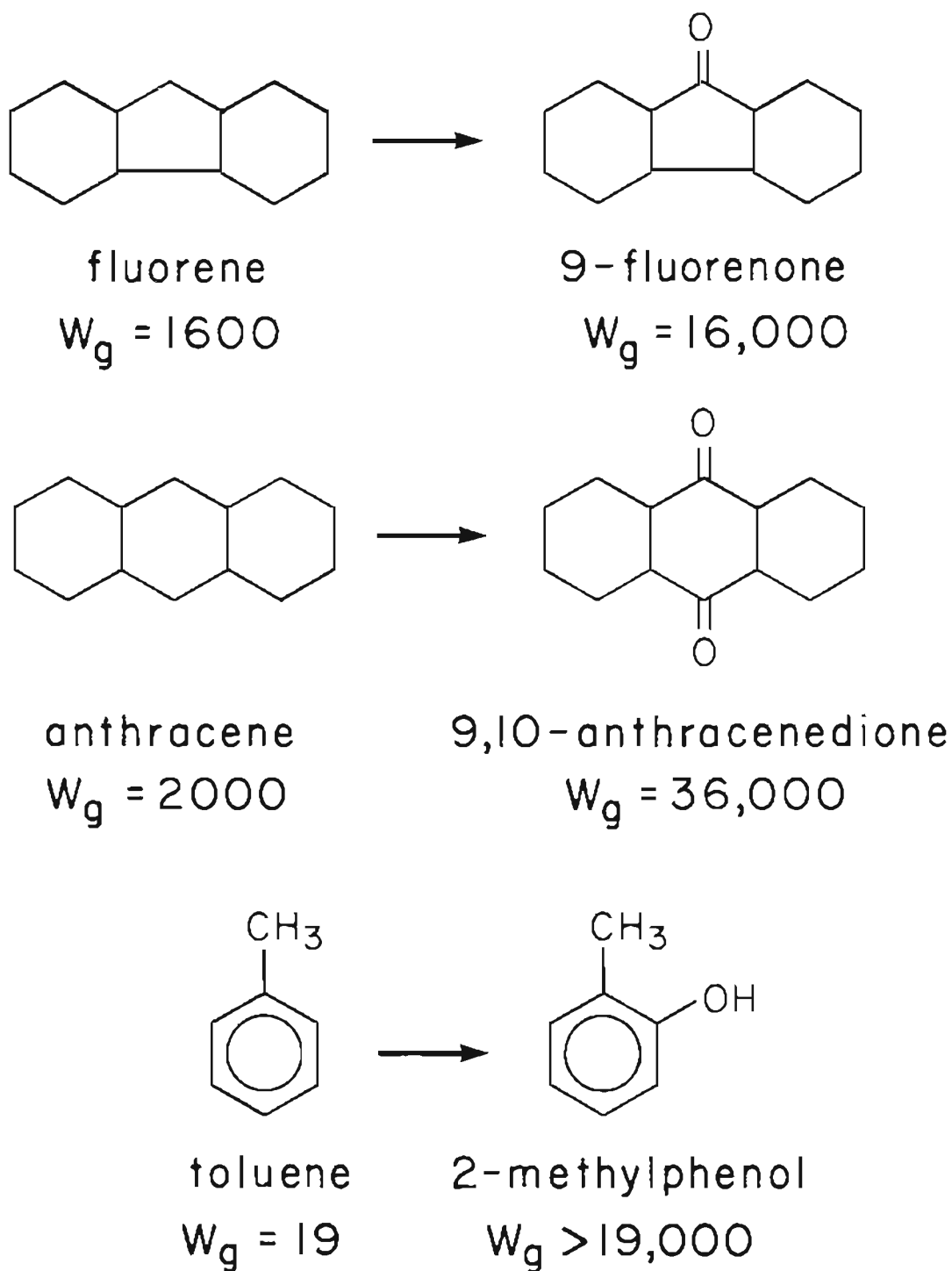
Figure 6.1. The effect of oxygen addition on the gas scavenging of aromatic compounds.

these calculated α values is shown in Figure 6.2. The agreement is excellent, supporting the suggestion of Pankow et al. (1984) that much of the discrepancy between typical urban atmospheric concentrations and those predicted from $25^{\circ}C$ H data and measured rain dissolved concentrations in that earlier study was due to the temperature dependence of the H values. The ratios of the measured to expected values in Figure 6.2 give an overall average of 0.99 with a standard deviation of 0.39. Considering the difficulties inherent in the determination of S and P for these relatively insoluble, nonvolatile compounds, as well as the uncertainties in the determinations of their ambient concentrations, this is remarkable agreement. The degree of agreement indicates that equilibrium gas scavenging occurred for PAHs, and therefore suggests that surface films did not exist on the raindrops. This conclusion is in agreement with the findings of Gill et al., (1983) who state that the quantities of surface-active organic material in rain are not sufficient for monolayer surface coverage. The factor of 3-6 difference in W_g and α values for the other compounds is consistent with expected variations due to temperature. Thus, equilibrium is likely to have existed for the other compounds as well. The W_g values in Table 6.1 may therefore be used to obtain estimates of the H values for these compounds at temperatures in the range of $3-10^{\circ}C$.

Solubility and vapor pressure data at low ambient temperatures are also available for some alkylphenols. Figure 6.3 shows the comparison of measured W_g values to α values at $8^{\circ}C$ for four alkylphenols. The agreement is good for the dimethylphenol, but not for the other com-
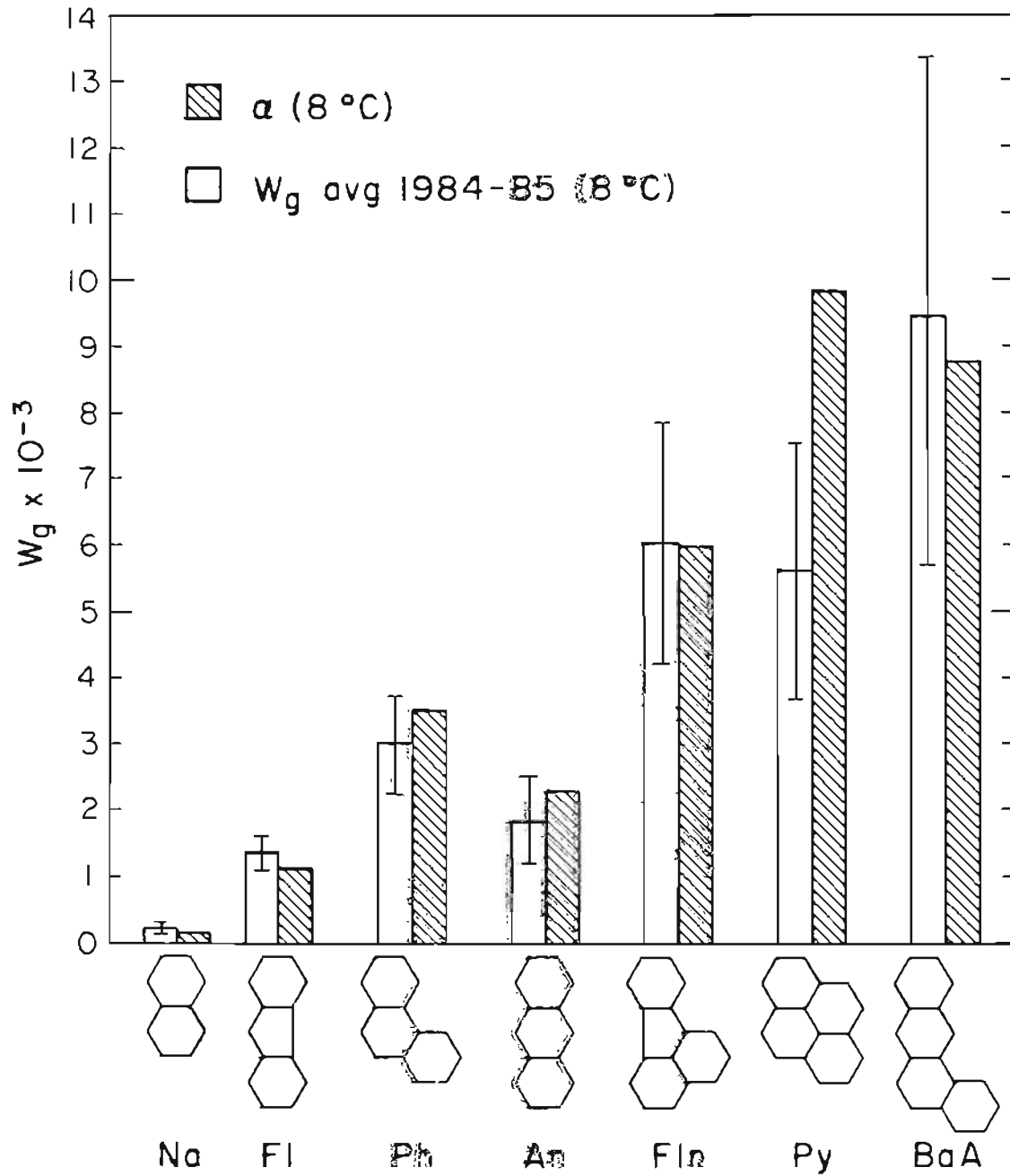
Figure 6.2. Comparison of PAH Wg values to the equilibrium values
evaluated at the same temperature. Na=naphthalene,
Fl=fluorene, Ph=phenanthrene, An=anthracene, Fln=fluor-
anthane, Py=pyrene, BaA=benz[a]anthracene.
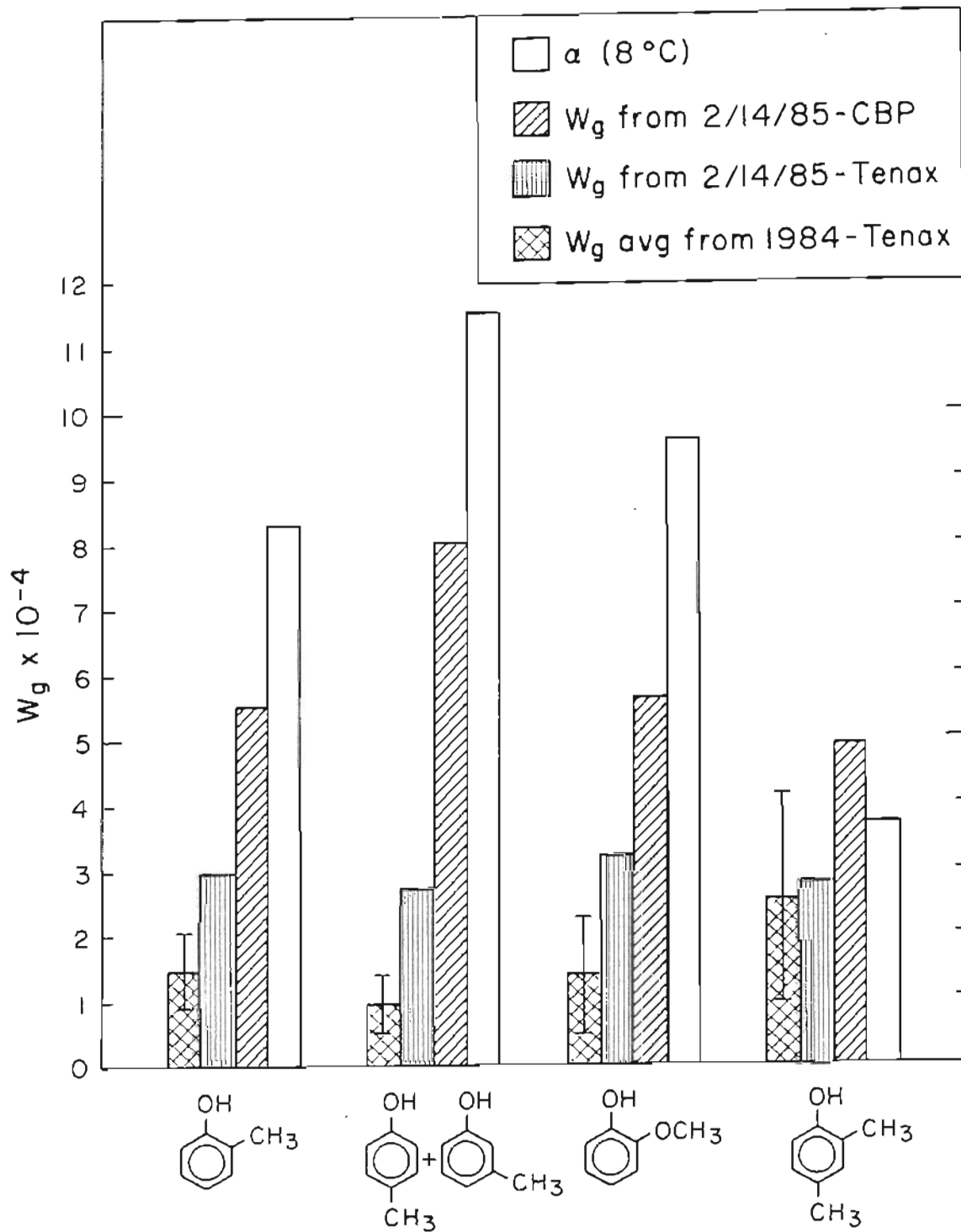
Figure 6.3. Comparison of Wg values for phenols to the equilibrium
values evaluated at the same temperature.

pounds. While the possibility of error in the α values exists, it is more likely that the discrepancy is due to one of two factors: 1) the sampling problems experienced for the alkylphenols and discussed in Section 5.2.4.4; or 2) the lack of attainment of rain/air equilibrium for compounds with very high α values. The latter possibility will be discussed in depth in Chapter 7. Figure 6.3 shows that higher rain dissolved concentrations, and hence higher W_g values, were measured on the CBP cartridges than on the Tenax cartridges. The higher W_g values found with the 1985 Tenax cartridges as compared to the 1984 cartridges can be attributed to the lower sample flow rates used in the 1985 sampling.

In Figures 6.4 - 6.10, the rain dissolved concentrations are plotted against atmospheric vapor phase concentrations for several compounds. Ideally, when these concentrations are plotted at constant T the points should fall on a line which passes through the origin and has slope equal to $\alpha(T)$. Although no temperature corrections were made in Figures 6.4 - 6.10, most of the compounds plotted in this manner show approximate linear behavior, with some scatter. In Figures 6.11 and 6.12, the temperature-corrected concentrations are plotted for phenanthrene and fluoranthene. The slopes in these plots represent the equivalent W_g values at $20^{\circ}C$. The correlations between the rain and air concentrations are 0.86 and 0.87 for the phenanthrene and fluoranthene plots, respectively. These are not better than the correlations for the plots which were not temperature corrected.
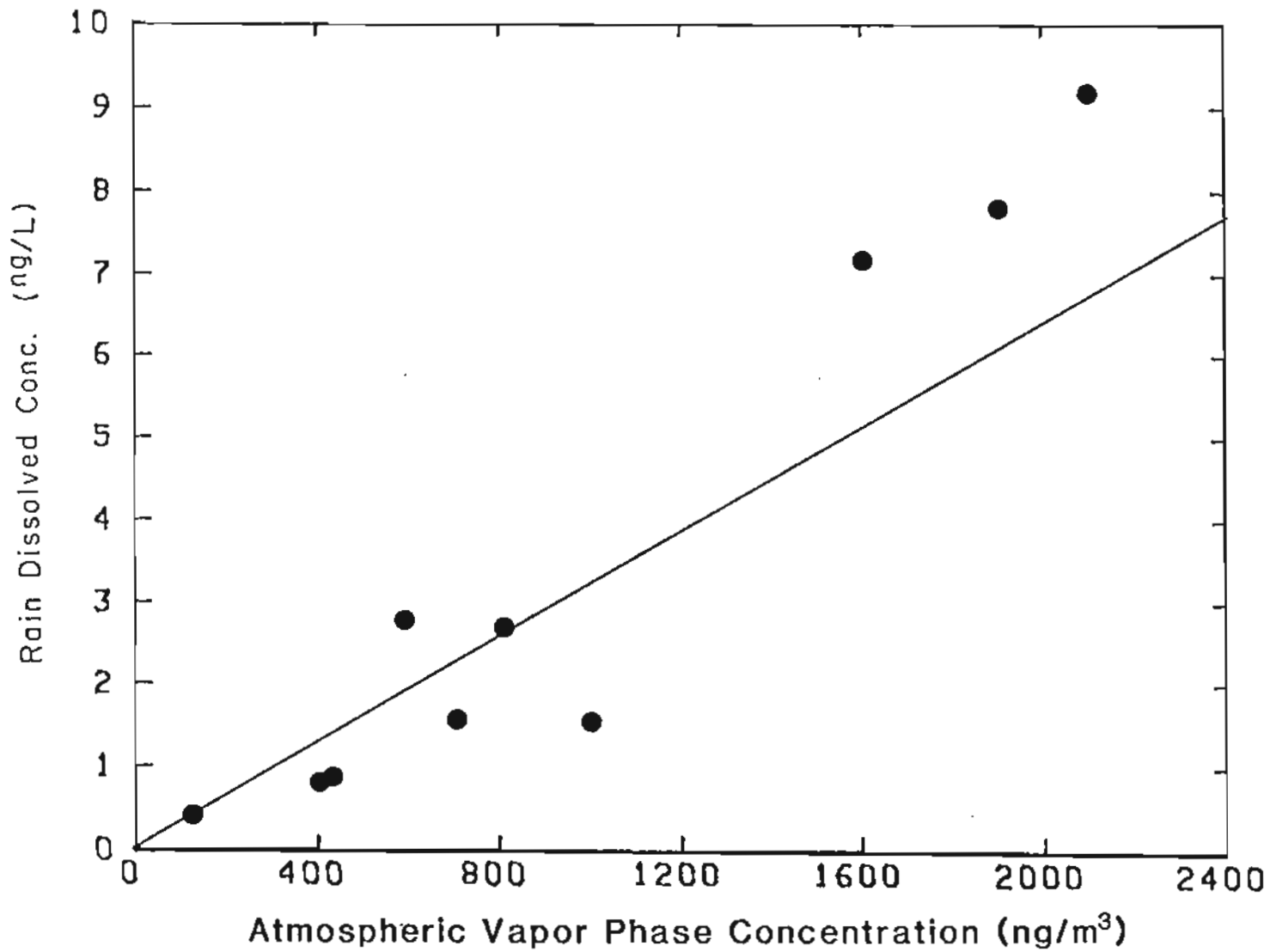
Figure 6.4. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for tetrachloroethene.
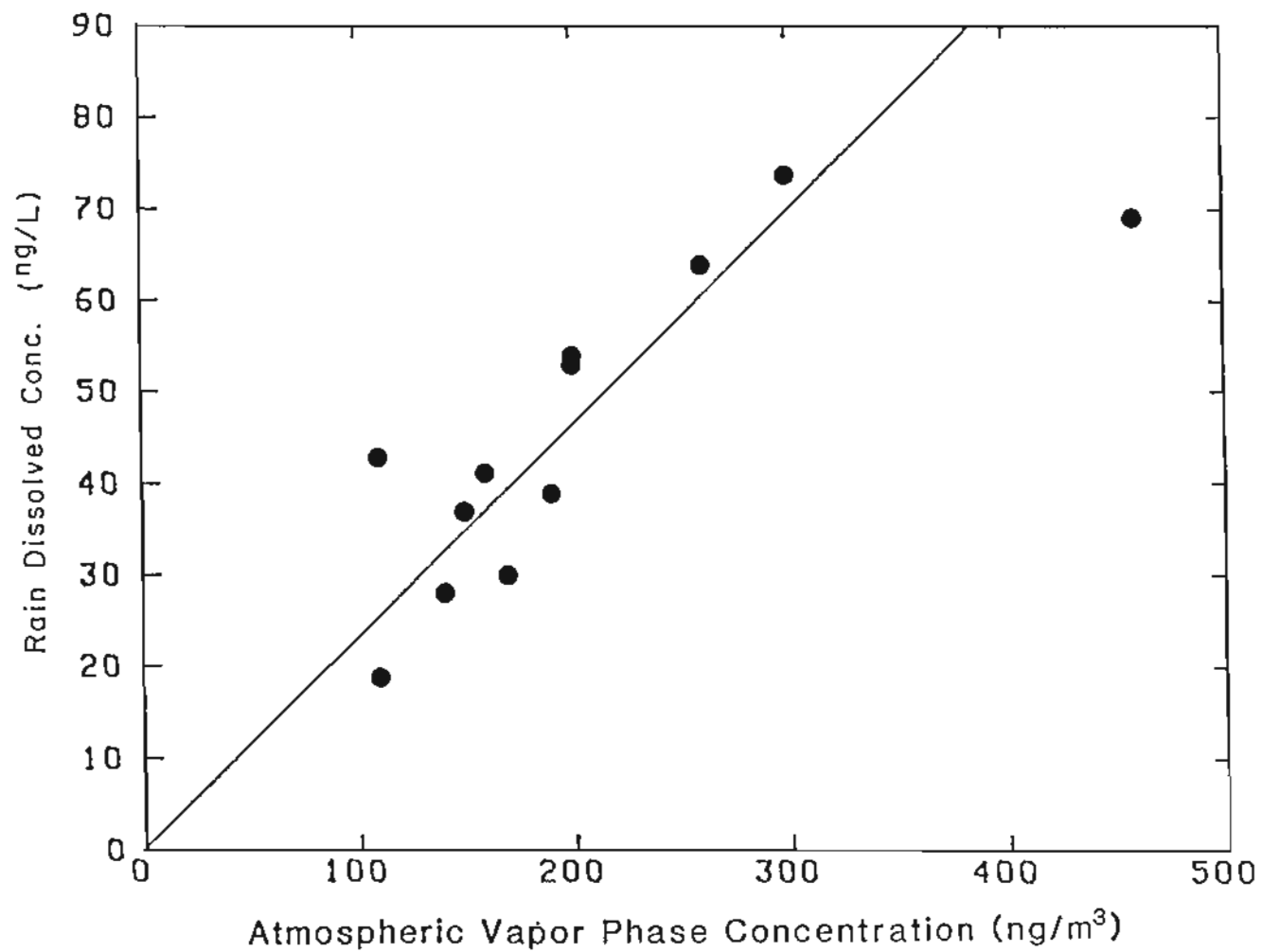
Figure 6.5. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for 2-methylnaphthalene.
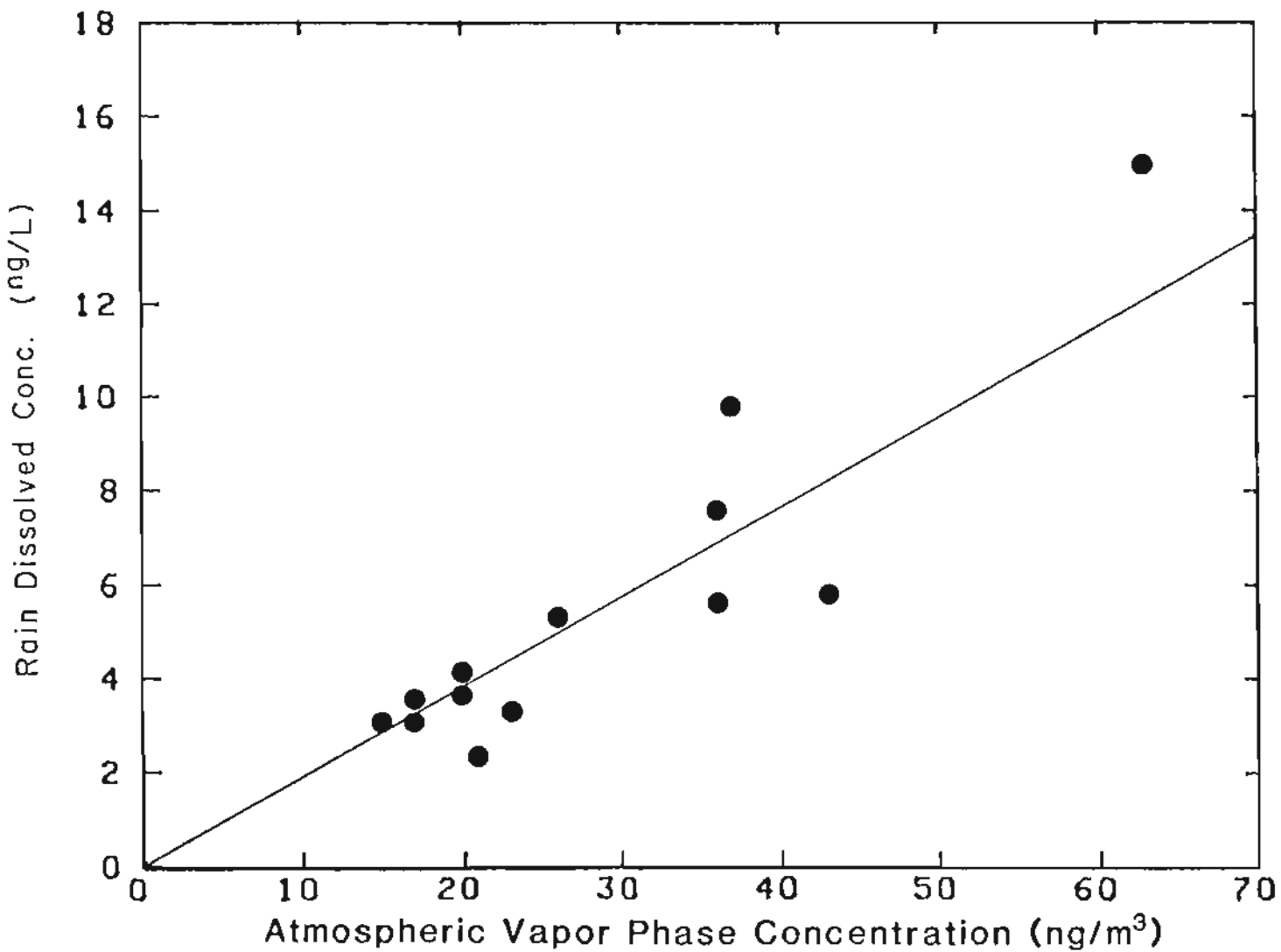
Figure 6.6. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for 2,6-dimethylnaphthalene.
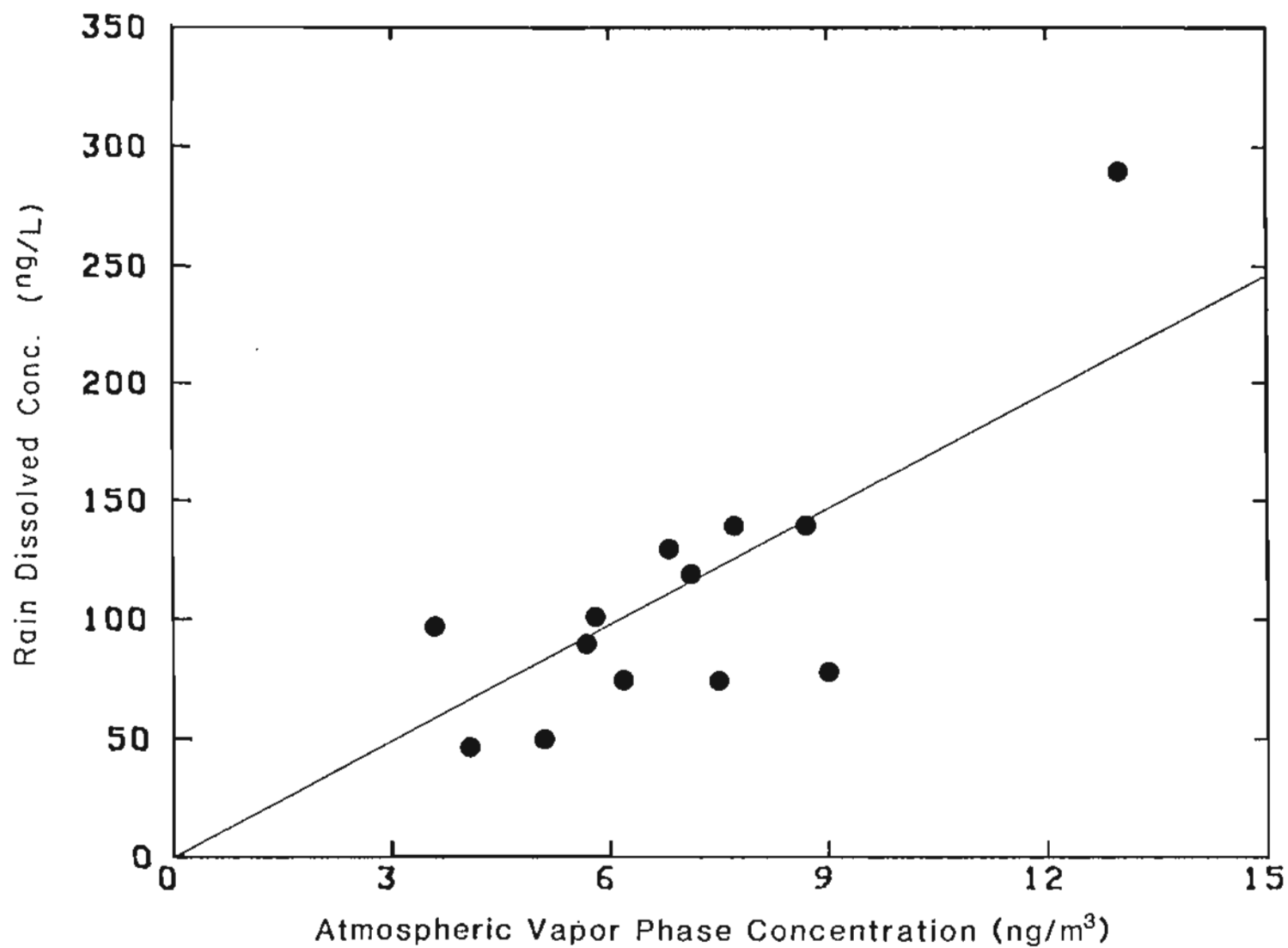
Figure 6.7. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for 9-fluorenone.
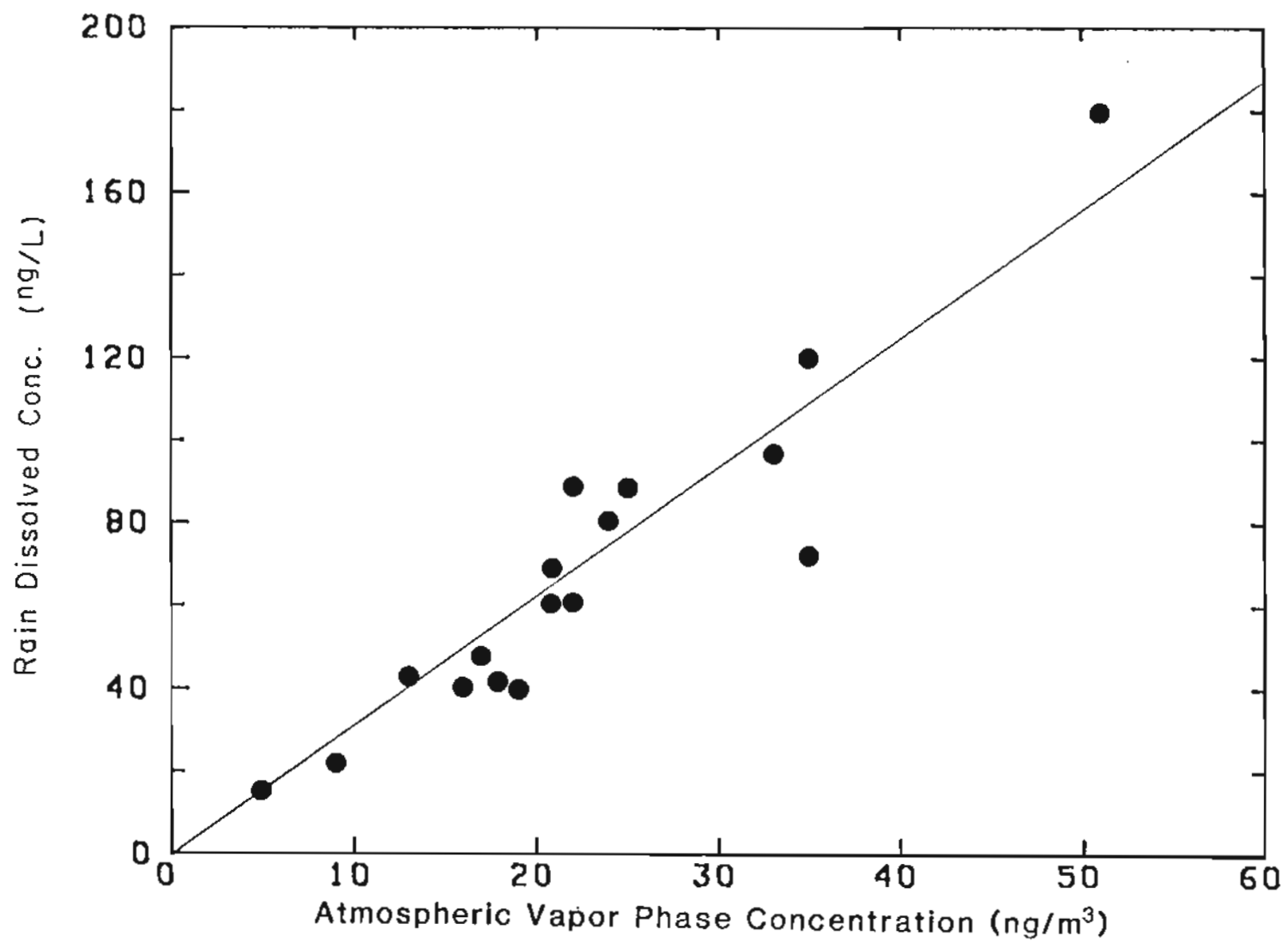
Figure 6.8. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for phenanthrene.
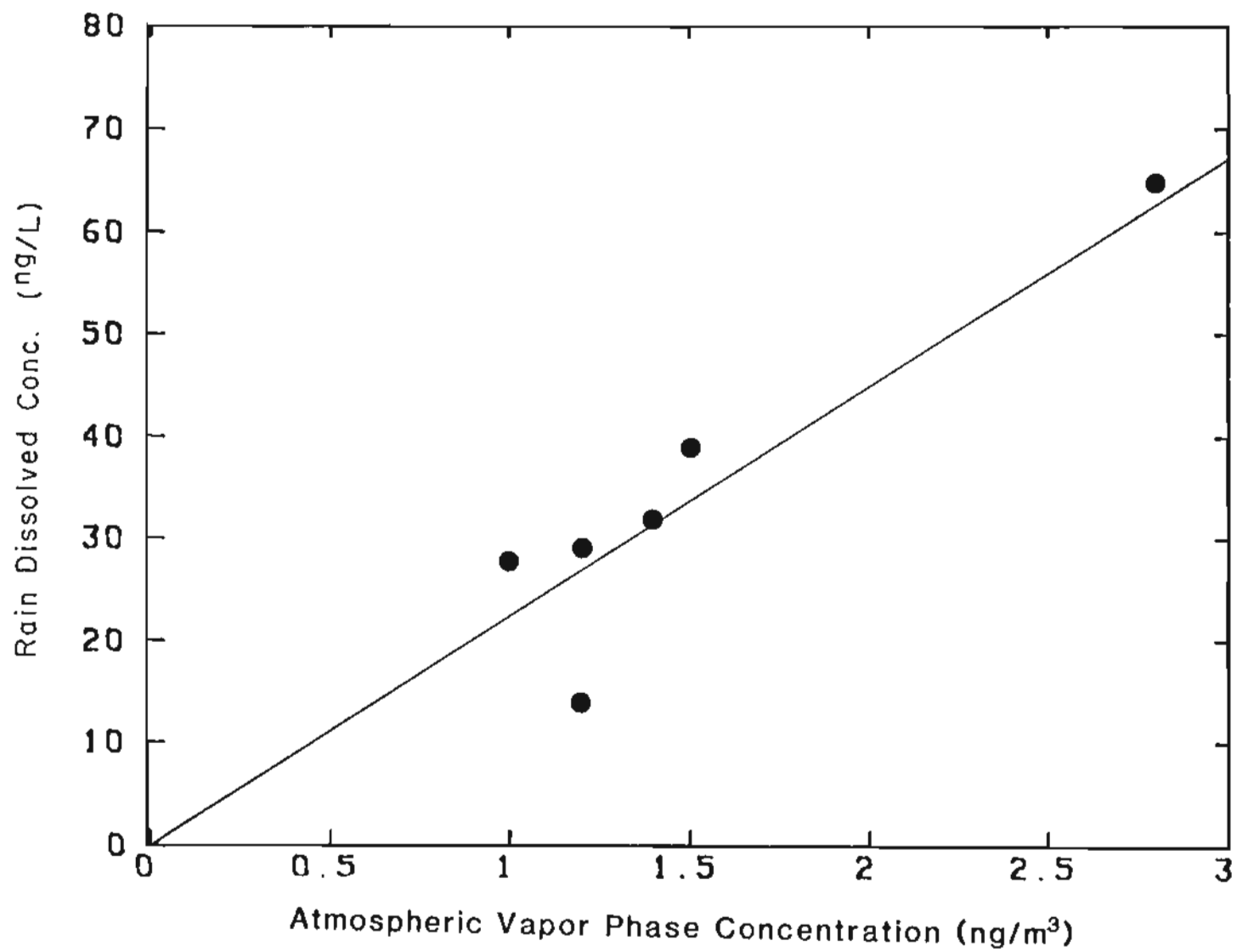
Figure 6.9. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for xanthone.
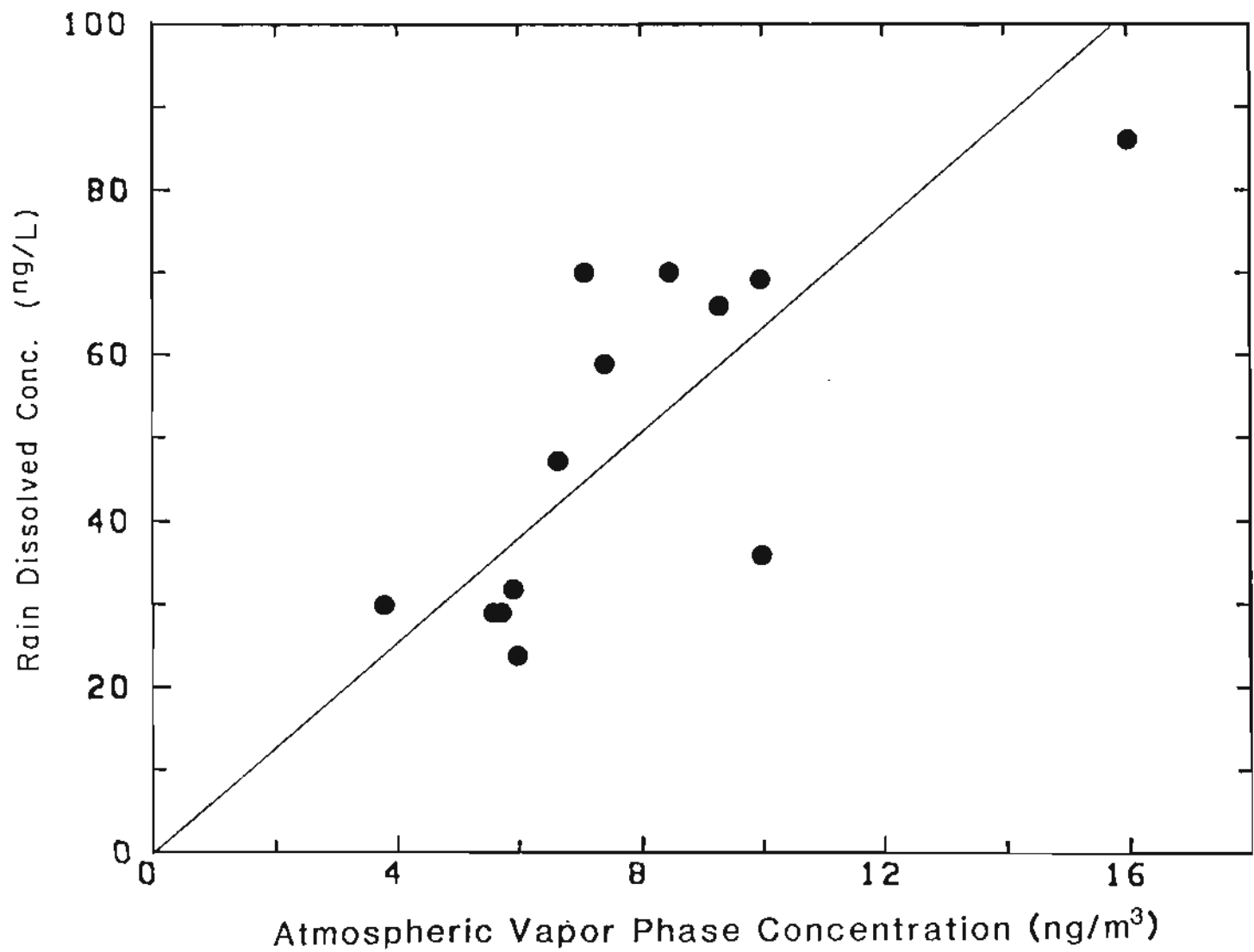
Figure 6.10. Correlation between rain dissolved concentrations and atmospheric vapor phase concentrations for fluoranthene.
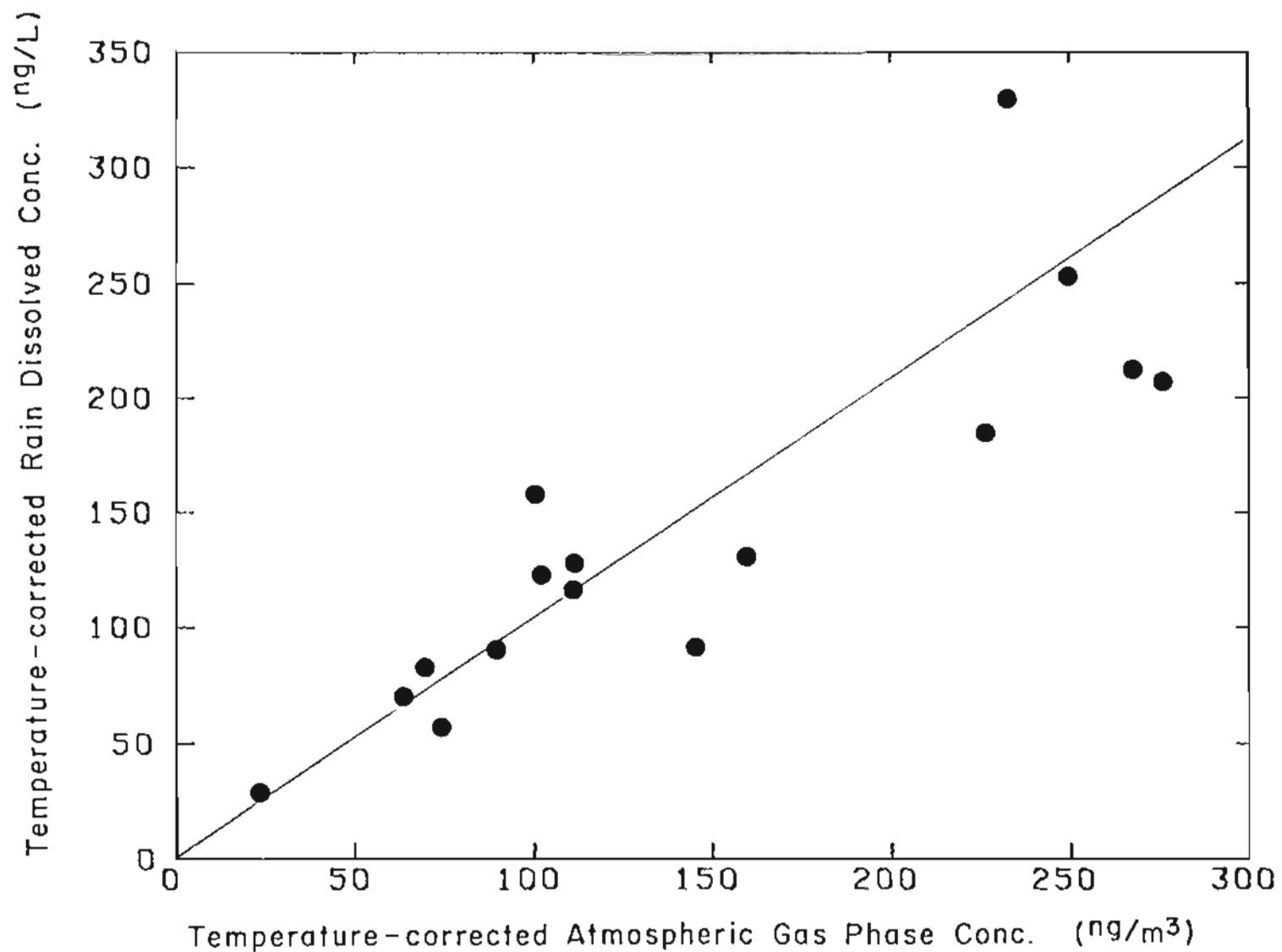
Figure 6.11. Correlation between temperature-corrected rain dissolved and vapor phase concentrations for phenanthrene.
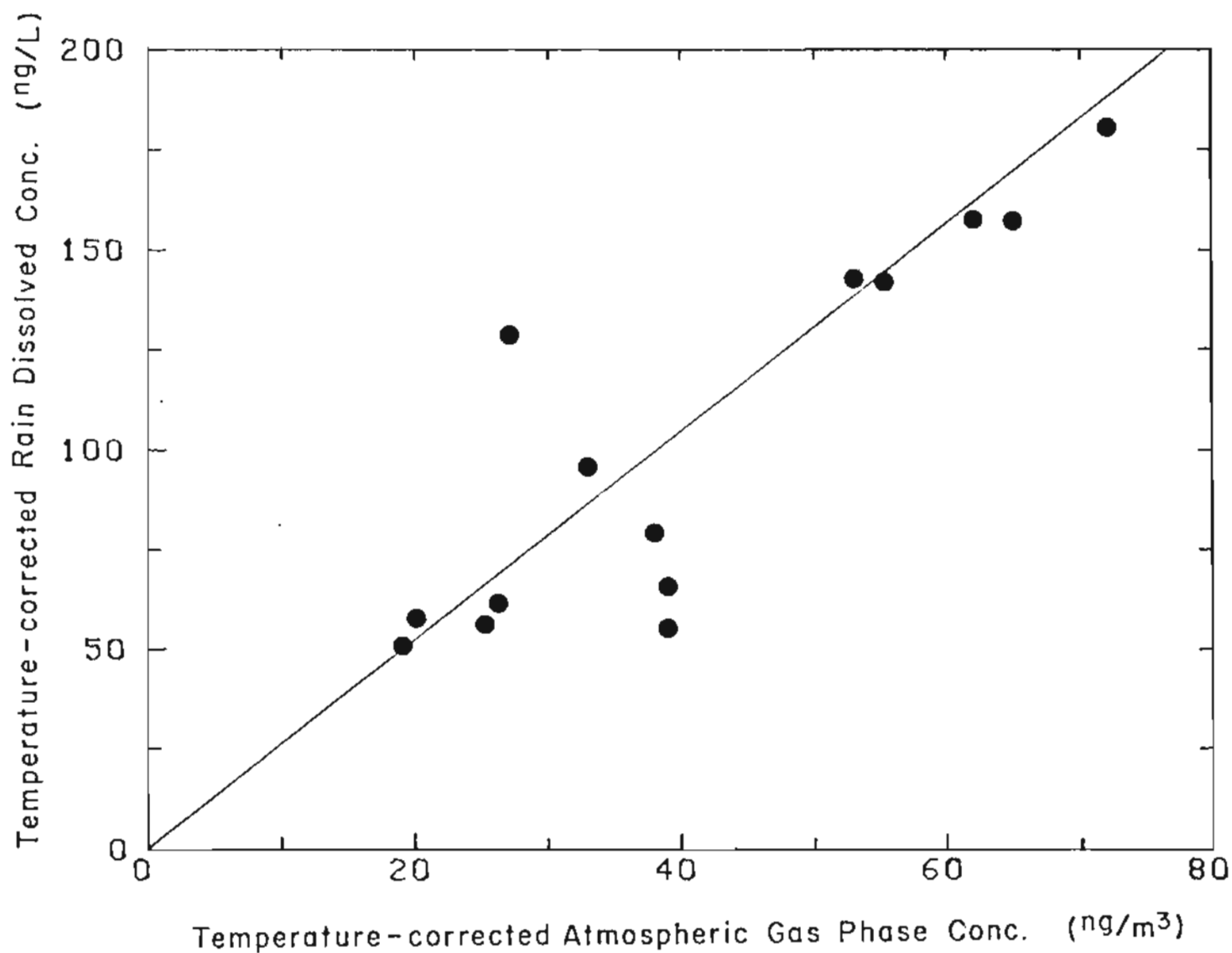
Figure 6.12. Correlation between temperature -corrected rain dissolved and vapor phase concentrations for fluoranthene.

If the range of concentrations over several events is large compared to the experimental uncertainty, a correlation coefficient close to unity for the rain/air concentration plot indicates that W_g is constant under that range of conditions. If the concentration range is comparable to the experimental uncertainty, the correlation coefficient will very likely be low, and no such conclusions will be possible. In this study, the average coefficient of variation due to sampling and analysis errors within each event was ~18% for the air samples (Tables 4.10 and 4.11). It was ~30% for the rain samples (Tables 5.8 and 5.9). The variation due to differences in the average temperature would produce a smaller effect. Compounds which demonstrated rain and vapor phase concentration coefficients of variation much greater than 20% should therefore show high inter-event correlations. The correlation coefficients given in Table 6.1 are indeed very high (r=0.96) for toluene and tetrachloroethene, two compounds which did show large variabilities between events. Correlation coefficients are low for compounds such as 1,4-dichlorobenzene (r=0.46) for which the variability between events was low. The fact that high correlations were found for many compounds for which a large range of rain and air concentrations were observed indicates that the W_g values were constant for most compounds over all of the storm events sampled in this study.

The determination of gas scavenging ratios can be confounded when particle-scavenged compounds are not completely separated from the rainwater. The dissolved rain concentrations will be overestimated if a significant fraction of adsorbed material resides on particles which

pass through the filter and are trapped by the Tenax cartridges. The results from Tables 5.5 and 5.7, indicating that 90% of the collected particulate material was >10 um, appear to ensure that this did not occur. The agreement between the measured W_g and laboratory α values for the compounds fluoranthene, pyrene, and benz[a]anthracene in Figure 6.2 is encouraging in this respect, since these compounds are scavenged from both the particulate and vapor phases. This indicates that the sampling system employed in this study was effective in differentiating particulate from dissolved material in rain.

6.1.2 Gas Scavenging Ratios at the Oregon Coast

The gas scavenging ratios from the coastal sampling, computed from the data in Tables A1.3 and A2.4, are presented in Table 6.2. The W_g values for most of the compounds were very similar to those found in Portland. However, the W_g values for the benz[a]anthracene and chrysene were about a factor of 3 lower in the coastal samples. This was apparently due to analytical difficulties with the rain samples, in which some water remained in the concentrated extracts. This problem was corrected for the April 25, 1985 sample, which subsequently yielded W_g values similar to those found in Portland.

Table 6.2. Mean Dissolved Rain Concentrations, Mean Atmospheric Vapor Phase Concentrations, and Gas Scavenging Ratios (W_g) at the Oregon Coast in 1985.

	Mean Concentrations		
	Rain (ng/L)	Air (ng/m^3)	W_g
Tetrachloroethene	0.44 (1)	210 ± 100	3.4 (1)
Toluene	11 ± 12 (2)	670 ± 260[a]	33 ± 5 (2)
Ethylbenzene	11 ± 7	210 ± 76	61 ± 53
2,6-Dimethylnaphthalene	4.0 ± 0.7	17 ± 3	240 ± 10
1,3+1,6-Dimethylnaphthalene	8.1 ± 1.8	29 ± 5	280 ± 30
2-Methylnaphthalene	18 ± 2	63 ± 13	290 ± 40
Naphthalene	32 ± 13	98 ± 31	320 ± 81
1-Methylnaphthalene	12 ± 1	33 ± 7	360 ± 70
1,4+1,5+2,3-Dimethyl naphthalene	3.0 ± 0.1	8.1 ± 1.5	380 ± 45
1,2-Dimethylnaphthalene	1.4 ± 0.2	2.9 ± 0.6	500 ± 50
Salicylaldehyde	100 ± 50	170 ± 50	700 ± 520
Benzonitrile	24 ± 4	35 (1)	830 (1)
Dibenzofuran	8.2 ± 4.1	6.9 ± 3.4	1200 ± 300
Acenaphthene	1.7 ± 0.8	1.2 ± 0.5	1300 ± 300
Acenaphthylene	12 ± 6	8.6 ± 6.3 (2)	1300 ± 600
2-Nitrophenol	23 ± 11	13 ± 7	1900 ± 800
Fluorene	7.4 ± 3.2	4.5 ± 2.1	1700 ± 200
2,4-Dimethylbenzaldehyde	14 ± 13	8.4 ± 2.5	1900 ± 1800
Benzo[b]fluorene	0.93 ± 0.18 (2)	0.82 ± 0.62	2000 ± 300 (2)

Table 6.2 (cont'd). Mean Dissolved Rain Concentrations, Mean Atmospheric Vapor
Phase Concentrations, and Gas Scavenging Ratios (W_g) at the Oregon Coast in 1985.

	Mean Concentrations		
	Rain (ng/L)	Air (ng/m^3)	W_g
Benzo[a]fluorene	1.7 ± 0.9	0.91 ± 0.69	2100 ± 700
2-Heptanone	29 ± 14	16 (1)	2100 (1)
Anthracene	5.0 ± 5.8 (2)	1.8 ± 1.4	2200 ± 800 (2)
3+2-Methylphenanthrene	6.0 ± 3.1	2.2 ± 0.9	2700 ± 400
Phenanthrene	30 ± 16	10.0 ± 6.3	3100 ± 300
1+4+9-Methylphenanthrene	5.0 ± 3.1	1.6 ± 0.8	3200 ± 600
Dibenzothiophene	1.4 ± 0.3	0.42 ± 0.10	3300 ± 500
Xanthone	4.9 ± 1.6	0.96 ± 0.45 (2)	4600 ± 200 (2)
Chrysene	2.1 ± 1.0	0.53 ± 0.22	4600 ± 3400
Benz[a]anthracene	1.3 ± 0.75	0.37 ± 0.22	4800 ± 5000
Coumarin*	60 ± 40	12 ± 8 (2)	4800 ± 1300 (2)
Butylbenzylphthalate	61 ± 57 (2)	4.3 ± 0.4 (2)	5000 (1)
Fluoranthene	28 ± 17	5.2 ± 3.1	6400 ± 4300
2,6-Dimethylphenol*	26 ± 20	3.8 ± 2.9	6600 ± 2900
7-Benz[de]anthracenone	0.72 ± 0.40 (2)	0.10 ± 0.03	7400 ± 1400 (2)
Pyrene	21 ± 13	4.1 ± 2.8	7600 ± 6900
9-Fluorenone	42 ± 37	3.1 ± 1.8	12000 ± 4000
4-Methyl-2-nitrophenol*	12 ± 2	1.1 ± 0.8	15000 ± 9000
2-Methoxyphenol*	880 ± 600	48 ± 17	16000 ± 8500

Table 6.2 (cont'd). Mean Dissolved Rain Concentrations, Mean Atmospheric Vapor Phase Concentrations, and Gas Scavenging Ratios (W_g) at the Oregon Coast in 1985.

	Mean Concentrations		
	Rain (ng/L)	Air (ng/m^3)	W_g
9,10-Anthracenedione	20 ± 16	1.3 ± 0.8	16000 ± 9000
Diethylphthalate*	57 ± 43	4.7 ± 4.6	18000 ± 17000
Methylfurfural*	750 ± 660	43 (1)	18000 (1)
2,4+2,5-Dimethylphenol*	270 ± 180	14 ± 8	19000 ± 2000
3,4-Dimethylphenol*	67 ± 47	4.3 ± 2.2 (2)	19000 ± 2000 (2)
2,4-Dichlorophenol*	5.9 ± 0.5	0.29 ± 0.05 (2)	20000 ± 3000 (2)
1-Indanone*	120 ± 100	5.1 ± 3.1	22000 ± 6000
Dibutylphthalate	49 ± 32	4.1 ± 2.8 (2)	23000 ± 21000 (2)
3+4-Methylphenol*	1100 ± 1200	44 ± 34	23000 ± 8000
2-Methylphenol*	550 ± 540	20 ± 10	24000 ± 12000
4-Ethyl+3,5-dimethylphenol*	400 ± 270	17 ± 10	25000 ± 1300
4-Methyl-2-methoxyphenol*	490 ± 390	19 ± 1 (2)	38000 ± 11000 (2)
α-HCH*	15 ± 3	0.37 ± 0.04	41000 ± 13000

*Indicates that breakthrough correction was applied to the determination of the rain dissolved concentrations. [a]No. of samples = 3 unless otherwise specified.

6.2 Particle Scavenging Ratios

6.2.1 Particle Scavenging Ratios in Portland

The particle scavenging ratios, W_p, obtained for each compound from the data in Tables A1.2 and A2.3 are presented in Table 6.3. Several interesting facts may be derived from Table 6.3: 1) The measured W_p values in Portland ranged over three orders of magnitude, from 10^2 to 10^5; 2) There was more similarity in the W_p values for different compounds within each event than for individual compounds between events; 3) The W_p values for individual compounds were quite variable, spanning a range of a factor of 10 to 50 over the thirteen events; and 4) The W_p values for the more volatile PAHs and all of the alkanes and phthalates were generally an order of magnitude larger than those for the less volatile PAHs.

The mean particulate concentrations in the air and rain and the mean W_p values ($\overline{W_p}$) in Portland are presented in Table 6.4. In Table 6.4, the standard deviations are calculated based on a normal distribution. The W_p data, however, are better described by a log-normal distribution. In Figure 6.13, the means and standard deviations are calculated on the basis of a log-normal distribution. Figure 6.13 shows the change in $\overline{\log W_p}$ with the log of the supercooled liquid vapor pressure ($\log P_L$) for the PAHs. While a linear relationship between $\overline{\log W_p}$ and $\log P_L$ can be fit to the data in Figure 6.13, the points appear to fall into two groups, with compounds having $P_L < 10^{-6}$ exhibiting $\overline{\log W_p}$ - 3.2 and compounds with $P_L > 10^{-6}$ exhibiting $\overline{\log W_p}$ - 4.2.

Table 6.3a. Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1984.

Compound	MW	$W_p \times 10^3$						
		2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
PAHs and Oxygenated PAHs								
Dibenzofuran	168	NA[a]	4.9	23	NA	9.3	5.5	NA
Fluorene	166	NA	NA	34	NA	8.2	2.4	NA
Phenanthrene+Anthracene	178	19	2.5	38	5.6	17	15	22
9-Fluorenone	180	29	NA	NA	9.0	17	1.9	18
2+3-Methylphenanthrene	192	13	NA	16	NA	NA	NA	NA
1+4+9-Methylphenanthrene	192	16	NA	10	NA	NA	NA	NA
Fluoranthene	202	4.5	2.4	15	3.5	12	23	18
Pyrene	202	2.6	1.7	13	3.6	10	20	14
9,10-Anthracenedione	208	1.7	NA	2.6	1.4	3.9	NA	NA
Benz[a]anthracene	228	0.64	0.41	1.3	0.40	2.3	2.6	1.1

Table 6.3a (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1984.

Compound	MW	$W_p \times 10^3$						
		2/12-2/13	2/14-2/15	2/20-2/21	2/23-2/24	2/29-3/1	3/16-3/20	4/11-4/12
Chrysene	228	1.7	1.1	3.5	1.2	4.5	3.8	2.4
7-Benz[de]anthracenone	230	0.56	NA	1.1	0.90	2.7	NA	NA
Benzo[b+j+k] fluoranthene	252	1.3	0.43	2.7	3.2	4.9	2.1	0.90
Benzo[e]pyrene	252	1.4	0.43	3.0	2.8	4.5	1.7	0.29
Benzo[a]pyrene	252	0.58	0.18	2.5	1.2	3.9	NA	NA
Perylene	252	0.63	NA	2.6	0.92	3.0	NA	NA
Benzo[ghi]perylene	276	1.3	NA	4.2	3.9	5.8	NA	0.29
Coronene	300	2.0	NA	1.8	NA	14	NA	NA
Average of PAHs with MW <202		15	2.9	24	5.0	12	11	18
Average of PAHs with MW >202		1.2	0.51	2.5	1.8	5.0	2.6	1.0

Table 6.3a (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1984.

Compound	MW	W_p x 10^3						
		2/12-2/13	2/14-2/15	2/20-2/21	2/23-2/24	2/29-3/1	3/16-3/20	4/11-4/12
Alkanes								
Eicosane	282	21	NA	15	89	44	NA	32
Heneicosane	296	14	NA	16	76	46	10	12
Docosane	310	15	NA	12	63	34	NA	6.3
Tricosane	324	27	3.9	16	29	44	NA	13
Tetracosane	338	10	NA	18	NA	27	NA	6.4
Pentacosane	352	47	5.0	11	26	29	NA	22
Hexacosane	366	NA	3.3	14	NA	36	NA	7.0
Average of alkanes		22	4.1	15	57	37	10	14

Table 6.3a (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1984.

Compound	MW	$W_p \times 10^3$						
		2/12-2/13	2/14-2/15	2/20-2/21	2/23-2/24	2/29-3/1	3/16-3/20	4/11-4/12
Phthalate Esters								
Butylbenzylphthalate		1.0	NA	13	10	NA	NA	NA
Bis[2-ethylhexyl]-phthalate		9.1	NA	37	15	NA	NA	NA
Dioctylphthalate		29	NA	15	65	NA	35	25
Average of phthalates		13	NA	22	30	NA	35	25

[a]NA = not available, due to lack of rain or air data.

Table 6.3b. Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1985.

Compound	$W_p \times 10^3$					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
PAHs and Derivatives						
Acenaphthylene	51	31	23	13	83	130
Dibenzofuran	21	22	38	11	110	110
Fluorene	32	11	11	6.0	95	58
Dibenzothiophene	41	4.4	NA	NA	110	50
Phenanthrene	45	27	31	12	99	110
Anthracene	27	17	19	6.2	NA	56
2+3-Methylphenanthrene	21	8.2	25	8.3	74	72
1+4+9-Methylphenanthrene	21	12	18	7.4	80	55
Fluoranthene	24	20	10	9.1	79	61
Pyrene	20	15	7.9	7.1	58	50

Table 6.3b (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1985.

Compound	$W_p \times 10^3$					
	2/14- 2/15	3/3- 3/4	3/21- 3/23	3/25- 3/27	4/17- 4/19	4/21- 4/23
Benzo[a]fluorene	9.8	7.3	5.5	5.0	52	32
Benzo[b]fluorene	7.9	6.2	5.4	3.9	43	21
Benz[a]anthracene	1.4	2.3	1.7	2.1	9.2	5.7
Chrysene	3.1	3.7	4.5	3.6	40	10.5
Benzo[b+j+k]fluoranthene	1.3	2.5	3.2	3.0	26	5.9
Benzo[e]pyrene	1.5	2.5	3.0	2.8	23	6.2
Benzo[a]pyrene	0.97	1.7	2.3	1.5	18	5.0
Perylene	1.05	1.7	3.0	3.9	21	5.3
Indeno[1,2,3-cd]pyrene	0.96	1.4	3.2	2.7	21	7.4
Benzo[ghi]perylene	1.4	1.9	3.4	2.4	17	6.7
Dibenz[a,c+a,h]anthracene	0.42	NA	2.5	2.0	NA	NA
Coronene	0.49	NA	3.1	1.3	33	15

Table 6.3b (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1985.

Compound	$W_p \times 10^3$					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Oxygenated PAHs						
9-Fluorenone	14	19	7.4	6.4	46	35
Xanthone	NA	1.1	NA	NA	36	16
9,10-Anthracenedione	7.9	2.9	4.9	3.7	42	16
7-Benz[de]anthracenone	0.48	1.2	1.5	1.5	11	2.3
7,12-Benz[a]anthracenedione	5.6	NA	NA	1.5	36	NA
Alkanes						
Eicosane	23	NA	10	NA	27	19
Heneicosane	9.6	NA	26	NA	56	NA
Docosane	NA	NA	13	NA	50	NA
Tricosane	NA	NA	38	NA	74	NA

Table 6.3b (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds in Portland, Oregon in 1985.

Compound	$W_p \times 10^3$					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Tetracosane	NA	6.6	25	NA	74	NA
Pentacosane	6.1	13	53	NA	73	NA
Hexacosane	NA	10	28	NA	72	NA
Heptacosane	NA	NA	NA	NA	120	NA
Octacosane	NA	18	37	NA	66	NA
Phthalate Esters						
Butylbenzylphthalate	7.3	5.4	6.5	20	17	17
Dioctylphthalate	52	17	68	13	NA	41

[a]NA = not available, due to lack of rain or air data.

Table 6.4. Mean Particulate Phase Concentrations and Mean W_p Values in Portland, Oregon in 1984–85.

Compound	Mean Concentrations Rain (ng/L)	Air (ng/m^3)	Mean W_p x 10^3
PAHs and Derivatives			
Acenaphthylene	0.86 ± 0.39 (6)[a]	0.021 ± 0.011 (6)	55 ± 44 (6)
Dibenzofuran	1.1 ± 0.7 (12)	0.10 ± 0.11 (12)	35 ± 40 (10)
Fluorene	0.64 ± 0.59 (10)	0.067 ± 0.076 (11)	29 ± 31 (9)
Dibenzothiophene	0.43 ± 0.42 (6)	0.039 ± 0.041 (9)	51 ± 44 (4)
Phenanthrene	5.7 ± 4.2	0.28 ± 0.25	34 ± 34
Anthracene	0.75 ± 0.45 (5)	0.035 ± 0.020 (6)	25 ± 19 (5)
2+3-Methylphenanthrene	4.0 ± 3.4 (8)	0.21 ± 0.14	30 ± 27 (8)
1+4+9-Methyl phenanthrene	2.7 ± 2.8 (9)	0.16 ± 0.10	27 ± 26 (8)
Fluoranthene	9.0 ± 8.4	0.53 ± 0.31	22 ± 23
Pyrene	8.2 ± 7.7	0.62 ± 0.37	17 ± 17
Benzo[a]fluorene	4.6 ± 3.1 (6)	0.43 ± 0.30 (6)	19 ± 19 (6)
Benzo[b]fluorene	4.1 ± 2.8 (6)	0.45 ± 0.32 (6)	15 ± 15 (6)
Benz[a]anthracene	2.5 ± 1.8	1.2 ± 0.8	2.4 ± 2.5
Chrysene	7.5 ± 8.3	1.5 ± 1.0	6.4 ± 10.4
Benzo[b+j+k] fluoranthene	14 ± 18	3.6 ± 1.9	4.4 ± 6.7
Benzo[e]pyrene	4.9 ± 5.6	1.3 ± 0.8	4.1 ± 5.9
Benzo[a]pyrene	5.4 ± 7.3 (11)	1.6 ± 1.1	3.4 ± 5.0 (11)
Perylene	0.99 ± 1.02 (10)	0.31 ± 0.21	3.8 ± 6.3 (10)

Table 6.4 (cont'd). Mean Particulate Phase Concentrations and Mean W_p Values in Portland, Oregon in 1984–85.

Compound	Mean Concentrations Rain (ng/L)	Air (ng/m^3)	Mean W_p x 10^3
Indeno[1,2,3-cd]pyrene	13 ± 18 (6)	2.1 ± 1.0 (6)	6.1 ± 7.6 (6)
Dibenz[a,c]anthracene+ Dibenz[a,h]anthracene	2.3 ± 3.4 (4)	0.36 ± 0.22 (5)	1.6 ± 1.1 (3)
Benzo[ghi]perylene	11 ± 14 (11)	2.4 ± 1.3	4.4 ± 4.6 (11)
Coronene	6.7 ± 9.4 (9)	0.94 ± 0.75 (12)	8.8 ± 11.4 (8)
Oxygenated PAHs			
9-Fluorenone	1.4 ± 0.9 (12)	0.14 ± 0.14 (12)	18 ± 13 (11)
Xanthone	0.59 ± 0.63 (3)	0.060 ± 0.035 (6)	18 ± 18 (3)
9,10-Anthracenedione	3.6 ± 3.0 (10)	0.59 ± 0.22	8.7 ± 12.5 (10)
7-Benz[de]anthracenone	4.1 ± 5.1 (10)	1.7 ± 1.2	2.3 ± 3.1 (10)
7,12-Benz[a]anthracene dione	5.0 ± 4.8 (3)	0.40 ± 0.20 (6)	14 ± 19 (3)
Alkanes			
Eicosane	22 ± 20 (10)	0.88 ± 0.63 (12)	31 ± 24 (9)
Heneicosane	44 ± 50 (10)	1.1 ± 1.1 (11)	30 ± 24 (9)
Docosane	46 ± 62 (10)	2.9 ± 2.6 (10)	28 ± 22 (7)
Tricosane	79 ± 110 (11)	3.5 ± 3.7 (11)	31 ± 22 (8)
Tetracosane	67 ± 95 (11)	4.6 ± 4.1 (9)	24 ± 24 (7)
Pentacosane	120 ± 140	4.6 ± 4.9 (11)	29 ± 23 (10)
Hexacosane	57 ± 84 (12)	3.6 ± 3.6 (9)	24 ± 24 (7)

Table 6.4 (cont'd). Mean Particulate Phase Concentrations and Mean W_p Values in Portland, Oregon in 1984-85.

Compound	Mean Concentrations		Mean $W_p \times 10^3$
	Rain (ng/L)	Air (ng/m^3)	
Octacosane	72 ± 62 (5)	3.5 ± 3.5 (5)	40 ± 24 (3)
Phthalates			
Butylbenzylphthalate	38 ± 37 (10)	4.1 ± 3.1 (11)	11 ± 6 (9)
Dioctylphthalate	18 ± 16 (12)	0.48 ± 0.25 (11)	36 ± 20 (10)

[a]Number in parentheses is number of samples, if other than 13.
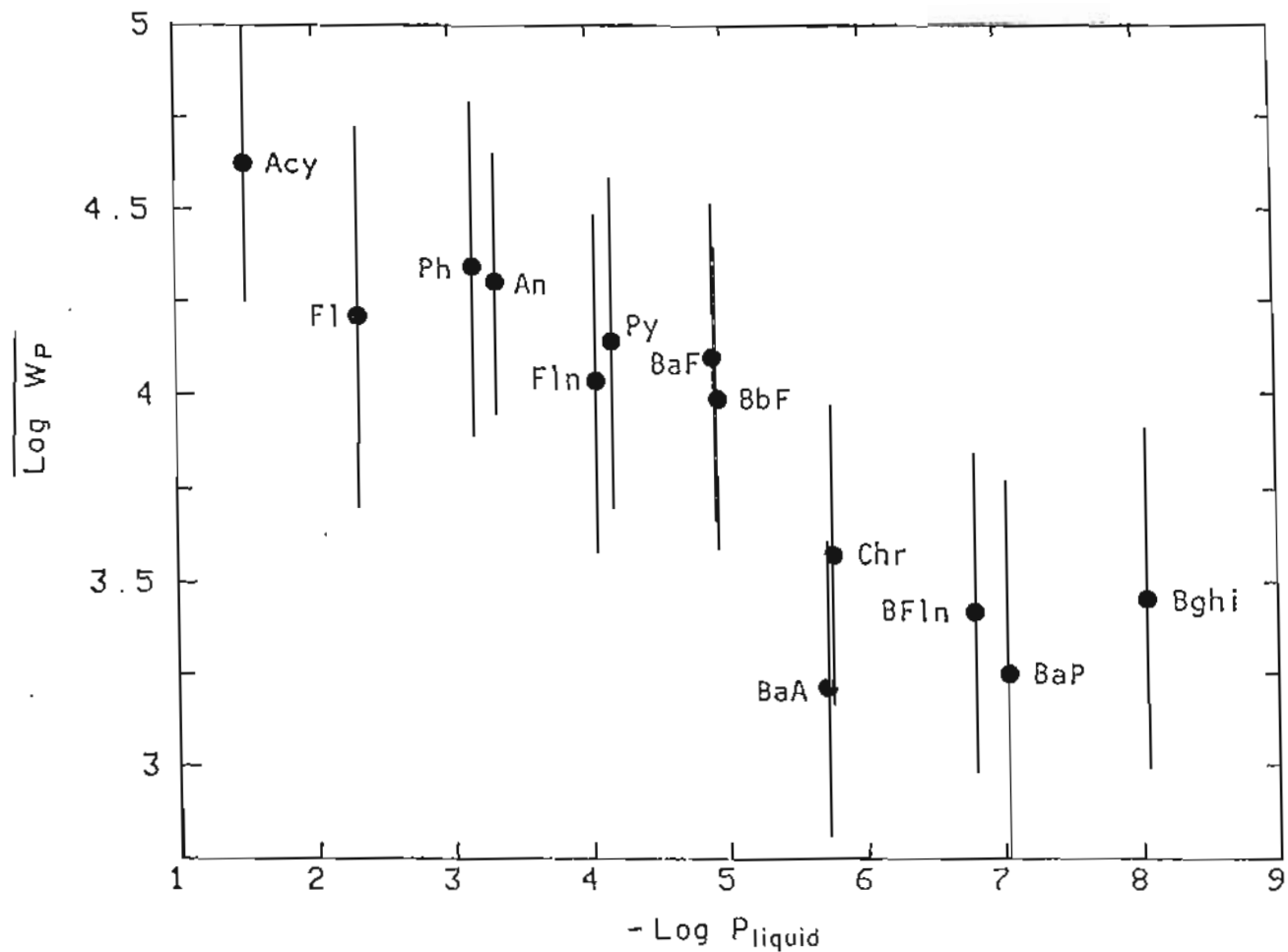
Figure 6.13   Mean particle scavenging ratios of PAHs as a function of supercooled liquid vapor
pressure in Portland, Oregon.   Acy = acenaphthylene, Fl = fluorene, Ph = phenan-
threne, An = anthracene, Fln = fluoranthene, Py = pyrene, BaF = benzo[a]fluorene,
BbF = benzo[b]fluorene, BaA = benz[a]anthracene, Chr = chrysene, BFln = benzo[b+j+k]-
fluoranthenes, BaP = benzo[a]pyrene, Bghi = benzo[ghi]perylene.

A portion of this effect may have been due to sampling losses of the more volatile compounds in the aerosol, as discussed in Sections 2.2.1 and 4.4.2. However, the losses found by Van Vaeck et al. (1984) were limited to roughly 50% for phenanthrene during winter sampling. Also, as shown in Figure 6.14, a similar trend in W_p with vapor pressure was not observed for the alkanes and phthalates. Thus this effect alone cannot account for the entire order of magnitude differences observed here. In addition, the vapor adsorption effect described in Section 4.2.2 would counteract the volatilization effect to some degree. Therefore, the differences in the W_p values appear to be real. A possible interpretation for the dependence of the PAH W_p values on vapor pressure will be discussed in Section 6.2.4.

While there were relative differences in the W_p values for the various compounds, they were nearly all low in comparison with the values of 10^5 to 10^6 reported for inorganics (Peirson, 1973; Gatz, 1974). This may have been due to actual differences in the scavenging mechanisms for the organic compounds, as discussed above. However, it is worthwhile to consider other possible reasons for the low W_p values. After sampling, even with the flushing procedure described in Section 5.2.3.4, some particulate material remained on the Teflon collection sheet and in the pressurized vessel in the rain sampler. In addition, there were events during which the filter became plugged during sampling. In those cases the flushing procedure could not be carried out. While the amount of residue was not measured, it is not likely to have affected the rain particulate concentrations. If the losses of par-
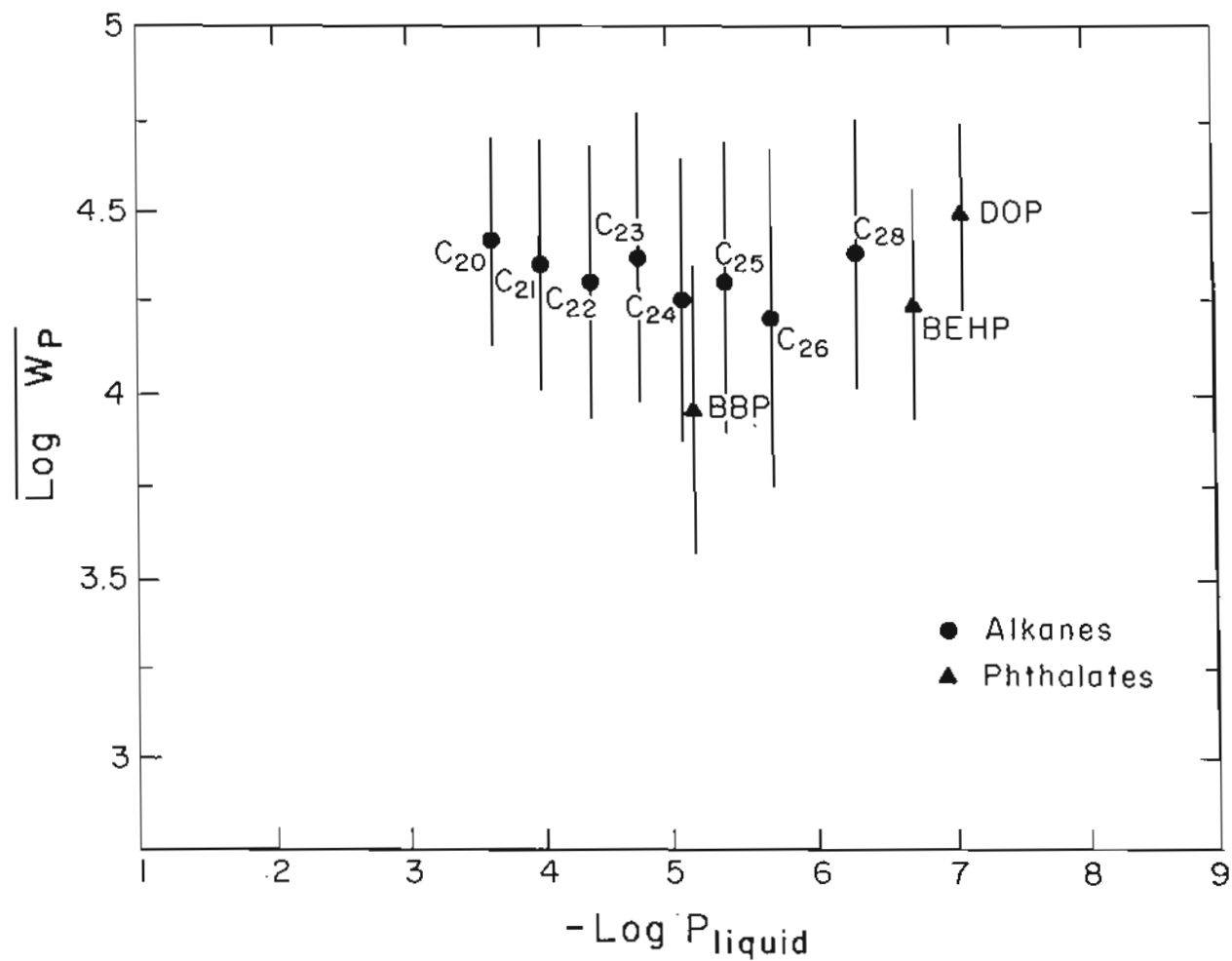
Figure 6.14. Mean particle scavenging ratios of alkanes and phthalates as a function of vapor pressure in Portland. Alkanes labelled C_{20}-C_{28}; BBP=butylbenzylphthalate; BEHP=bis (2-ethylhexyl)phthalate; DOP=dioctylphthalate.

ticles were large enough to cause an order of magnitude error in the W_p values, the variability between samplers would also be large. Table 5.10 shows that good agreement was observed between the samplers. Also, only particles greater than ~20 μm in diameter would settle out of the standing water on the Teflon collection sheet. Such particles are not likely to be important in the rain scavenging of organic compounds.

Erroneously low W_p values would also be observed if dissolution of adsorbed material occurred either in the raindrop or after collection. The equilibrium distribution between adsorbed material and the dissolved phase is governed by the K_{oc} partition coefficients of the compounds, where

$$K_{oc} = [adsorbed]/[dissolved] \qquad 6.3$$

at equilibrium. It is unlikely that sufficient time is available for equilibrium to be achieved between these phases in rain. Still, the relative values of the K_{oc} coefficients of the PAHs should give some indication as to which compounds would be likely to dissolve off of the suspended particulate matter. The K_{oc} values for the PAHs range from 10^3 to 10^6 (Mabey et al., 1982), with the less volatile compounds exhibiting the higher K_{oc} values and the more volatile compounds exhibiting the lower values. Thus the less volatile PAHs have less of a tendency to dissolve than the more volatile PAHs. Since all of the PAHs were present in the particulate samples in roughly equal amounts, dissolution cannot be the cause of the differences in W_p values among the

PAHs.

6.2.2 Particle Scavenging Ratios at the Oregon Coast

The particle scavenging ratios for the three events sampled at the Oregon coast, calculated from the data in Tables A1.3 and A2.4, are presented in Table 6.5. The variation of log W_p with vapor pressure for the PAHs in the coastal samples is shown in Figure 6.15. The same general trends of W_p values ranging from 10^3 to 10^5 and the behavior of W_p with vapor pressure for the PAHs are observed in the coastal samples.

6.2.3 Influence of Meteorological Parameters

The degree of variability between storm events observed in the W_p values suggests that: 1) the meteorology of individual storm events has a substantial effect on the scavenging of particles; or 2) in-cloud particulate phase concentrations bear little relation to concentrations at ground level. Two 1985 storm events were sampled simultaneously in Portland and at the coast. Both events were cold fronts. However, the W_p values for Portland and the coast for these two events did not show any greater degree of similarity to each other than seen in the unrelated samples. In Figures 6.16 and 6.17, the W_p values are plotted against precipitation amount. Previous studies (Gatz, 1976; van Noort and Wondergem, 1985) have found strong decreases in W_p with increasing precipitation amount. That trend was not observed in this study.

Table 6.5. Particle Scavenging Ratios (W_p) for Organic Compounds at the Oregon Coast in 1985 and Comparison to Mean Portland W_p Values.

Compound	W_p (x 10^3)				
	4/17	4/21	4/25	Mean	Portland
Acenaphthylene	13	250	100	120	55
Dibenzofuran	57	110	51	72	36
Fluorene	NA[a]	NA	50	50	31
9-Fluorenone	47	62	39	49	19
Phenanthrene	98	82	38	73	34
Anthracene	56	40	21	39	25
3+2-Methylphenanthrene	57	34	24	38	26
1+4+9-Methylphenanthrene	58	32	34	41	24
9,10-Anthracenedione	NA	19	NA	19	8.7
Eicosane	NA	NA	68	68	31
Fluoranthene	48	13	14	25	22
Pyrene	30	9.7	16	19	17
Benzo[a]fluorene	7.8	2.7	3.5	4.7	19
Benzo[b]fluorene	9.5	2.3	4.4	5.4	15
Butylbenzylphthalate	NA	NA	29	29	11
Benz[a]anthracene	3.3	1.8	1.6	2.3	2.4
Chrysene	7.0	4.3	4.0	5.1	6.4
7-Benz[de]anthracenone	0.90	1.3	4.3	2.2	2.3
7,12-Benz[a]anthracenedione	NA	NA	8.4	8.4	15

Table 6.5 (cont'd). Particle Scavenging Ratios (W_p) for Organic Compounds at the Oregon Coast in 1985 and Comparison to Mean Portland W_p Values.

Compound	W_p (x 10^3)				
	4/17	4/21	4/25	Mean	Portland
Benzo[b+j+k]fluoranthene	1.5	1.5	2.8	2.0	4.4
Benzo[e]pyrene	1.6	2.2	2.7	2.2	4.1
Benzo[a]pyrene	1.1	2.0	2.3	1.8	3.4
Indeno[1,2,3-cd]pyrene	2.7	1.0	2.2	2.0	6.1
Benzo[ghi]perylene	3.1	1.8	2.6	2.5	4.4
Coronene	8.8	NA	NA	8.8	8.9

[a]NA = not available, due to lack of rain or air data.
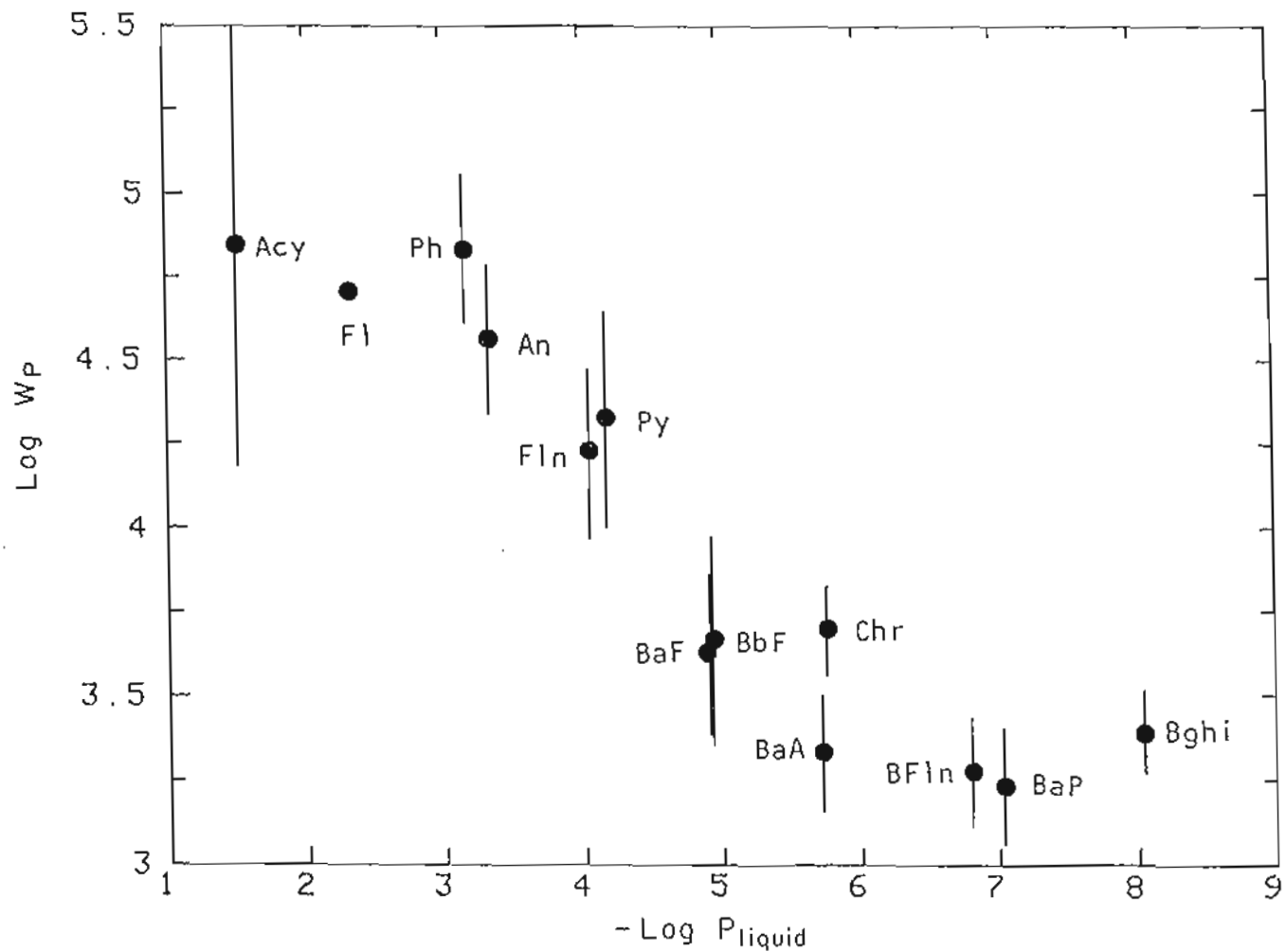
Figure 6.15. Mean particle scavenging ratios of PAHs as a function of supercooled liquid vapor pressure at the Oregon coast. Abbreviations are as in Figure 6.13.
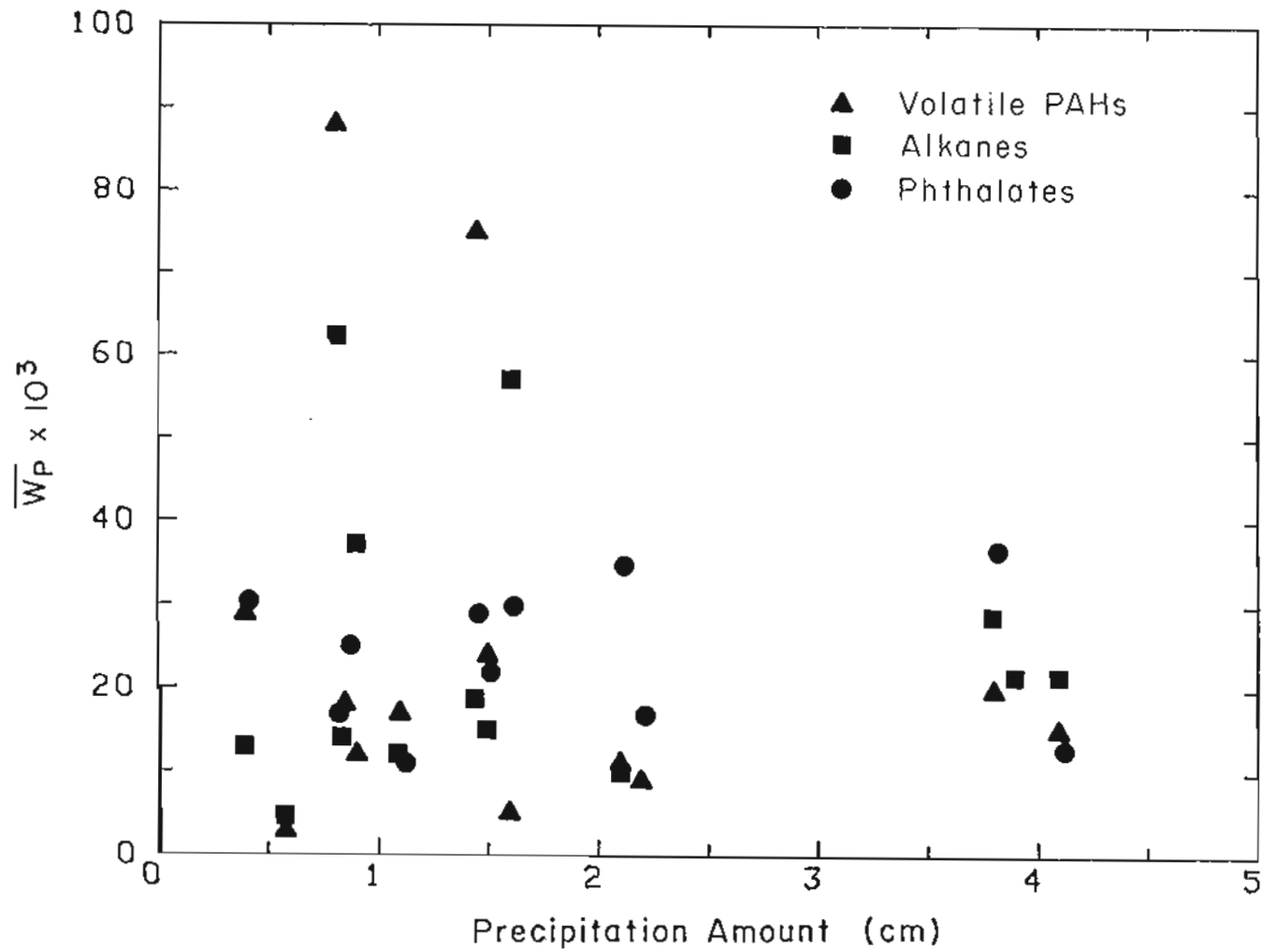
Figure 6.16. Mean W_p values as a function of precipitation amount for volatile PAHs, alkanes, and phthalates.
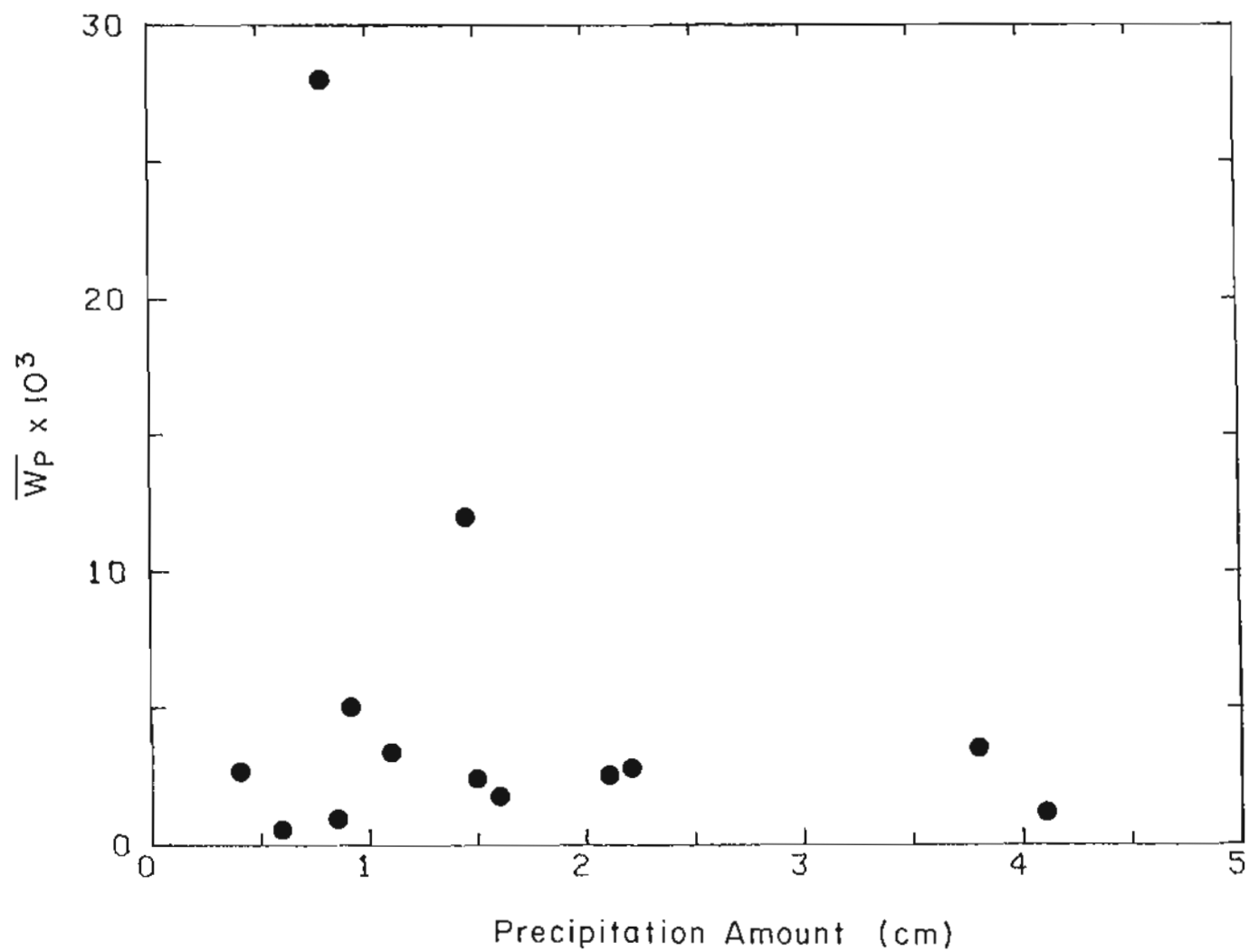
Figure 6.17. Mean W_p values as a function of precipitation amount for nonvolatile PAHs.

Furthermore, neither storm type nor precipitation intensity showed any correlation with the W_p values. Thus it appears that the meteorological data collected in this study was not sufficient to draw any conclusions about the effects of meteorology on particle scavenging.

6.2.4 Interpretation of Particle Scavenging Ratios

The larger W_p values found for the more volatile PAH compounds may be due to the presence of these compounds on larger particles. DeWiest (1978) found that 44% of the aerosol-bound fluoranthene was associated with particles larger than 1 μm, while no benzopyrenes were associated with that fraction. This may be attributed to the greater tendency of the more volatile compounds to re-distribute onto larger particles in the atmosphere while the less volatile compounds remain on the small particles on which they were emitted. However, the re-distribution would occur gradually as the aerosol ages. The resulting size distribution will vary depending upon the proximity of the sources to the sampling point.

The data presented in Tables 5.5 and 5.7 suggest that the majority of scavenged PAHs may be associated with large particles, because roughly 90% were trapped by the 10 μm pre-filter. As discussed in Section 5.2.4, an alternate interpretation for the predominance of large particles on the filter is that coagulation of smaller particles occurs within the raindrop. However, if a majority of the scavenged PAHs were genuinely associated with larger particles and the less volatile PAHs are less likely to be associated with that fraction, then the

observed difference in W_p values among the PAHs makes sense. A decrease in W_p values with decreasing particle size in the 0.1 to 10 μm range has been reported for inorganics (Gatz, 1976). Furthermore, since below-cloud scavenging rates are low for micron-sized particles and increase with particle size, both the observed increase in W_p values for compounds associated with larger particles and the overall magnitude of the scavenging ratios are consistent with a below-cloud removal mechanism for PAHs.

Recent work by Ogren et al. (1984) has suggested that elemental carbon particles can be scavenged by the same mechanisms as are hygroscopic particles, due to the coating of the carbonaceous particles with hygroscopic substances. Those authors reasoned that in urban areas where carbonaceous particles have not had time to become coated, elemental carbon would be scavenged less readily than in remote areas. While elemental carbon scavenging was not measured directly in the present study, the concentrations of elemental carbon and PAHs were strongly correlated in the Portland air particulate samples (Table 6.6). The fact that measured W_p values were very low compared to typical values for hygroscopic substances indicates that the coating effect on scavenging of carbonaceous particles was not significant in Portland. Furthermore, the similarity in the W_p values at the non-urban coastal site indicates that the coating effect was not apparent at that location either.

Table 6.6. Concentrations of Atmospheric Particulate Organic and Elemental Carbon, Benzo[a]pyrene and Total PAHs in Portland, Oregon in 1983-1985.

Date	OC (μg/m^3)	EC (μg/m^3)	BaP (ng/m^3)	PAHs[a] (ng/m^3)
4/21/83	2.4	1.3	0.59	4.4
2/23/84	5.8	1.6	0.99	9.5
2/29/84	17	4.0	2.2	22
3/16/84	4.9	2.7	0.88	8.8
4/11/84	7.5	2.2	0.61	6.7
2/14/85	18	8.8	4.9	38
3/3/85	7.1	2.4	1.5	13
3/21/85	5.2	2.2	1.5	14
3/26/85	5.3	2.0	1.9	17

Correlation (r) of BaP/EC   0.95

PAH/EC   0.93

[a] Sum of phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, benzopyrenes, benzo[ghi]perylene and coronene.

Finally, as discussed in Section 3.3.1, some researchers feel that W_p values are not useful parameters to measure because they do not remain constant throughout storm events. Certainly the W_p values do vary from event to event for a given compound. However, for the storms sampled in this study, there is no correlation between size of storm event and W_p value. The W_p values measured here are storm averages and as such are not useful for eliciting information on the mechanisms involved in particle scavenging. They do, however, provide average values which can be used in modeling wet deposition, and are valuable for that reason. Mean W_p values which are weighted by precipitation amount are calculated and discussed in Chapter 8.

6.3 Overall Scavenging Ratios

The mean W_p values are compared to the mean W_g values for the Portland sampling in Table 6.7, and for the coastal sampling in Table 6.8. Also presented are the mean ϕ values from Table 4.13 and the resulting mean overall scavenging ratios, W. Because ϕ is small for the more volatile PAHs, W values are similar (3000-9000) for all PAHs despite the large differences in the W_p values.

The dominant scavenging mechanism for each compound is determined by the relative magnitudes of $W_g(1-\phi)$ and $W_p\phi$. The relative contributions of gas and particle scavenging for the PAHs in the Portland samples are shown graphically in Figure 6.18. Gas scavenging dominated over particle scavenging for all PAHs and oxo-PAHs of MW < 228. Particle and gas scavenging were equally important for PAH of MW = 228,

Table 6.7. Mean φ Values, Mean Particle (Wp), Gas (W_g) and Overall (W) Scavenging Ratios, and Dominant Scavenging Mechanisms (DSM) for Organic Compounds in Portland, Oregon in 1984-85.

Compound	Mean φ	Mean W_p	Mean W_g	Mean W^a	DSM
α-HCH	0.0	NA[c]	42000	42000	g
Diethylphthalate	0.0	NA	24000	24000	g
Dibenzofuran	0.002	36000	950	1000	g
Fluorene	0.006	31000	1600	1600	g
Phenanthrene	0.010	34000	3100	3400	g
9-Fluorenone	0.018	19000	16000	16000	g
2+3-Methylphenanthrene	0.025	26000	2700	3400	g
1+4+9-Methylphenanthrene	0.027	24000	3100	3600	g
Xanthone	0.039	18000	22000	22000	g
Fluoranthene	0.061	22000	6300	7300	g
Pyrene	0.083	17000	6100	7000	g
Eicosane	0.15	31000	NA	4700	p
Benzo[a]fluorene	0.19	19000	5100	7700	g
9,10-Anthracenedione	0.19	8700	36000	31000	g
Benzo[b]fluorene	0.22	15000	5400	7500	g
Heneicosane	0.33	30000	NA	10000	p
Butylbenzylphthalate	0.42	11000	14000	13000	g
Docosane	0.47	28000	NA	13000	p
Dioctylphthalate	0.56	36000	20000	30000	p
Tricosane	0.6 (est)	31000	NA	19000	p
Chrysene	0.72	6400	17000	9400	g/p
Benz[a]anthracene	0.76	2400	10000	4200	g
Tetracosane	0.8(est)	24000	NA	19000	p

Table 6.7 (cont'd). Mean ϕ Values, Mean Particle (W_p), Gas (W_g) and Overall (W) Scavenging Ratios, and Dominant Scavenging Mechanisms (DSM) for Organic Compounds in Portland, Oregon in 1984-85.

Compound	Mean ϕ	Mean W_p	Mean W_g	Mean W^a	DSM
Benzo[b+j+k]fluoranthene	0.96	4400	10000	4600	p
7-Benz[de]anthracenone	0.97	2300	180000	7600	g
Benzo[e]pyrene	0.98	4100	5800	4100	p
Benzo[a]pyrene	0.99	3400	NA	3400	p
Perylene	1.0	4300	NA	4300	p
Pentacosane	1.0	29000	NA	29000	p
Hexacosane	1.0	24000	NA	24000	p
Octacosane	1.0	40000	NA	40000	p
7,12-Benz[a]anthracene dione	1.0	14000	NA	14000	p
Indeno[1,2,3-cd]pyrene	1.0	6100	NA	6100	p
Dibenz[a,c]anthracene+ Dibenz[a,h]anthracene	1.0	1600	NA	1600	p
Benzo[ghi]perylene	1.0	4400	NA	4400	p
Coronene	1.0	8900	NA	8900	p

$^a W = W_p\phi + W_g(1-\phi)$. $^b g$ = gas; p = particle. ^{c}NA = not available.

Table 6.8. Mean ϕ Values, Mean Particle, Gas and Overall Scavenging Ratios (W_p, W_g, and W), and Dominant Scavenging Mechanisms (DSM) for Organic Compounds at the Oregon Coast in 1985.

Compound	Mean ϕ	Mean W_p	Mean W_g	Mean W^a	DSM
a-HCH	0	NA^c	41000	41000	g
Diethylphthalate	0	NA	9600	9600	g
Dibenzofuran	0.002	72000	1200	1300	g
Fluorene	0.002	50000	1700	1700	g
Phenanthrene	0.006	73000	3100	3500	g
9-Fluorenone	0.010	49000	12000	12000	g
2+3-Methylphenanthrene	0.023	38000	2700	3500	g
1+4+9-Methylphenanthrene	0.027	41000	3200	4200	g
Fluoranthene	0.047	25000	6400	7300	g
9,10-Anthracenedione	0.073	19000	16000	16000	g
Pyrene	0.075	19000	7600	8500	g
Butylbenzylphthalate	0.11	29000	5000	7600	g
Benzo[a]fluorene	0.13	4700	2100	2400	g
Benzo[b]fluorene	0.14	5400	2000	2500	g
Chrysene	0.44	5100	5100	5100	g/p
Benz[a]anthracene	0.48	2300	5500	4000	g
7-Benz[de]anthracenone	0.79	2200	7400	3300	g/p
7,12-Benz[a]anthracene dione	1.0	8400	NA	8400	p
Benzo[b+j+k]fluoranthene	1.0	2000	NA	2000	p

Table 6.8. Mean ϕ Values, Mean Particle, Gas and Overall Scavenging Ratios (W_p, W_g, and W), and Dominant Scavenging Mechanisms (DSM) for Organic Compounds at the Oregon Coast in 1985.

Compound	Mean ϕ	Mean W_p	Mean W_g	Mean W[a]	DSM
Benzo[e]pyrene	1.0	2200	NA	2200	p
Benzo[a]pyrene	1.0	1800	NA	1800	p
Indeno[1,2,3-cd]pyrene	1.0	2000	NA	2000	p
Benzo[ghi]perylene	1.0	2500	NA	2500	p
Coronene	1.0	8800	NA	8800	p

[a]$W = W_g (1-\phi) + W_p \phi$. [b]g = gas; p = particle. [c]NA = not available.
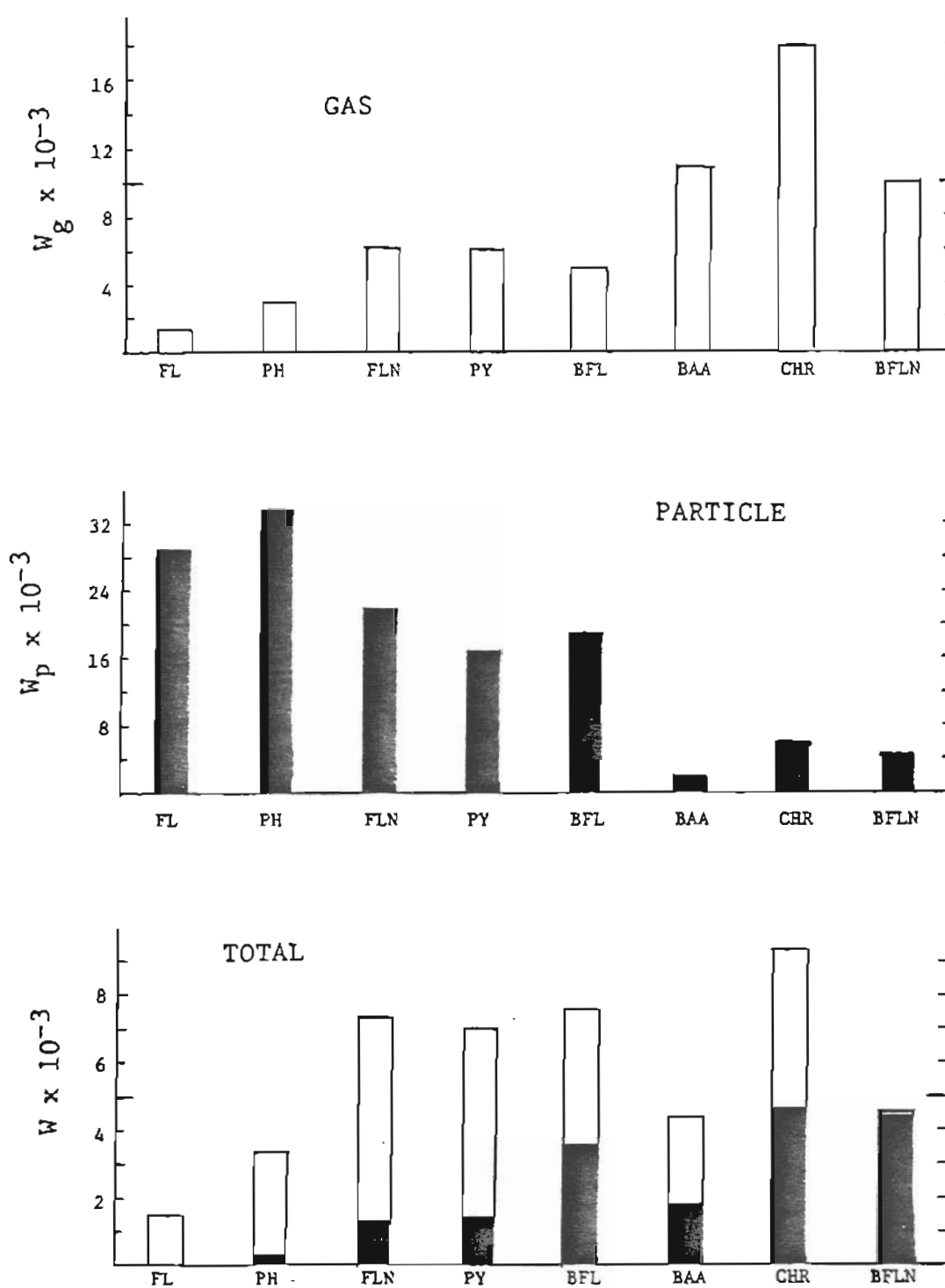
Figure 6.18. Absolute and relative magnitudes of the gas and particle scavenging contributions for PAHs.

and particle scavenging dominated for PAHs of MW > 228. Particle sca-
venging also dominated for the alkanes, which are essentially insoluble
in water and hence have W_g values too low to measure. For the phtha-
lates and oxo-PAHs, the W_g and W_p values were of similar magnitudes and
the dominant scavenging mechanism simply depended on the physical form
of the compound. For the coastal samples, the same trends were ob-
served with the exception of the decreased W_g values for the least
volatile vapor phase PAHs. As discussed in Section 6.1.2, these low W_g
values are believed to have been caused by analytical errors.

Only a few measurements are available in the literature with which
to compare the scavenging data. At Enewetok Atoll, Atlas and Giam
(1981) measured α-HCH and dibutylphthalate at $28^{\circ}C$. They obtained
atmospheric vapor phase concentrations of 0.25 ng/m^3 and 0.87 ng/m^3 and
rain concentrations of 3.1 ng/L and 31 ng/L, respectively. Resulting W
values were 12000 for α-HCH and 36000 for dibutylphthalate. Eisenreich
et al. (1980) have compiled non-concurrent rain and air measurements
for the Great Lakes area. They cite average air concentrations
(ng/m^3), rain concentrations (ng/L), and W values of: α-HCH 0.3, 15,
50000; phenanthrene 0.6, 2, 3300; pyrene 1.1, 2, 1800; and benz[a]-
anthracene 0.5, 3, 6000. Simmonds (1984) found vapor phase concentra-
tions for tetrachloroethene averaging 400 ng/m^3, rain concentrations of
0.92 ng/L, and a W value of 2.3. Pankow et al. (1983), utilizing a
previous version of the sampling system employed here, found the fol-
lowing atmospheric vapor concentrations (ng/m^3), rain dissolved concen-
trations (ng/L) and W_g values in Portland, Oregon: 1,4-dichlorobenzene

210, 9.2, 44; naphthalene 530, 120, 230; acenaphthylene 57, 100, 1800; fluorene 18, 26, 1600; and phenanthrene 43, 260, 6000. Most of these W values agree quite well with those determined in the present study.

Past research on the importance of particle vs. gas scavenging for organic compounds has generally focused on the PCBs and pesticides. Most researchers have concluded that particle scavenging is more important than gas scavenging for these compounds (Eisenreich et al., 1981; Atkins and Eggleton, 1971). This is likely to be true for the PCBs, which have gas scavenging ratios of only 10-100. However, this work has shown that many higher MW organic compounds do not behave in this manner. In particular, compounds such as α-and γ-HCH, PAHs, PAH ketones and quinones, and phthalate esters have W_g values equal to or larger than their W_p values. Gas scavenging will dominate for most of these compounds.

6.4 Predictive Equations for Scavenging Ratios

As discussed in Section 6.1.1, gas scavenging of many non-reactive trace organic compounds can be predicted using the Henry's Law Constant applied at the appropriate temperature. The value of ϕ can be estimated to a reasonable degree of certainty using Equation 2.1. As discussed in Sections 6.2.1 and 6.2.4, particle scavenging is more difficult to predict. When measurements cannot be made at the site of interest, a constant W_p value of 2×10^4 is the best choice for alkanes and

phthalates. The W_p values for the PAHs and oxo-PAHs are likely to be site-dependent, but may vary from 10^3 to 5×10^4. Values for the higher molecular weight PAHs are likely to be lower than for the other compounds. Values for the vapor/particle distribution of the compound of interest may be obtained from its vapor pressure and the data in Figures 4.8-4.10, or, if TPC information is available, from Figure 4.11. Thus the vapor pressure and solubility, along with the compound class, are sufficient to predict the scavenging of organic compounds. Even if the vapor pressure and solubility are not available for the compound of interest, these parameters can be estimated from more basic properties (Lyman et al., 1982; Mackay et al., 1982).

CHAPTER 7 A MODEL FOR THE RATE OF MASS TRANSFER
OF ORGANIC VAPORS INTO RAINDROPS

In Chapter 6, equilibrium gas scavenging was found to have occur-
red for PAHs. However, some deviations from equilibrium behavior were
found for the phenols, which have the highest α values of all the tar-
get compounds. Thus, the possibility that equilibrium gas scavenging
has a dependence upon α values was investigated using a mass transport
model. The results are presented in this chapter.

7.1 Background

The first major study of the dynamics of gas scavenging was done
by Hales (1972), who pointed out that gas scavenging, unlike particle
scavenging, can be a reversible process. He calculated the conditions
under which equilibrium between the rain and air would be approached.
Converted to the notation used here, these conditions are given by:

$$\left| \frac{dy_A}{dz} \right| << - \frac{3\, k_A}{U\, r\, \alpha}\, y_A \qquad\qquad 7.1$$

where y_A is the mixing ratio, or mole fraction, of the gaseous compound
in air and dy_A/dz is the vertical mixing ratio gradient, U is the rain-
drop's terminal fall velocity, r is the drop radius, and k_A is the gas

phase mass transfer coefficient. From Equation 7.1 it can be seen that even large vertical gradients do not affect equilibrium for compounds with α values less than about 10^4. The conclusion from this analysis, stated by Slinn et al. (1978) was that for most compounds equilibrium between the rain and air would be achieved within a fall distance of "tens of meters". No dependence of this value on Henry's Law constant was discussed. Scott (1981) also predicted a short time ($^-$1s) for equilibrium and no dependence on Henry's Law constants.

Several authors (Baboolal et al., 1981; Barrie, 1981; Garland, 1978; Kumar, 1984) have formulated models dealing specifically with the gas scavenging of SO_2. Modelling of the scavenging of SO_2 is difficult, mainly due to complications introduced by inclusion of dissociation and reaction in the aqueous phase. For most phenols and other organic compounds these aqueous phase processes are negligible. This model therefore examines specifically the gas scavenging of atmospheric phenols and other organic compounds with low H values. In addition, possible deviations of measured W_g values from α which are not due to a lack of equilibrium, but rather to the consequences of obtaining a storm-averaged sample, are examined.

7.2 Model Formulation

This model calculates atmospheric and raindrop concentrations as a function of altitude and time. The only processes considered are vertical atmospheric mixing and transfer of vapors between the atmosphere

and the raindrops. The rate of transfer out of the atmosphere and into a raindrop is assumed proportional to the gradient between atmospheric concentration and the equivalent equilibrium concentration, as given by the two-film diffusion model (Whitman, 1923; Liss and Slater, 1974)

$$\text{Flux} = K \ (c_A - c_R/\alpha) \qquad\qquad 7.2$$

In this equation, K contains components of the resistance to mass transfer both in the air surrounding the raindrop and inside the raindrop itself

$$1/K = 1/k_A + 1/\alpha k_R \qquad\qquad 7.3$$

For a stagnant raindrop, the resistances in the air and inside the raindrop will contribute equally to the total resistance for $\alpha = 6500$. However, internal circulation currents develop inside falling raindrops (Pruppacher et al., 1980). These currents tend to greatly increase the value of k_R along certain regions of the drop surface. From the model of Baboolal et al. (1981) it can be calculated that for a falling drop of radius 0.3 mm the gas and aqueous phase resistances are equal for $\alpha = 500$. Since the present model is concerned with compounds which exhibit α values of 10^4 or greater the aqueous phase resistance will be neglected here and K will be replaced by k_A. However, it should be noted that k_R cannot be neglected in the modelling of SO_2 scavenging (Baboolal et al., 1981; Barrie, 1981).

The vertical mixing of an atmospheric compound is dependent upon the change in the mixing ratio of the compound (y_A) rather than the

concentration. For example, the concentration of a well-mixed vapor (constant y_A) at an altitude of 2000 m is approximately 80% of its value at ground level. The use of y_A in the mixing portion of the concentration equation introduces only a small correction and could possibly be neglected. However, for the sake of correctness and because it introduces no particular computational difficulties, it was included here. The concentration and mixing ratio are related by the equation

$$y_A = \frac{RT}{M_A} \; \frac{c_A}{\exp(-z/Z)} \qquad 7.4$$

where M_A is the molecular weight and Z is the altitude at which the atmospheric density is reduced to 1/e of its ground-level value. The value of Z used here was 8000 m. The equation for the change in vapor phase concentration, c_A, as a function of altitude and time is

$$\frac{\partial c_A}{\partial t} = D \; \frac{M_A}{RT} \exp(-z/Z) \; \frac{\partial^2 y_A}{\partial z^2} - k_A \, (4\pi r^2 N) \, (c_A - c_R/\alpha) \qquad 7.6$$

where r is the drop radius, N is the number of drops per m^3, and the quantity $4\pi r^2 N$ thus represents the total raindrop surface area concentration. D is an eddy diffusion coefficient. The first term on the right-hand side of Equation 7.6 represents turbulent vertical mixing and the second term represents flux into raindrops. The equation for the change in raindrop concentration, c_R, is

$$\frac{\partial c_R}{\partial t} = U \frac{\partial c_R}{\partial z} + \frac{3}{r} k_A (c_A - c_R/\alpha) \qquad 7.7$$

where U is the terminal raindrop fall velocity. Note that Equation 7.7 is written from an Eulerian viewpoint; i.e., the concentration is expressed as a function of absolute height in the atmosphere rather than as a function of the distance travelled by any particular raindrop. The first term on the right-hand side of Equation 7.7 represents advection of concentration by falling raindrops. The $3/r$ factor in the second term is the surface area to volume ratio of a sphere.

Equations 7.6 and 7.7 comprise a set of coupled, second-order partial differential equations, for which an analytical solution is difficult to obtain. However, it is not difficult to discretize these equations and solve them numerically. To accomplish this, the model atmosphere was divided into homogeneous layers of depth h. To a first-order approximation, Equation 7.6 can be rewritten in the following discrete form

$$\frac{c_A(z,t+k)-c_A(z,t)}{k} = D \frac{M_A}{RT} \exp(-z/Z) \frac{y_A(z+h,t)-2y_A(z,t)+y_A(z-h,t)}{h^2}$$
$$- k_A (4\pi r^2 N) (c_A(z,t) - c_R(z,t)/\alpha) \qquad 7.8$$

where k is the time step and the first term on the right now represents mixing between adjacent layers. Equation 7.7 becomes:

$$\frac{c_R(z,t+k)-c_R(z,t)}{k} = U \frac{c_R(z+h,t)-c_R(z,t)}{h}$$

$$+ \frac{3}{r} k_A (c_A(z,t) - c_R(z,t)/\alpha) \qquad 7.9$$

For simplicity, this model assumes spherical raindrops of a uniform size falling at their terminal velocity. Mean raindrop radius can be estimated from the precipitation rate P by the following relationship (Mason, 1971)

$$r = 0.3659 \ P^{0.21} \qquad 7.10$$

where P is in mm/h and r is in mm. The drop fall velocity U may then be calculated from the data of Beard and Pruppacher (1969). Once that is known, the number of drops per cubic meter, N, can then be calculated from a flux balance on P and U as follows

$$N = \frac{3P}{4\pi r^2 U} \qquad 7.11$$

The value of k_A for spherical raindrops of radius 0.02 - 0.6 mm under "forced convection " conditions is given by the Frossling equation (Barrie, 1981)

$$\frac{k_A \ r}{D_A} = 1 + 0.3 \ Re^{1/2} \ Sc^{1/3} \qquad 7.12$$

where D_A is the molecular diffusion coeffcient in air, Re is the rain-

drop Reynolds number (Re = $2Ur/\nu$), and Sc is the Schmidt number (Sc = ν/D_A). In the preceding equations, ν is the kinematic viscosity of air. The values of these parameters which were used in the present study are given in Table 7.1.

Two initial atmospheric concentration profiles were examined. The first is a well-mixed atmosphere. This profile is appropriate for compounds such as the pesticide α-HCH, which is globally distributed and has a long atmospheric lifetime. The second initial profile includes a ground-level polluted layer with a 10% background well-mixed concentration. The second profile may be appropriate for compounds such as the alkylphenols, which are formed during combustion processes (Hubble et al., 1982) as well as through photochemical oxidation of aromatic compounds (Atkinson et al., 1980). The polluted layer model was examined for the case of no source during the rainstorm, as would occur if photochemistry provided the dominant source of phenols, and with a ground-level source which continued throughout the storm. The two initial profiles are shown in Figure 7.1.

The boundary conditions selected were that no mixing occurs across the upper (cloud base) and lower (ground) boundaries of the model. The rain is assumed to be organic-free initially as it descends from the cloud. The initial ground-level concentration ($c_A(0,0)$) is set to a value of 100. The cloud base height chosen was 2000 m (Kumar, 1984).

The effect of variation of precipitation rate during the course of a storm was also investigated. Precipitation rate profiles for three actual rainstorms in Portland, Oregon are shown in Figure 7.2 as exam-

Table 7.1. Model Parameters.

D	20 m^2/s	
D_A	0.15 cm^2/s	
u	0.0176 cp (10^oC)	
v	0.14 cm^2/s (10^oC)	
h	40 m	
P	5 mm/h	1 mm/h
r	0.51 mm	0.37 mm
U	4.1 m/s	2.9 m/s
N	600 drops/m^3	470 drops/m^3
k_A	0.177 m/s	0.188 m/s
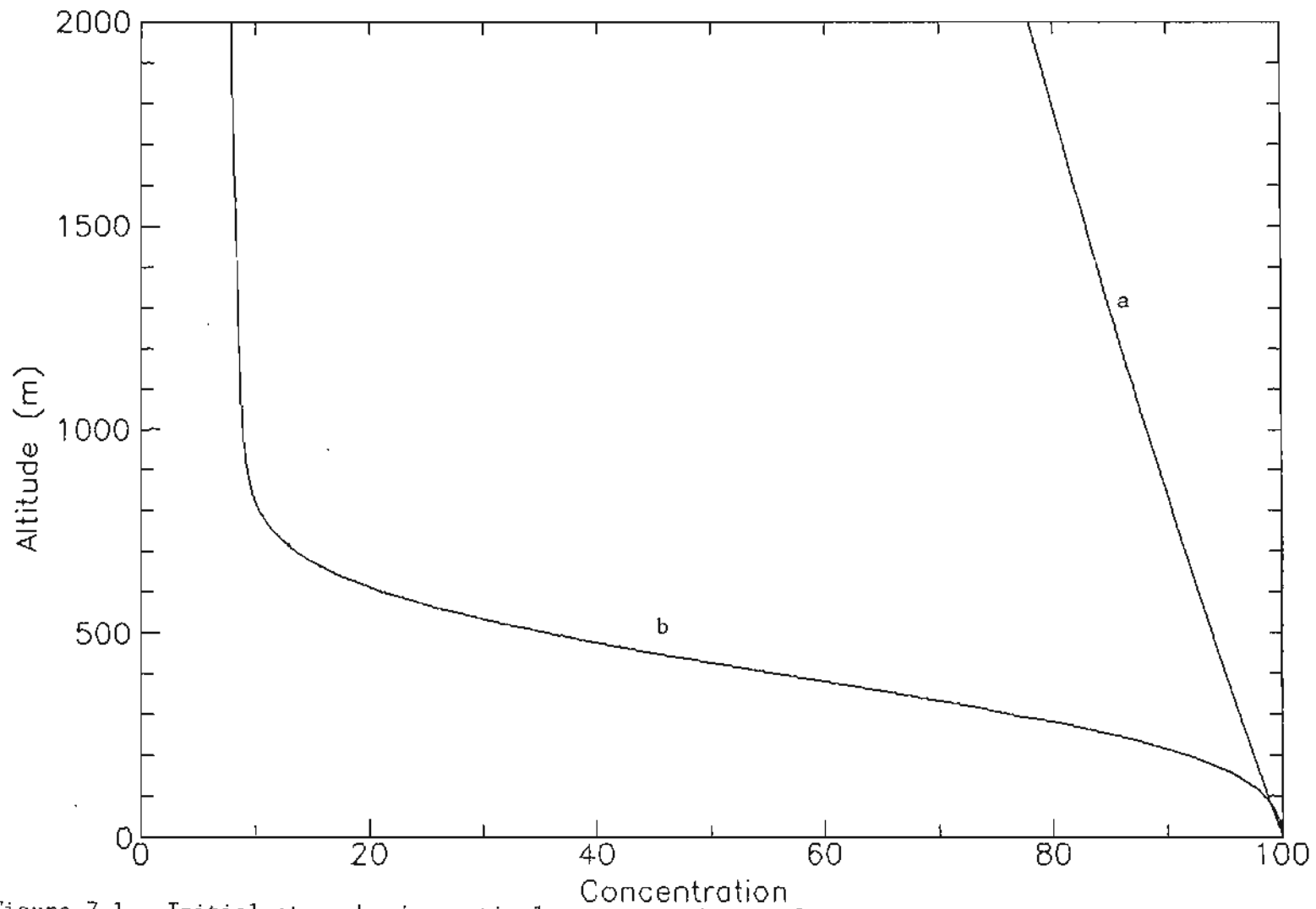
Figure 7.1. Initial atmospheric vertical concentration profiles: a)well-mixed; b)polluted layer.
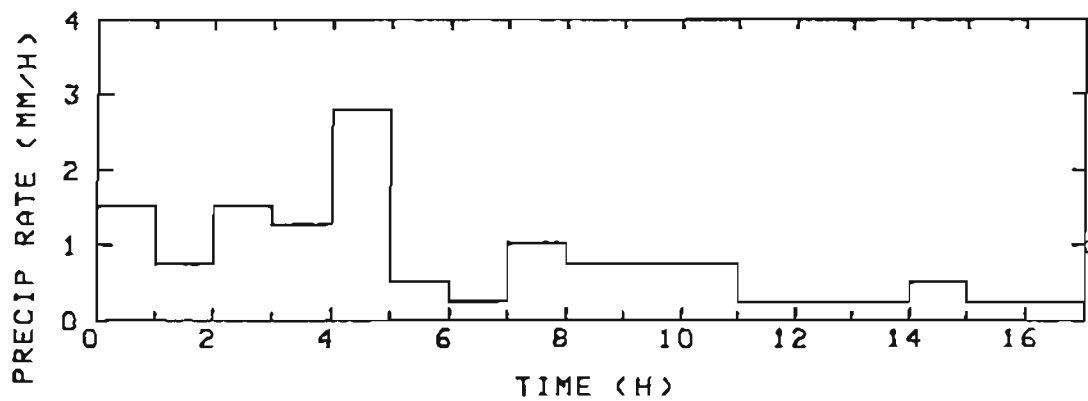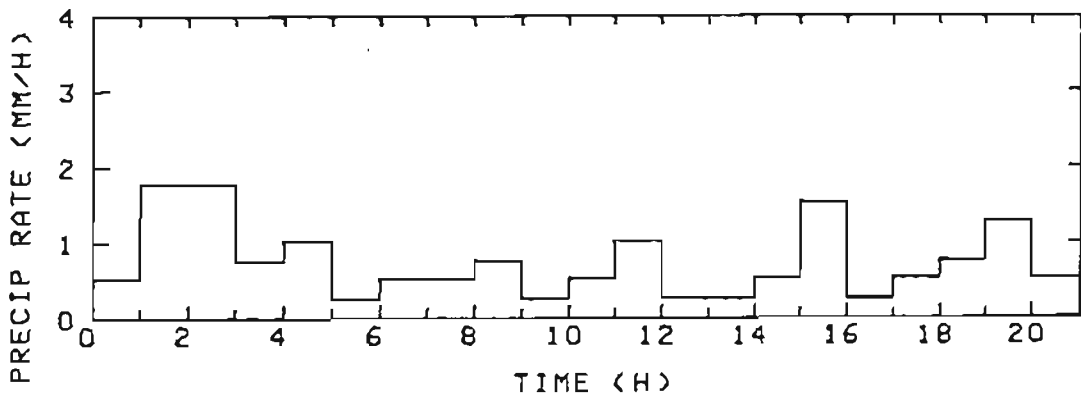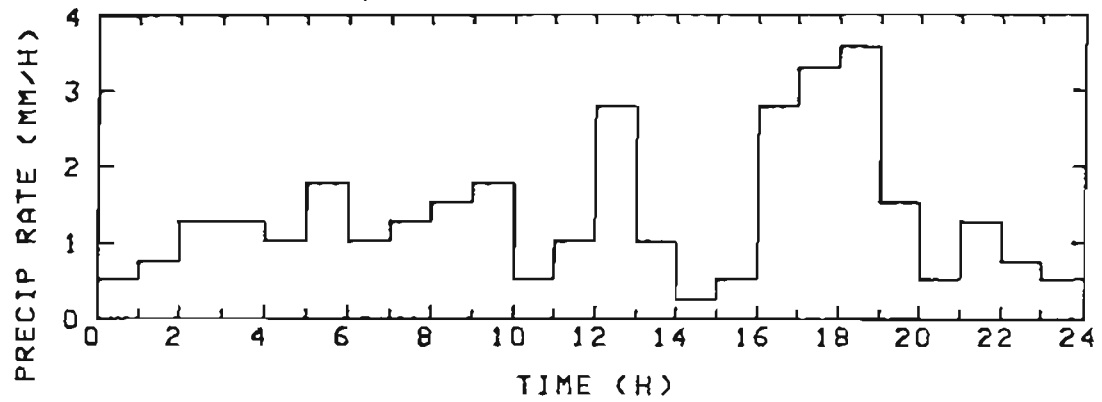
Figure 7.2. Precipitation rate profiles for several Portland storms in 1984.
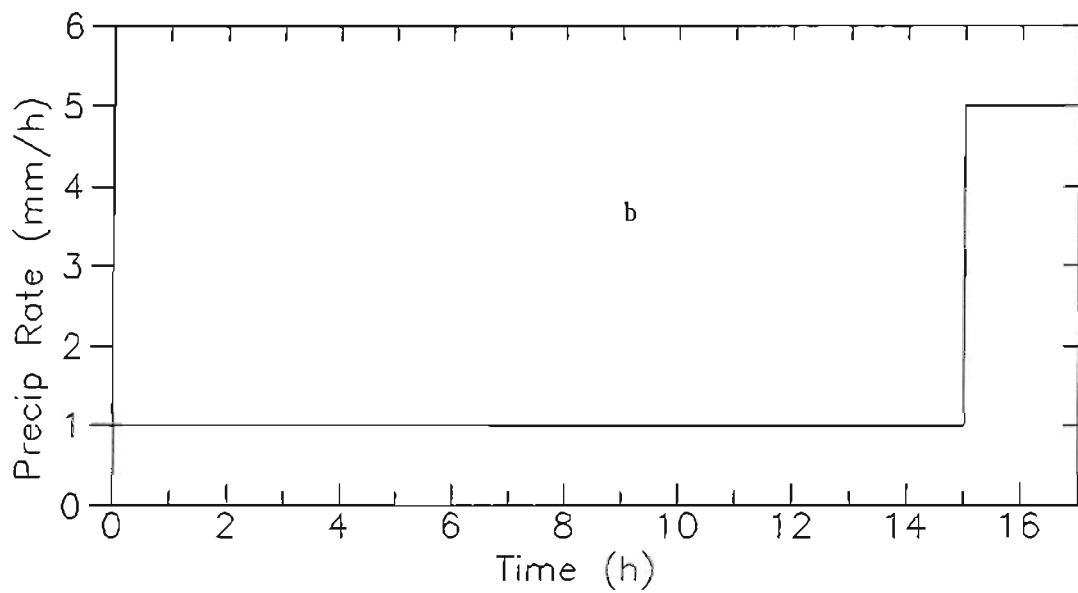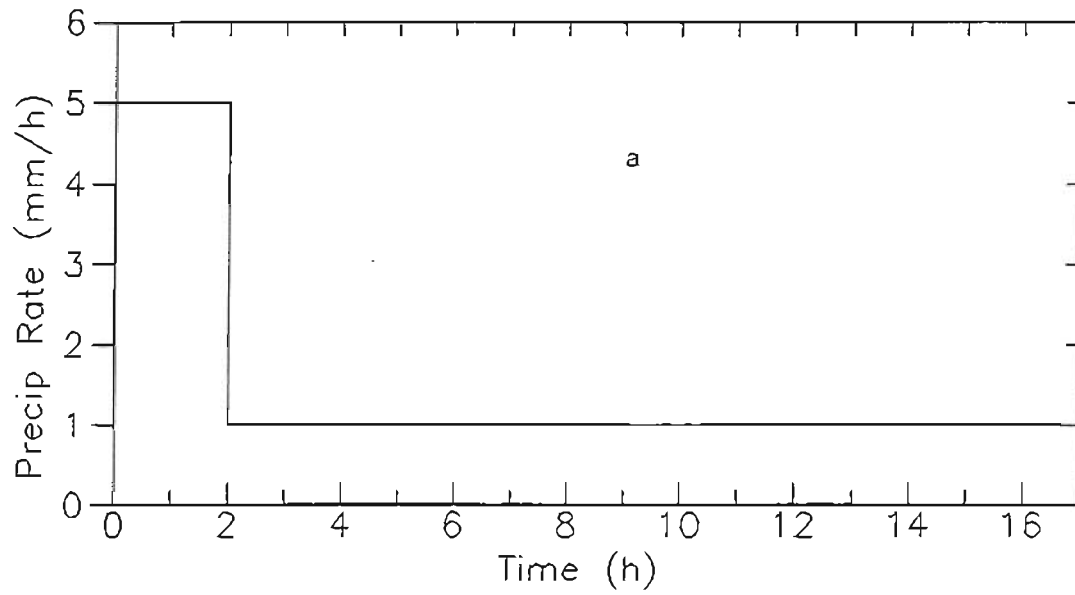
Figure 7.3. Hypothetical precipitation profiles used to determine the effects of variable precipitation rates on storm-averaged Wg values: a) CF profile; b) FC profile.

ples of the degree of variation of P during a storm. In general, cold front-type storms are characterized by initial heavy rainfall, followed by lighter variable showers. Warm front-type storms exhibit steadier, light rain. A frontal cyclone, which is characterized by a warm front followed by a cold front, exhibits the heaviest rain at the end. The rain sampler collected an integrated samples in which the raindrop concentrations during periods of heavy rainfall had more weight than the concentrations during periods of light rainfall. That is,

$$c_{R,meas} = \frac{\int c_R(t)\ P(t)\ dt}{\int P(t)\ dt} \qquad 7.13$$

The air sampler, by contrast, sampled at a steady rate. The storm-averaged W_g value which is obtained from these measured concentrations is thus given by

$$W_{g,meas} = \frac{c_{R,meas}}{c_{A,meas}} = \frac{\left(\int c_R(t)\ P(t)\ dt\right)\left(\int dt\right)}{\left(\int c_A(t)\ dt\right)\left(\int P(t)\ dt\right)} \qquad 7.14$$

It is clear from Equation 7.14 that $W_{g,meas}$ may differ from α even if equilibrium exists at all times throughout the storm unless c_A, c_R and P remain constant.

Two hypothetical precipitation rate profiles (Figure 7.3) were used to investigate the magnitude of this effect. One is the extreme of a cold front (CF) situation, with a brief period of heavy rain followed by a longer period of light rain. The other is the extreme of a

frontal cyclone (FC) in which the period of heavy comes at the end of the storm. Each storm had total rainfall of 2.5 cm. The results will be discussed in terms of the deviation of measured W_g values from α in the event that equilibrium is maintained at all points during the storm, and in terms of the combined effects of storm averaging and lack of equilibrium.

7.3 Time Required for Rain/Air Equilibration of a Falling Drop

In the absence of mixing and vertical concentration gradients, the time required for a falling raindrop to achieve equilibrium with a constant vapor phase concentration can be computed by solving the Lagrangian form of Equation 7.7

$$\frac{\partial c_A}{\partial t} = \frac{3K}{r} (c_A - c_R/\alpha) \qquad 7.15$$

The solution is

$$c_R(t) = \alpha c_A (1 - \exp(-3Kt/\alpha r)) \qquad 7.16$$

The time required for c_R to reach 63% (1-1/e) of its equilibrium value is given by

$$t^* = \alpha r/3K \qquad 7.17$$

The distance travelled by the raindrop in this period of time is

$$z^* = U\ t^* = U\alpha r/3K \qquad 7.18$$

If resistance inside the raindrop limits the mass transfer, then from Equation 7.4 it can be seen that

$$K = \alpha \, k_R \qquad\qquad 7.19$$

and Equation 7.18 becomes independent of the value of α:

$$z^* = Ur/3k_R \qquad\qquad 7.20$$

Equation 7.20 is similar to the equation for equilibration distance reported by Scott (1981). However, this equation is only valid at extremely low α values ($\alpha < 50$). The distance required for equilibration of raindrops, given by Equation 7.18, is shown as a function of α in Figure 7.4 for two precipitation rates. At low α values this distance is indeed less than 10 m, but for α values $> 10^4$ the distance is considerably larger. From Figure 7.4 it is clear that the assumption of equilibrium, without regard to the α value of the compound in question, could lead to serious error.

7.4 Results from Model Storm Simulations

7.4.1 Well-mixed Atmosphere

Rainstorms were simulated at two precipitation rates and several values for α, ranging from 2×10^4 to 2×10^5. The atmospheric concentration (c_A) was calculated as a function of time and altitude. Figure 7.5 shows vertical profiles of the atmospheric vapor phase concentration for the well-mixed case at various times throughout a model storm.
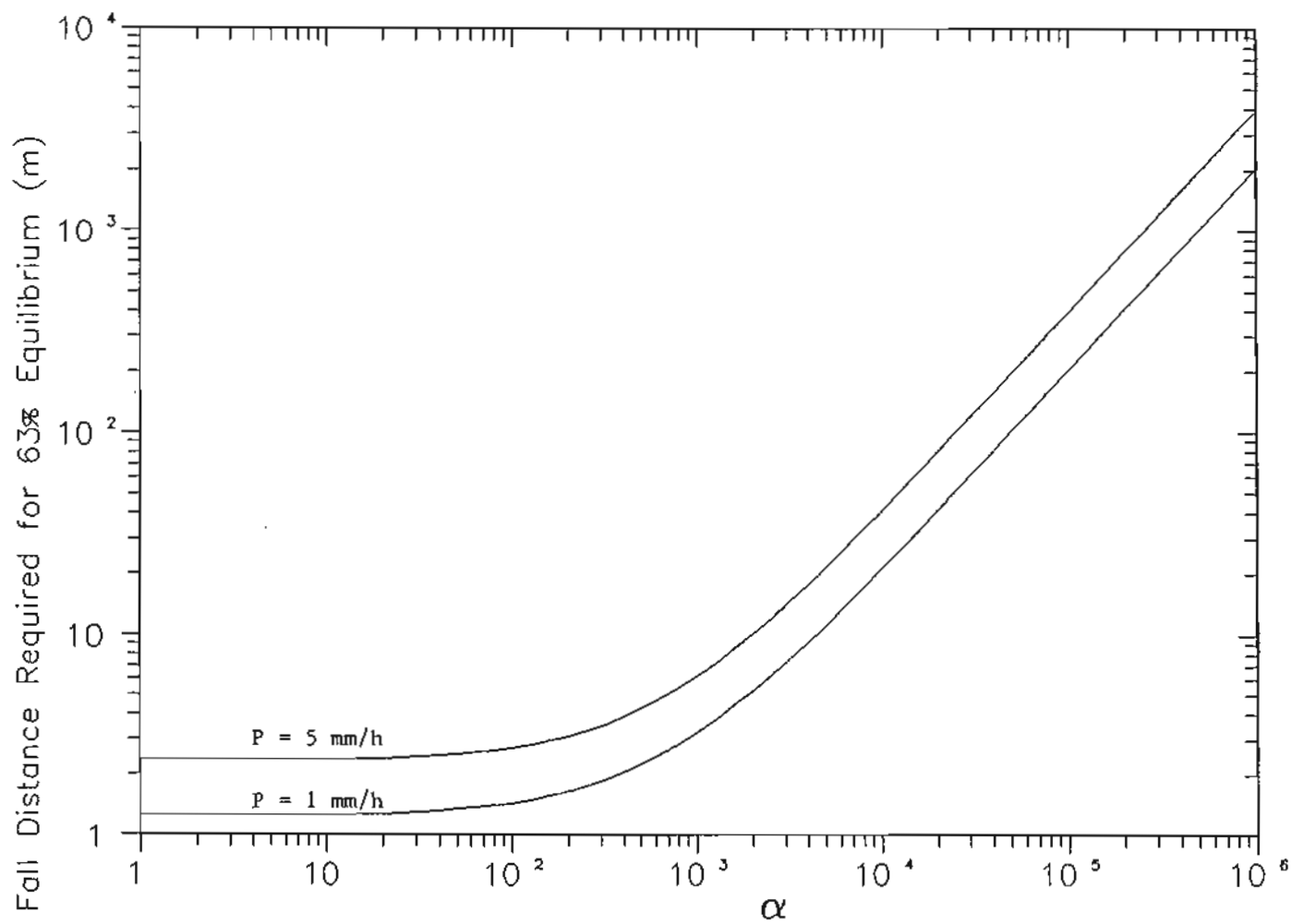
Figure 7.4. Distance required for equilibration of a raindrop falling in a constant-concentration atmosphere.
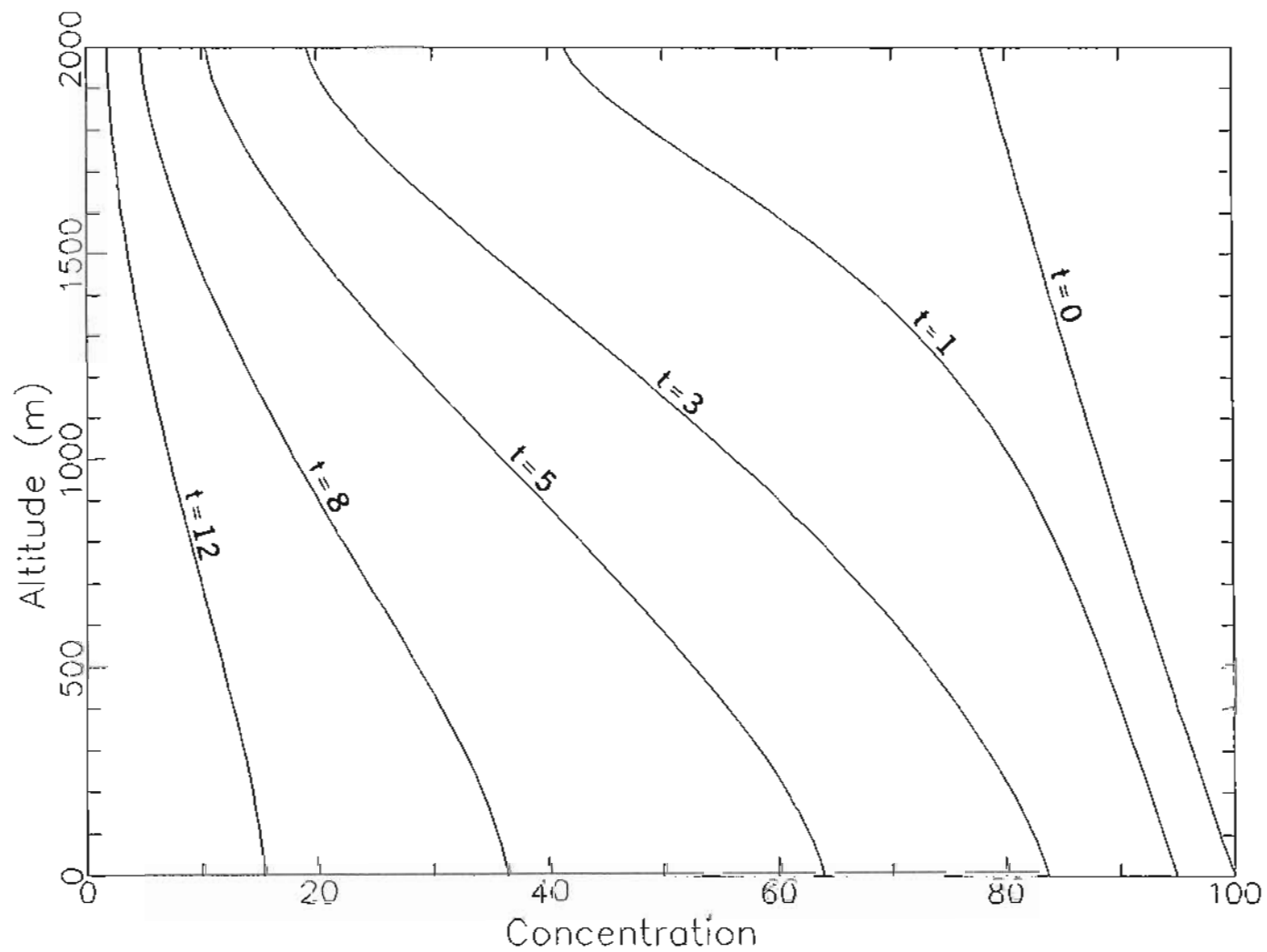
Figure 7.5. Vertical atmospheric concentration profiles throughout the storm: well-mixed initial profile, P=5 mm/h, α=5 x 10^4.

A P value of 5 mm/hr and an α value of 5×10^4 were used for the calculation shown. It can be seen that the concentration in the upper layers of the atmosphere is depleted more rapidly than at ground level. This is due to a rapid uptake of material by the clean raindrop leaving the cloud, followed by much slower uptake as equilibrium with the vapor phase is approached. Because of this depletion, even though the initial concentration profile was well-mixed, concentration gradients develop as the storm progresses. The extent of the gradient formation depends upon the value chosen for the vertical mixing parameter, D: large values of D lead to rapid mixing and hence to smaller gradients.

In Figure 7.6 the ground level atmospheric concentration is plotted as a function of time for various input α values. The ground level concentration changes gradually in the early portion of the storm while the upper atmospheric layers are being depleted, then more rapidly as gradients reach ground level. For $\alpha > 10^5$, the concentration is reduced to <5% of its initial value after 5 cm of rain.

To examine the degree of attainment of rain/air equilibrium, the ratios of the W_g values at ground level to the input α values throughout the storm are plotted in Figure 7.7. Initially, this ratio is close to unity for α values $\leq 10^5$. However, as the storm progresses and the vertical gradients develop, the ratio decreases. It reaches a low of 0.65 for $\alpha = 2 \times 10^5$.

Further calculations were done in order to determine the storm-averaged rain and air concentrations which would be measured by ground-based samplers during these model storms. From these concentrations,
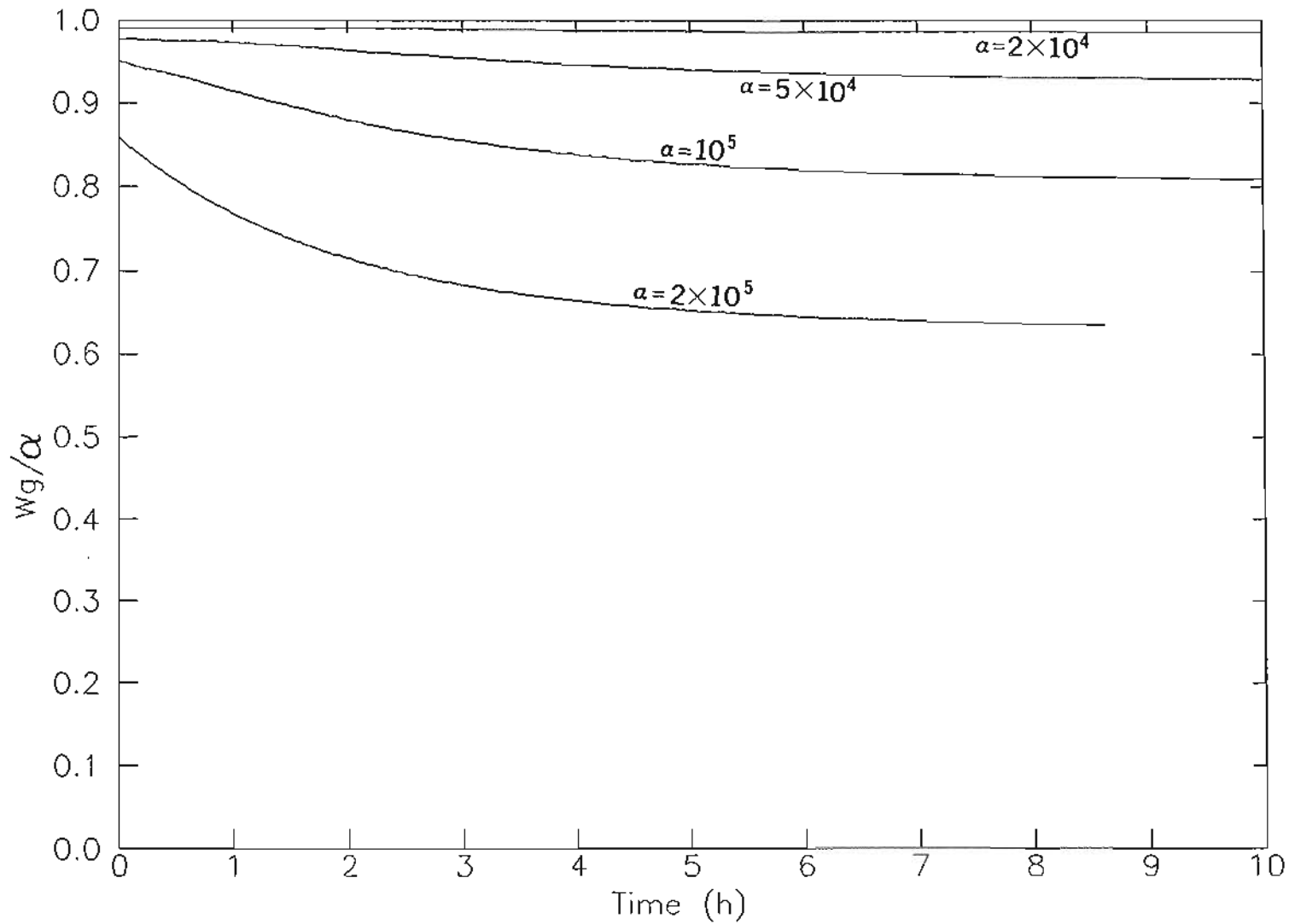
Figure 7.6.   Ground-level atmospheric concentration as a function of time for various α values: well-mixed initial profile, P=5 mm/h.
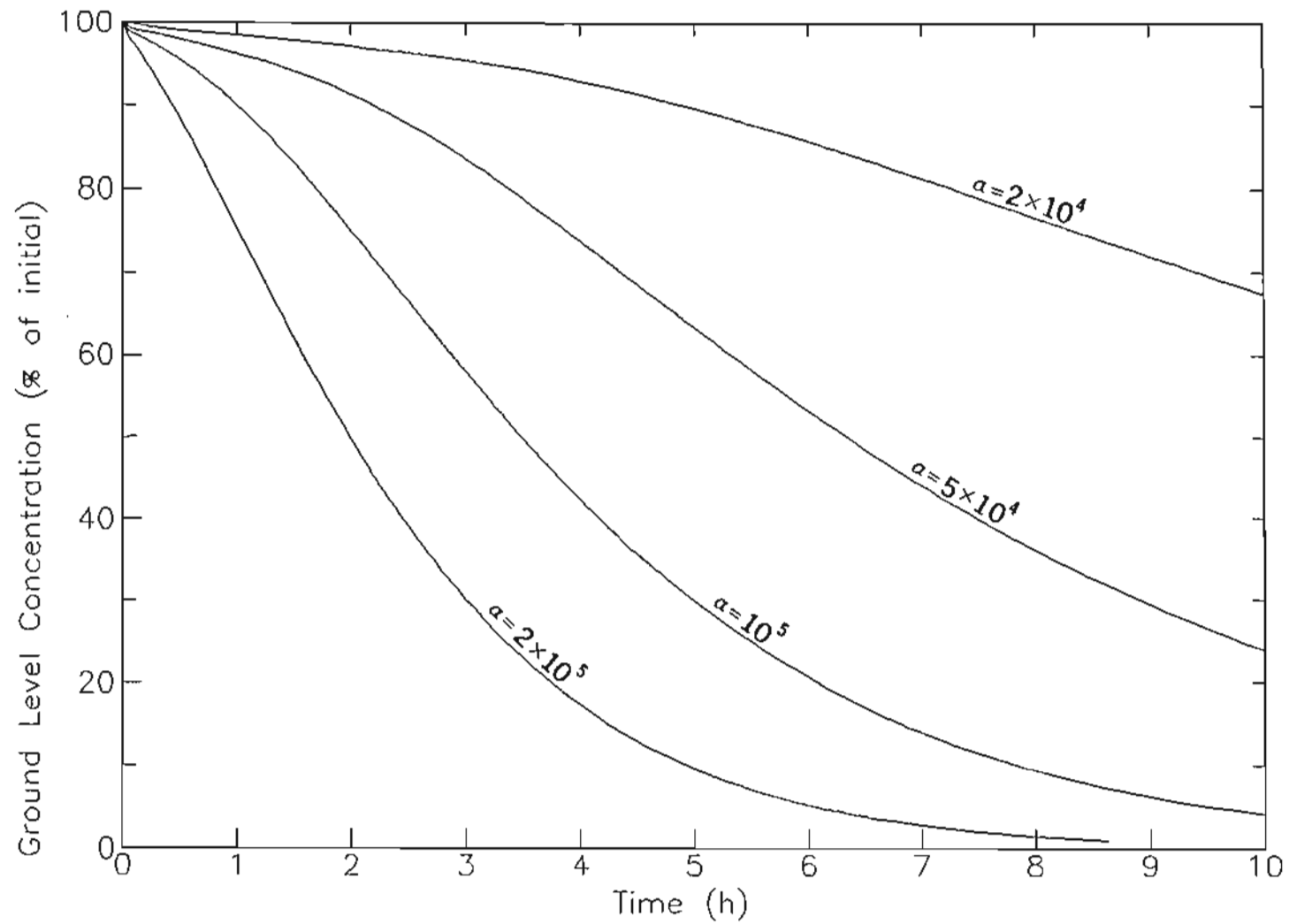
Figure 7.7. Extent of attainment of rain/air equilibrium at ground level for various α values: well-mixed initial profile, P=5 mm/h.

storm-averaged W_g values were obtained from Equation 7.14. Figure 7.8 shows these storm-averaged W_g values as a function of the input α values for constant rainfall rates of 5 mm/h and 1 mm/h, and for the variable precipitation rate profiles CF (heaviest rain at the beginning of the storm) and FC (heaviest rain at the end of the storm).

The absolute magnitude of the rainfall rate affects the degree of attainment of equilibrium because it affects the mean drop size, and hence the drop fall velocity. From Figure 7.8 it can be seen that noticeable deviation of W_g from α begins at about $\alpha = 5 \times 10^4$ for the 5 mm/h case, and at about 1×10^5 for the 1 mm/h case. For the CF precipitation profile $W_{g,meas}/\alpha$ ratios were roughly 1.01 for α values $< 10^4$, for which equilibrium existed at all points during the storm. For $\alpha = 10^5$, $W_{g,meas}/\alpha$ was 1.18. For the FC profile the $W_{g,meas}/\alpha$ ratios were 0.99 for $\alpha < 10^4$, and decreased to 0.81 for $\alpha = 1 \times 10^5$. Thus, for the well-mixed initial profile, deviations due to variation of precipitation rate are not large.

7.4.2 Polluted Layer-No Source

The polluted layer model assumes that an inversion layer at about 400 m exists prior to the onset of rain. This inversion layer dissipates as the storm progresses, allowing mixing with the upper layers. At the same time, the polluted layer is depleted by scavenging. Not surprisingly, the polluted layer is eliminated by a combination of these two effects in a short period of time. For $\alpha = 1 \times 10^5$, only four hours of rainfall at 5 mm/h were required. After this point in
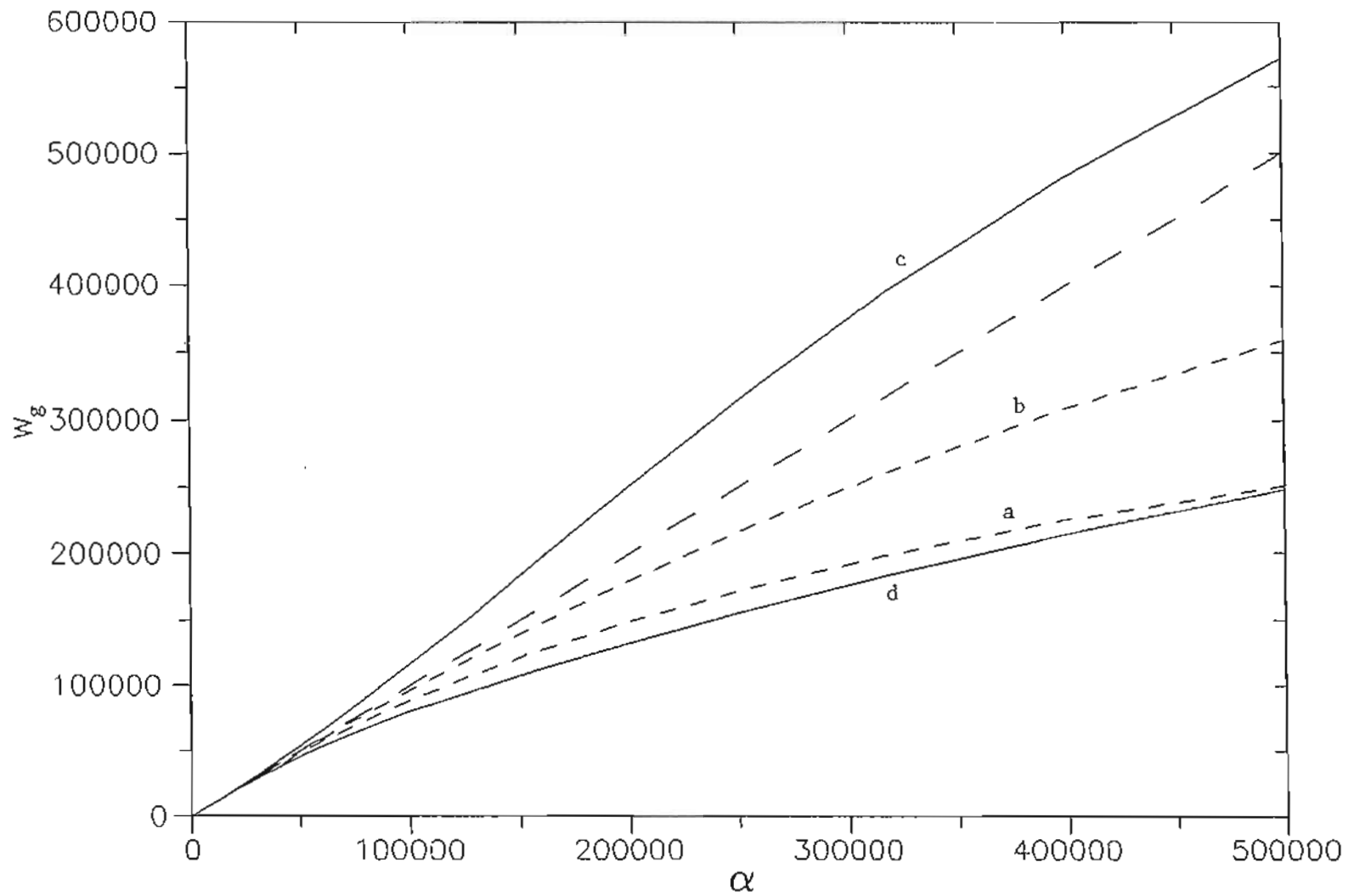
Figure 7.8. Storm-averaged Wg values as a function of α, well-mixed initial profile: a)P=5 mm/h, b)P=1 mm/h, c)CF precipitation profile, d)FC precipitation profile.

the storm, the washout continues in a similar manner to the well-mixed case. Because of the larger initial concentration gradients in the polluted layer case, the degree of attainment of rain/air equilibrium early in the storm is less than for the well-mixed case. As shown in Figure 7.9, for $\alpha = 2 \times 10^5$, the minimum W_g/α value of 0.44 occurs after 1/2 hour of rain. By the end of the storm, this ratio has increased to 0.63, similar to the well-mixed case. The storm-averaged W_g values for this model for constant P values of 1 and 5 mm/h, and variable precipitation rate profiles CF and FC are shown in Figure 7.10. By comparison to Figure 7.8 it can be seen that the deviation of W_g from equilibrium is much greater for the polluted layer case. For the CF precipitation profile, the W_g/α ratio is >1 for $\alpha < 4 \times 10^5$. For $\alpha = 1 \times 10^5$, the ratio is 1.39. For the FC profile, the ratio is 0.73 for $\alpha = 1 \times 10^5$. In contrast to the well-mixed case, here the measured W_g value can vary by nearly a factor of two depending solely upon the precipitation rate profile.

7.4.3 Polluted Layer-With Source

The addition of a continuing ground level source to the polluted layer model causes the vertical gradients to be maintained longer and thus reduces the degree of attainment of equilibrium at ground level. Figure 7.11 shows the ground level concentrations as a function of time for this case. The ground level concentrations for all values of α reach a steady-state with the source after 3 to 6 hours. After this time period, the ground level concentration does not change appreciably
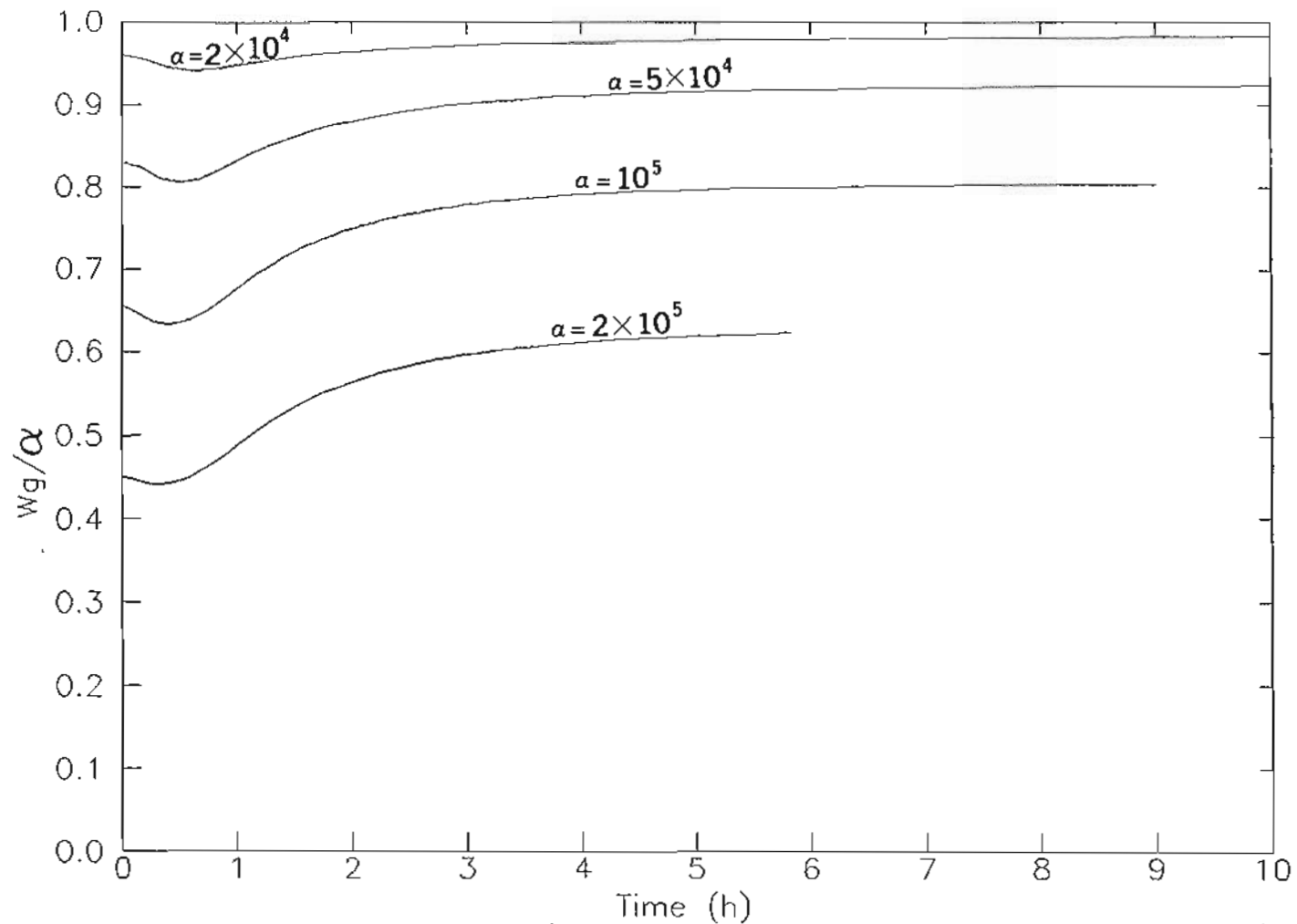
Figure 7.9. Extent of attainment of rain/air equilibrium at ground level for various α values: polluted layer without ground-level source, P=5 mm/h.
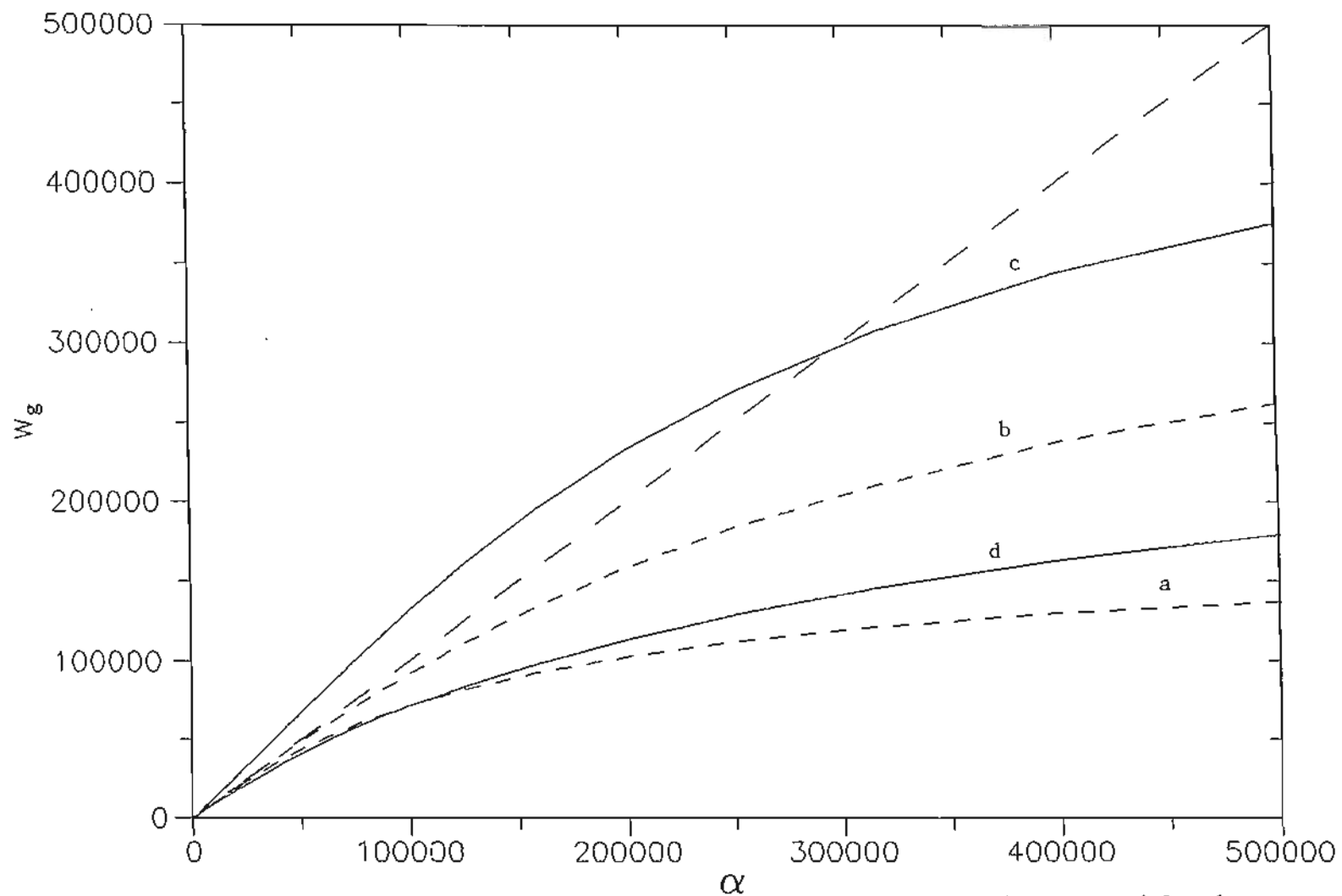
Figure 7.10. Storm-averaged Wg values as a function of α. polluted layer without ground level source: a)P=5 mm/h, b)P=1 mm/h, c)=CF precipitation profile, d)FC precipitation profile.
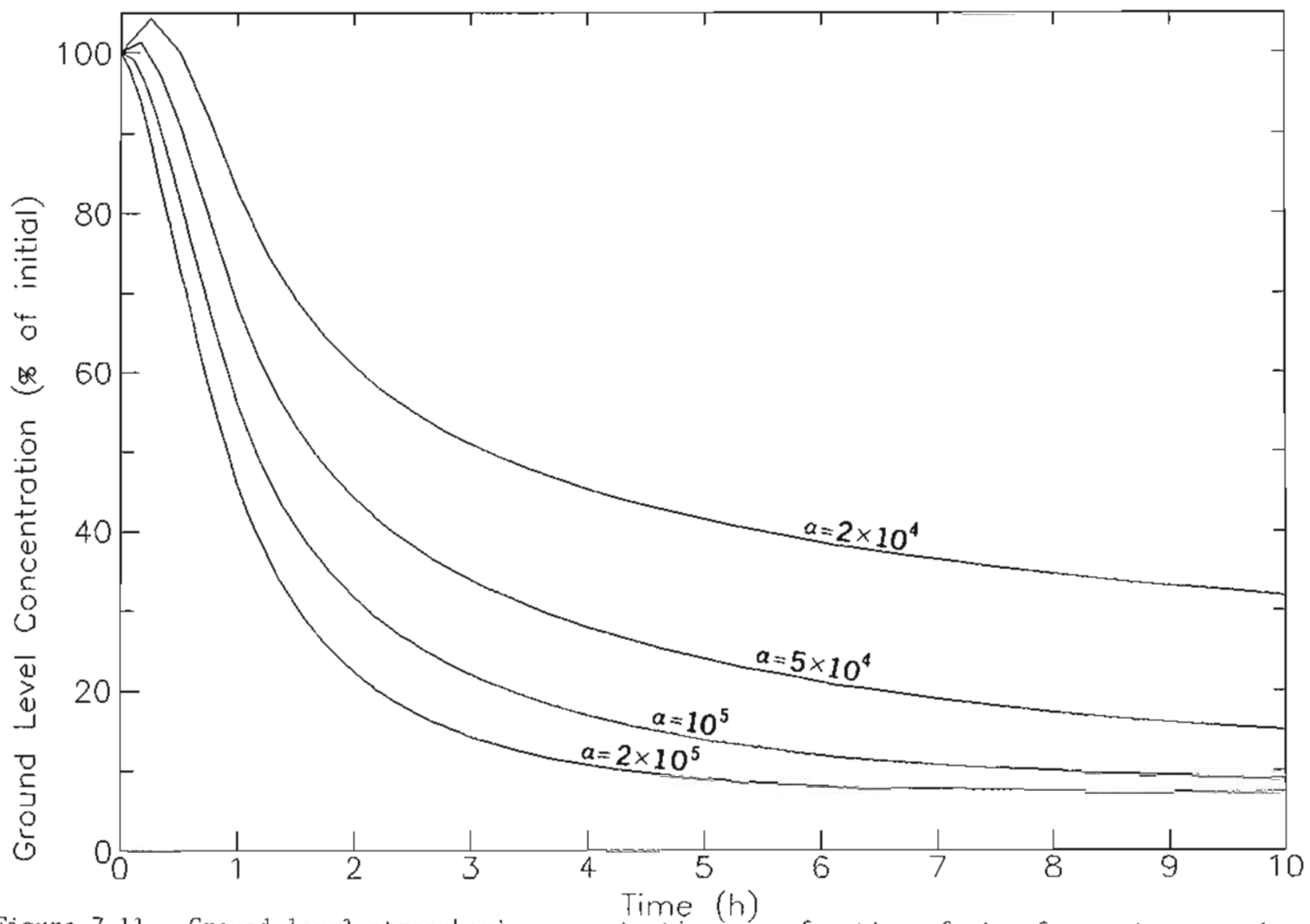
Figure 7.11.   Ground-level atmospheric concentration as a function of time for various α values: polluted layer initial profile with ground-level source, P=5 mm/h.

for the remainder of the storm.

In Figure 7.12 the degree of attainment of rain/air equilibrium is shown for this case. By comparison to Figures 7.7 and 7.9, it can be seen that this model results in the largest deviations from equilibrium, and that the deviations remain large throughout the storm. For $\alpha = 2 \times 10^5$, the minimum W_g/α value is 0.3, compared to 0.47 for the polluted layer with no source, and 0.67 for the well-mixed atmosphere.

The storm-averaged W_g values are plotted as a function of α for both the constant and variable precipitation rates in Figure 7.13. By comparison to Figures 7.8 and 7.10, it can be seen that the deviations from equilibrium are the largest in this case, as might be expected. The predicted W_g values are significantly smaller than α for most profiles. Even for the CF precipitation profile, the W_g/α ratio is only slightly greater than unity for $\alpha < 8 \times 10^4$. For $\alpha > 2 \times 10^5$, the curves for both the CF and FC profiles become almost flat, indicating that W_g shows little dependence on α. If sampling was conducted in this regime, the gas scavenging ratios would show the same pattern as the particle scavenging ratios, varying more with the meteorology of the individual storm events than with the chemistry of the compounds involved.

7.5 Applications to Field Sampling of Phenols and other Low-H Organic Compounds

Several alkylphenols which are found in rain have α values in the 10^5 range. From Table 6.1, W_g/α ratios of roughly 0.25 were found for
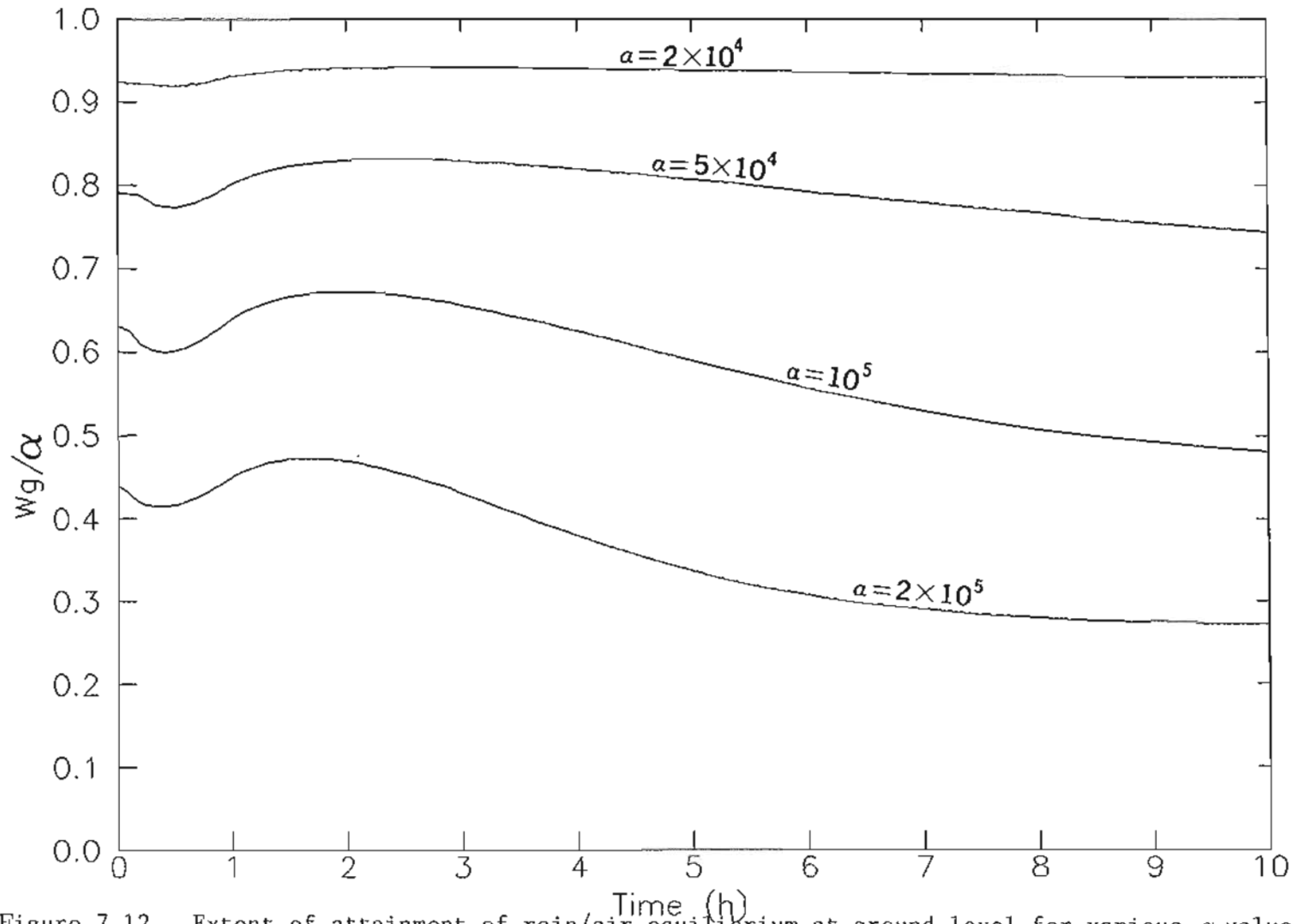
Figure 7.12. Extent of attainment of rain/air equilibrium at ground level for various α values: polluted layer initial profile with ground-level source, P=5 mm/h.
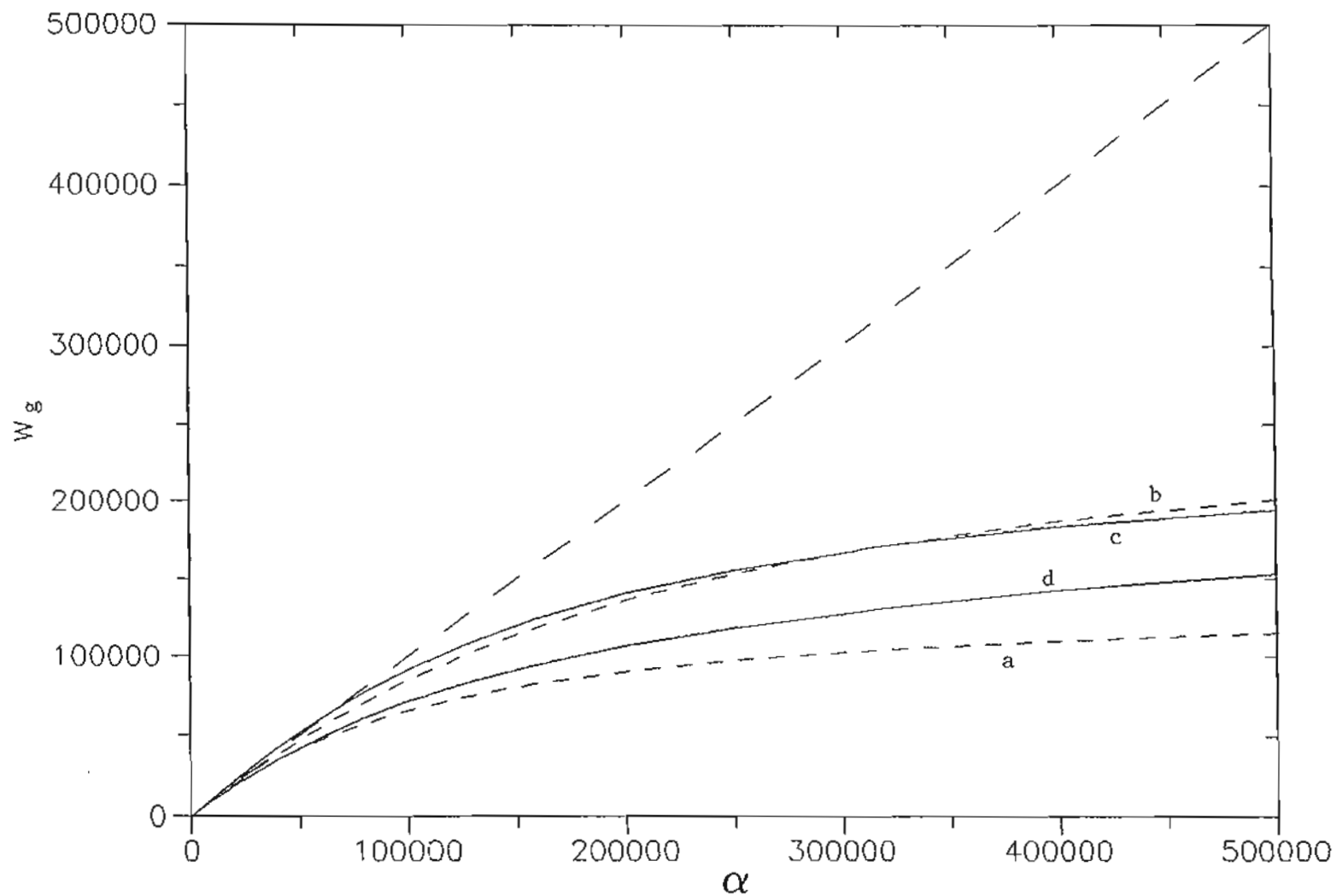
Figure 7.13. Storm-averaged Wg values as a function of α polluted layer with ground-level source:
a)P=5 mm/h, b)=1 mm/h, c)CF precipitation profile, d)FC precipitation profile.

the methylphenols and 2-methoxyphenol in Portland. In Table 7.2 the field W_g/α values are compared to those predicted by this model in the polluted layer case with source and P = 2 mm/h. Although lack of attainment of equilibrium can cause W_g values 20-40% lower than α under these conditions, it cannot explain the entire discrepancy found in the samples. Also shown in Table 7.2 is the percent depletion of the atmospheric concentration after the first hour of rainfall and after the entire model storm (12.5 h). The importance of rain scavenging as a removal pathway for these compounds can be seen by the 24 - 45% depletion for these compounds after only one hour of relatively light rain.

The P value of 2 mm/h used in Table 7.2 is an average value for samples obtained in Portland (Table A2.1) and the range of P = 1 - 5 mm/h is typical of frontal storms. However, thunderstorms are often characterized by P values as large as 20 mm/h. For $\alpha = 10^5$, after one hour of 20 mm/h rainfall, the depletion of the atmospheric concentration is 78% with a W_g/α ratio of only 0.45. Future studies of the gas scavenging of compounds with high α values should therefore take into account the effects of concentration gradients and precipitation rates on the measured W_g values.

Table 7.2. Comparison of Field W_g/a Values for Phenols to those predicted by the Model with Polluted Layer Profile and Ground-Level Source.

Compound	a (8°C)	Field W_g/a	Model W_g/a [a]	% Depletion[b]	
				1 h	12.5 h
phenol	2.2×10^5	NA[e]	0.59	45	90
3+4-methylphenol	1.1×10^5	0.20	0.79	36	84
2-methoxyphenol	9.6×10^4	0.28	0.81	34	82
2-methylphenol	8.2×10^4	0.23	0.85	32	79
2,4-dimethylphenol	3.6×10^4	0.75	0.94	24	63

[a] P = 2 mm/h, total rainfall 2.5 cm. [b] percent depletion of the vapor phase concentration. [c] field data for phenol are not available.

CHAPTER 8   COMPARISON OF RAIN SCAVENGING

TO OTHER ATMOSPHERIC TRANSPORT AND REMOVAL MECHANISMS

In this chapter, the magnitude of the deposition rates and the atmospheric removal rates due to gas and particle scavenging are compared to those from two other dominant processes: dry deposition and chemical reactions.

8.1   Dry Deposition

As discussed in Section 3.3.2, fluxes of organic compounds due to wet deposition can be expressed

$$F_{wet} = [rain,total] \ P \qquad\qquad 8.1$$

where P is the precipitation rate (cm/yr).   In terms of scavenging ratios,

$$F_{wet} = [air,total] \ W \ P \qquad\qquad 8.2$$

and the individual gas and particle scavenging contributions ($F_{wet,gas}$ and $F_{wet,part}$) are given by

$$F_{wet,gas} = [air,vapor] \ W_g \ P \qquad\qquad 8.3$$
$$= [air,total] \ W_g \ (1\text{-}\phi) \ P \qquad\qquad 8.4$$

and

$$F_{wet,part} = [air,particulate]\ W_p\ P \qquad\qquad 8.5$$

$$= [air,total]\ Wp\ \phi\ P \qquad\qquad 8.6$$

When calculating the cumulative depositional fluxes from several rain events, some error may be introduced by simply multiplying the mean concentrations by the total precipitation amount.

$$F'_{wet} = P\sum\ [rain] \qquad\qquad 8.7$$

where F'_{wet} is the flux calculated by this method, and n is the number of events. The actual cumulative wet depositional flux is given by

$$F_{wet} = \sum\ (P_i\ [rain]) \qquad\qquad 8.8$$

In order to calculate depositional fluxes, therefore, precipitation-weighted concentrations and scavenging ratios should be calculated. These are presented for the Portland data in Table 8.1. These mean values ($W_{g,pw}$ and $W_{p,pw}$) can then be multiplied by mean air concentrations and yearly precipitation amounts to give yearly wet depositional fluxes. These values are also given in Table 8.1. These fluxes can be compared to fluxes from other predominant transport mechanisms. Generally referred to as "dry deposition", these mechanisms include both the fallout of particulate material and the direct transfer of vapors to water or soil. The term "dry deposition" is somewhat inappropriate in describing the transfer of vapors since, as with the scavenging of vapors, this process is reversible and may occur in either direction

Table 8.1 Precipitation-Weighted W_g, W_p, and W Values, and Resulting Wet Depositional Flux[a] ($\mu g/m^2$-yr) in Portland, Oregon.

Compound	$W_{g,pw}$	$W_{p,pw}$	W_{pw}	Flux$_{wet}$
PAHs				
Naphthalene	230	NA[b]	230	92
2-Methylnaphthalene	230	NA	230	51
1-Methylnaphthalene	280	NA	280	31
2,6-Dimethylnaphthalene	170	NA	170	4.9
1,3+1,6-Dimethyl naphthalene	210	NA	210	10.9
1,4+1,5+2,3-Dimethyl naphthalene	290	NA	290	4.6
1,2-Dimethylnaphthalene	370	NA	370	2.3
Acenaphthylene	1500	45000	1540	49
Acenaphthene	1100	NA	1100	6.1
Fluorene	1500	21000	1600	18
Phenanthrene	3000	30000	3300	85
Anthracene	1800	22000	2000	6.8
2+3-Methylphenanthrene	2700	24000	3200	24
1+4+9-Methylphenanthrene	3000	22000	3500	21
Fluoranthene	6300	17000	7000	58
Pyrene	6000	14000	6700	49
Benzo[a]fluorene	5000	13000	6500	13
Benzo[b]fluorene	5600	11000	6800	13

Table 8.1 (cont'd) Precipitation-Weighted W_g, W_p, and W Values, and Resulting Wet Depositional Flux ($\mu g/m^2$-yr) in Portland, Oregon.

Compound	$W_{g,pw}$	$W_{p,pw}$	W_{pw}	$Flux_{wet}$
Heterocycles				
Dibenzofuran	890	34000	970	18
Dibenzothiophene	2600	48000	3600	6.7
Phthalate Esters				
Diethyl	19000	NA	19000	86
Dibutyl	46000	NA	46000	220
Butylbenzyl	8900	9100	9000	82
Bis(2-ethylhexyl)	NA	16000	16000	
Dioctyl	19000	35000	28000	11
Alkanes				
Eicosane	NA	27000	4100	24
Heneicosane	NA	29000	9600	35
Docosane	NA	20000	9400	40
Tricosane	NA	29000	20000	102
Tetracosane	NA	20000	18000	92
Pentacosane	NA	34000	34000	160
Hexacosane	NA	22000	22000	79
Octacosane	NA	32000	32000	112

Table 8.1 (cont'd) Precipitation-Weighted W_g, W_p, and W Values, and Resulting Wet Depositional Flux ($\mu g/m^2$-yr) in Portland, Oregon.

Compound	$W_{g,pw}$	$W_{p,pw}$	W_{pw}	$Flux_{wet}$
Phenols				
2-Methyl	19000	NA	19000	1600
2,6-Dimethyl	12000	NA	12000	170
2-Nitro	1900	NA	1900	65
2-Ethyl	15000	NA	15000	180
2,4 + 2,5-Dimethyl	24000	NA	24000	1100
2,4-Dichloro	9900	NA	9900	12
4-Ethyl + 3,5-Dimethyl	25000	NA	25000	990
2,6-Dichloro	9000	NA	9000	1.3
3,4-Dimethyl	24000	NA	24000	360
4-Methyl-2-methoxy	22000	NA	22000	2000
C_3-Phenols	30000	NA	30000	
4-Methyl-2-nitro	6200	NA	6200	105
2,4,6- + 2,4,5-Trichloro	18000	NA	18000	2.7

[a] Flux based on 100 cm of rainfall per year. [b] NA = not available.

across the interface.

8.1.1 Particles

Dry depositional fluxes of particles are generally expressed

$$F_{dry,part} = [air] \; \phi \; v_D \qquad\qquad 8.9$$

where v_D is called the deposition velocity. Wind tunnel studies of the deposition velocity have been conducted by Sehmel and Sutter (1974). The theoretical development of v_D has been reported by Slinn et al. (1978), Slinn and Slinn (1981), and Williams (1982). A review of deposition velocities is given by Sehmel (1980).

Values of v_D vary with particle size and composition, wind speed, relative humidity, and surface roughness. For 1 μm particles, reported values of v_D range from 10^{-2} to 10^0 cm/s (Slinn and Slinn, 1981). Hydrophilic particles, such as sulfates, will grow in the high humidity region near an air-water interface, and thus deposit more rapidly than hydrophobic particles of the same initial size. The presence of waves on the water surface increases the value of v_D and decreases the difference due to particle size (Williams, 1982). For the ocean, the value of v_D is roughly 10^{-1} cm/s for particles between 0.01 and 2 μm in diameter. Values of v_D increase to 10^0 to 10^1 cm/s for 10 μm particles, and are less dependent on particle composition.

To compare the magnitude of wet vs. dry deposition of particulate phase organic compounds, the ratio of

$$\frac{F_{wet,part}}{F_{dry,part}} = \frac{W_{p,pw} \, \phi \, P}{\phi \, v_D} = \frac{W_{p,pw} \, P}{v_D} \qquad 8.10$$

must be computed. For a typical organic compound with $W_{p,pw}$ of 10^4, a precipitation rate P of 100 cm/yr, and a deposition velocity of $\sim 10^{-1}$ cm/s, this ratio is equal to 0.3. Due to the uncertainties in these values, the wet and dry depositional fluxes for such a compound are comparable. Because scavenging ratios and deposition velocities exhibit similar behavior with respect to particle size, the differences in W_p values observed for the PAHs are likely to be reflected in the v_D values as well. If that is true, then wet and dry depositional fluxes will be comparable regardless of the magnitude of W_p.

8.1.2 Vapors

Transfer of vapors will occur in the direction of the phase which is undersaturated with respect to the Henry's Law equilibrium. As described in Section 7.2 and Equations 7.2 and 7.3. For the case of large bodies of water such as lakes or oceans, the gas and aqueous phase resistances are equal for $\alpha = 10^3$.

When the aqueous concentration is negligible, Equation 7.2 becomes linear

$$Flux_{dry,gas} = K \, [air, vapor] \qquad 8.11$$

and the flux can be compared directly to the wet depositional flux. This comparison is discussed in Pankow et al. (1983). The ratio of the

fluxes is

$$\frac{F_{wet,gas}}{F_{dry,gas}} = \frac{W_{g,pw} \, P \, [air,vapor]}{k_g \, [air,vapor]} = \frac{W_{g,pw} \, P}{k_g} \qquad 8.12$$

For a compound with $W_{g,pw}$ = 5000, P = 100 cm/yr, and k_g = 16 cm/s, this ratio is equal to 10^{-3}. However, it must be recalled that this is an upper limit for the dry depositional flux, in the case of negligible aqueous concentration. The flux is likely to be less than this value in most environmental situations. In fact, if the atmosphere and the aqueous system are in equilibrium, this flux vanishes completely and the wet depositional flux becomes the only mechanism for transport of vapor phase material to the aqueous system. At steady-state, wet deposition into the aqueous system during rainy periods will exactly balance the evaporative flux out of the aqueous system during dry periods. Mackay et al. (1986) describe this process in terms of short periods of rapid deposition to bodies of water from wet deposition, followed by longer periods of slow re-evaporation.

8.2 Chemical Reactions

As discussed in Section 3.3.1, atmospheric lifetimes of organic compounds are generally determined by the chemical reactivity of the compounds, as well as the wet and dry deposition. Information on the reactivity of organic compounds in the atmosphere is fragmentary, but a few things are known. Relevant atmospheric chemical reactions can include direct photolysis and reaction with OH radical, O_3, or NO_x. For

a chemical reaction of the following form

$$\frac{dC}{dt} = -k \, [OH] \, C \qquad\qquad 8.13$$

with solution

$$C = C_o \, \exp[-k \, [OH] \, t] \qquad\qquad 8.14$$

the atmospheric lifetime due to this chemical loss mechanism is given by

$$T_{chem,OH} = 1/(k[OH]) \qquad\qquad 8.15$$

The rate constants for the reactions of several organic compounds with OH are given in Table 8.2. Also given are the corresponding atmospheric lifetimes, assuming an average OH concentration of $8 \times 10^5 \, cm^{-3}$. These lifetimes are in the hours-to-days range. As discussed in Section 3.3.1, the gas scavenging lifetimes of organic compounds which are well-mixed in the atmosphere and have a values in the range of 10^1 to 10^4 are in the months-to-years range. For compounds which are concentrated near ground level gas scavenging lifetimes can be as short as an hour for compounds with a values of 10^5 (Section 7.5) The latter case is more likely to apply to the compounds listed in Table 8.2. For the phenols, gas scavenging, especially during the winter months, may be the dominant atmospheric removal process. For most of the other vapor phase organic compounds listed in Table 8.2, however, chemical reac-

Table 8.2. Rate Constants for the Reaction of Organic Compounds with OH
and the Resulting Atmospheric Lifetimes (T_{OH}).

Compound	$k \times 10^{12}$ (cm^3/molecule-sec)	ref	T_{OH}[a]
Trichloroethene	2.0	1	7 days
Tetrachloroethene	0.17	1	85 days
Benzaldehyde	13	1	27 hours
Methylisobutyl ketone	14	1	25 hours
Toluene	6	1	2 days
Ethylbenzene	8	1	43 hours
o-Xylene	14	1	25 hours
m-Xylene	23	1	15 hours
p-Xylene	12	1	29 hours
1,2,4-Trimethylbenzene	33	1	11 hours
1,3,5-Trimethylbenzene	48	1	7 hours
2-Methylphenol	40	1	9 hours
3-Methylphenol	67	1	5 hours
4-Methylphenol	52	1	7 hours
Naphthalene	24	2	15 hours
Phenanthrene	34	2	10 hours
Anthracene	110	2	3 hours

[a] [OH] of 8×10^5 molecules/cm^3 assumed. 1 Atkinson et al., 1979. 2 Biermann et al., 1985.

tions and not gas scavenging determine the atmospheric lifetimes. For some compounds not listed in Table 8.2, such as α- and γ-HCH, the lifetimes due to rain scavenging are likely to be comparable or shorter than the chemical lifetimes.

Several studies have reported on the reactivity of particulate PAHs (Fox and Olive, 1979; Korfmacher et al., 1980,1981; Butler and Crossley, 1981; Cimberle et al., 1983; Van Vaeck and Van Cauwenberghe, 1984; Behymer and Hites, 1985). Early studies reported rapid photodegradation of PAHs adsorbed onto silica gel (NAS, 1972). Photodegradation of anthracene collected on glass fiber filters has also been reported (Fox and Olive, 1979.) Studies of the reactivity of PAHs adsorbed on fly ash and soot, however, indicate that PAHs are highly resistant to photodegradation in those states (Korfmacher et al., 1980; Behymer and Hites, 1985).

The reactivity of particulate phase PAHs with ozone was investigated by Van Vaeck and Van Cauwenberghe (1984). Using an ozone concentration of 1.5 ppm, half-lives of 0.5-1 hour were found for most PAHs. Assuming that the reaction rates are first-order in $[O_3]$, the atmospheric lifetimes corresponding to 50 ppb O_3 ranged from 12 hours for perylene to 150 hours for the benzofluoranthenes. In Table 8.3, the lifetimes of particulate PAHs due to reaction with O_3 are compared to those due to rain scavenging for typical summer and winter conditions. For the calculation of the particle scavenging lifetime T_{rain}, the depth of the vertical mixed layer is assumed to be 500 m. Thus,

Table 8.3. Atmospheric Lifetimes (Days) of Particulate Phase PAHs due to Reaction with O_3[a] (T_{chem}) and Rain Scavenging[b] (T_{rain}).

Compound	Summer[c]		Winter[d]	
	T_{chem}	T_{rain}	T_{chem}	T_{rain}
Perylene	0.42	79	1.7	26
Benz[a]anthracene	0.50	130	2.0	42
Benzo[a]pyrene	0.67	88	2.6	29
Benzo[ghi]perylene	1.0	68	4.0	23
Benzo[e]pyrene	1.0	72	4.2	24
Chrysene	1.3	47	5.2	16
Indeno[1,2,3-cd]pyrene	1.4	49	5.5	16
Benzo[b+j+k]fluoranthenes	1.7	68	6.7	23

[a] Reaction rates from Van Vaeck and Van Cauwenberghe, 1984. [b] T_{rain} = $500/(W_p P)$. W_p values from Table 6.5. [c] Summer values: $[O_3]$ = 80 ppb, P = 5 cm/month. [d] Winter values: $[O_3]$ = 20 ppb, P = 15 cm/month.

$$T_{rain} = \frac{500}{W_p \, P} \qquad\qquad 8.16$$

In Table 8.3, the W_p values are from Table 6.5. Summer and winter lifetimes are calculated using the following $[O_3]$ and P values: summer, 80 ppb and 5 cm/month; winter, 20 ppb and 15 cm/month. The winter values for T_{rain} are within an order of magnitude of the T_{chem} values for many compounds. However, for most PAHs, particle scavenging does not appear to be critical in determining the atmospheric lifetimes.

CHAPTER 9   CONCLUSIONS

A method has been developed for the quantitative analysis of orga-
nic compounds in air and rain samples.   Field sampling for these com-
pounds took place over a two year period at an urban residential site
in Portland, Oregon.   Several samples were also obtained at a non-
urban coastal site at Ft. Stevens, Oregon.   Concentrations of neutral
organic compounds and phenols were obtained in the atmospheric vapor
and particulate phases and in the rain dissolved and particulate
phases.   This information was used to determine gas, particle, and
overall scavenging ratios for each compound.

Phenols were the dominant organic compounds found in the rain
samples, with concentrations in the μg/L range for many alkylphenols in
Portland.   PAHs and phthalate esters were also major constituents, at
levels of 10 to 100 ng/L.   Aromatics were the dominant organic com-
pounds found in the air samples.   About 90% of the compounds associated
with suspended particulate material in rain were trapped by the 10 um
pre-filter.   This indicates either that only very large particles were
scavenged, or that smaller particles coagulated after capture by the
raindrop.   Rain and air concentrations at the coastal site were gener-
ally a factor of 2 to 7 lower than concentrations in Portland.   Concen-
trations measured with duplicate samplers generally agreed within 15%

for the air samples and 25% for the rain samples, indicating good sampling precision.

Measured gas scavenging ratios (W_g) ranged from 10^0 to 10^5 for neutral organic compounds. Measured W_g values for phenols were ~10^4, but may have been underestimates, due to the incomplete retention of phenols on the rain adsorbent cartridges. In addition to alkyl- and chlorophenols, the largest W_g values were found for oxo-PAHs and phthalate esters. The W_g values, obtained at ambient temperatures of 3-10^0C, were generally a factor of 2 to 5 larger than the α values calculated from laboratory solubility (S) and vapor pressure (P) data obtained at 25^0C. This discrepancy was due to the temperature dependence of the α values. For several PAHs, S and P data were available at the actual sampling temperatures. For these compounds, the agreement between the measured values and the equilibrium values was excellent, demonstrating that equilibrium did exist between the rain and the atmospheric vapor phase.

Measured particle scavenging ratios (W_p) at both sampling sites ranged from 10^2 to 10^5 and averaged ~10^4. W_p values were generally an order of magnitude larger for PAHs of MW $\leq$ 202, alkanes and phthalates than for PAHs of MW > 202. The measured W_p values for some compounds were as much as 3 orders of magnitude lower than those found by other researchers for inorganic species. These results are consistent with a below-cloud scavenging mechanism for PAHs, in which the compounds with higher scavenging ratios were associated more frequently with large

particles.

Compounds with vapor pressures between 10^{-8} and 10^{-4} torr were present in both the vapor and particulate phases. Compounds with vapor pressures higher than 10^{-4} torr were present exclusively in the vapor phase, while compounds with vapor pressures lower than 10^{-8} were present exclusively in the particulate phase. In addition, measured particulate phase concentrations of PAHs were the same whether glass fiber or Teflon filters were used. Since adsorption of atmospheric vapors on glass fiber filters is expected to be much more significant than on Teflon filters, this result indicates that a vapor adsorption artifact did not significantly affect the measurement of the vapor/particle distribution of PAHs.

The overall scavenging ratios were very similar for all PAHs, although the contributions of gas and particle scavenging were very different. Particle scavenging was less important than gas scavenging for most PAHs, but more important than gas scavenging for alkanes and the most volatile PAHs. Because gas and particle scavenging ratios were very similar for phthalates, the dominant scavenging mechanism depended only upon their vapor pressures.

A mass transport model of the transfer of vapor phase compounds into raindrops was applied to the case of phenols and other compounds with α values of 10^4 or greater. For compounds with α values of 10^5, especially those such as phenols which are present in a shallow polluted layer near ground level, significant deviations from equilibrium can occur under typical frontal storm conditions. Thus, to understand

and predict the gas scavenging behavior of these compounds, the precipitation rate and vertical concentration profile of the compounds must be known in addition to the Henry's Law constants at the appropriate temperatures.

Wet deposition to bodies of water due to gas and particle scavenging was compared to dry deposition. For a typical compound in this study, wet and dry depositional fluxes of particles were found to be roughly equal. In order to compare the wet and dry deposition of vapors, information on the aqueous concentration is required. If the body of water is extremely undersaturated with respect to the Henry's Law equilibrium, dry deposition will dominate for virtually all compounds in this study. However, if the aqueous concentration is in equilibrium with the atmosphere, there is no flux due to dry deposition and wet deposition is the only mechanism for the introduction of vapor phase species into the body of water.

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APPENDIX 1 AIR CONCENTRATION DATA

In this appendix, the procedures for identification and quantification of target compounds on the Finnigan GC/MS Incos data system are presented, along with the entire set of concentration data in the atmospheric vapor and particulate phases, in Portland and at the Oregon coast.

```
Trace of procedure THRECR
   *SETN
THRCR1
   *
   GETN
   ISFD1
      * SETL IS;GETL #1;SEAR/V (I;$;&;N1,100,100;D-50,50;E)
      *
   SETL IS
   GETL #1
   SEAR  (I;$;&;N1,100,100;D-50,50;E)/V
SETL S1
THRCR2
      * GETL; SET1 !17;CHRO (I;-;/;%;#;H-40,40;E);LOOP
      *
      GETL
      SET1 !17
      CHRO (I;-;/;%;#;h-40,40;E)
      LOOP
   ISFD2
      *   SETL IS;GETL #2;SEAR/V (I;$;&;N1,100,100;D-50,50;E)
      *
      SETL IS
      GETL #2
      SEAR (I;$;&;N1,100,100;D-50,50;E)/V
   SETL S2
   THRCR2
      *GETL;SET1 !17;CHRO(I;-;/;%;#;h-40,40;E);LOOP
      *
      GETL
      SET1 !17
      CHRO (I;-;/;%;#;H-40,40;E)
      LOOP
   ISFD3
      *SETL IS;GETL #3;SEAR/V (I;$;&;n1,100,100;D-50,50;E)
      *
      SETL IS
      GETL #3
      SEAR (I;$;n1,100,100;D-50,50;E)/V
   SETL S3
   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.

```
Trace of procedure QUSLRN
   *
   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 IDOS target compound integration and quantifica-
tion procedure QUSLRN.

Table A1.1a. Atmospheric Vapor Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Monocyclic Aromatic Compounds							
Toluene	1800	5200	2800	2600	8600	2400	2900
Ethylbenzene	950	940	1400	780	2800	1000	1000
m+p–Xylene	3300	2900	3200	2000	7800	2000	2700
o–Xylene	990	930	1300	780	2800	1200	1000
Styrene	57	61	130	38	210	79	29
Cumene	45	56	87	48	150	59	46
n–Propylbenzene	160	260	300	160	520	260	190
Mesitylene	330	440	450	250	890	360	270
1,2,4–Trimethylbenzene	1200	1100	1300	900	3100	1000	820
1,2,3–Trimethylbenzene	310	360	540	310	1100	420	150
p–Cymene	64	120	91	51	140	89	70
n–Butylbenzene	49	78	100	61	220	NA	NA
Durene	72	86	130	77	270	100	78
1,2,3,5–Tetramethyl benzene	110	140	200	120	430	170	130
1,2,3,4–Tetramethyl benzene	43	53	79	46	150	61	44

Table A1.1a (cont'd). Atmospheric Vapor Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Chlorinated Compounds							
Trichloromethane	96	120	260	110	110	82	110
1,2-Dichloropropane	23	38	37	21	40	24	26
Trichloroethene	240	2300	3900	600	2300	760	660
Dibromochloromethane	1.3	ND[a]	1.2	0.36	ND	1.2	0.56
Tetrachloroethene	400	700	1900	590	2100	1600	810
Chlorobenzene	6.1	9.6	12	8.2	12	11	9.7
Tribromomethane	9.6	9.6	13	12	12	9.1	10.4
2-Chlorotoluene	3.6	4.7	12	7.4	9.9	10.1	4.7
1,4-Dichlorobenzene	120	140	170	73	130	99	95
1,2-Dichlorobenzene	3.3	6.7	5.5	4.0	10	7.1	4.2
Hexachloroethane	3.2	3.5	3.7	4.1	3.1	2.9	2.8
1,2,4-Trichlorobenzene	3.7	3.7	4.7	3.6	3.8	3.5	3.4
Hexachlorobutadiene	0.62	0.69	0.60	0.55	0.32	0.38	0.60
α-HCH	0.36	0.35	0.30	0.29	0.32	0.33	0.44
Hexachlorobenzene	0.09	0.05	0.11	0.07	0.07	0.08	0.06
p,p'-DDE	0.04	ND	0.12	0.12	0.42	0.06	ND

Table A1.1a (cont'd). Atmospheric Vapor Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Phenols							
Phenol	220	430	350	270	410	280	250
2-Methylphenol	52	88	88	51	130	46	51
3+4-Methylphenol	87	170	160	89	230	86	100
2-Methoxyphenol	110	190	170	89	290	91	130
2,6-Dimethylphenol	8.4	11	14	8.0	24	6.4	8.3
2-Nitrophenol	17	15	39	11	28	34	24
2,4+2,5-Dimethylphenol	24	30	37	26	70	15	29
2,4-Dichlorophenol	0.88	1.3	1.7	0.93	2.3	1.9	2.0
4-Ethyl+3,5-dimethyl phenol	13	26	23	15	42	9.7	13
3,4-Dimethylphenol	ND	ND	5.4	ND	ND	ND	3.5
2,6-Dichlorophenol	0.01	0.15	0.14	0.12	0.31	0.12	0.13
C$_3$-Phenols	20	40	34	21	57	7.5	8.8
2,4,6+2,4,5-Trichloro- phenol	0.04	ND	0.31	0.06	0.13	0.11	0.29
2,3,4,6-Tetrachlorophenol	ND	ND	0.38	0.07	0.62	0.23	0.06

Table A1.1a (cont'd). Atmospheric Vapor Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Phthalate Esters							
Diethylphthalate	3.0	2.7	2.1	ND	ND	2.8	ND
Dibutylphthalate	0.37	ND	ND	ND	ND	ND	ND
Dioctylphthalate	ND	0.16	0.65	0.94	ND	0.12	0.06
Polycyclic Aromatic Hydrocarbons (PAHs) and Derivatives							
Naphthalene	280	410	490	310	940	350	300
Benzothiazole	10	ND	11	6.3	ND	13	8.8
2-Methylnaphthalene	110	150	200	110	460	200	160
1-Methylnaphthalene	57	75	110	54	210	92	73
Biphenyl	16	19	27	14	28	31	15
2,6-Dimethylnaphthalene	21	20	36	17	43	23	17
1,3+1,6-Dimethyl naphthalene	35	37	66	31	76	41	33
1,4+1,5+2,3-Dimethyl naphthalene	11	12	18	8.1	20	12	9.2
1,2-Dimethylnaphthalene	4.4	4.4	6.6	3.1	8.4	3.9	3.2
Acenaphthylene	15	35	>27[b]	15	47	>11	>14
Acenaphthene	3.8	4.4	5.9	6.1	9.0	5.9	3.3
Dibenzofuran	14	22	25	14	24	13	15

Table A1.1a (cont'd). Atmospheric Vapor Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12– 2/13	2/14– 2/15	2/20– 2/21	2/23– 2/24	2/29– 3/1	3/16– 3/20	4/11– 4/12
Fluorene	7.6	10	11	7.8	14	8.6	7.4
Dibenzothiophene	1.3	1.3	2.5	1.3	1.6	1.8	1.2
Phenanthrene	21	35	33	22	35	22	21
Anthracene	2.0	3.7	2.4	1.9	4.5	2.6	2.4
2+3–Methylphenanthrene	5.8	7.0	9.1	5.4	9.4	5.0	4.6
1+4+9–Methylphenanthrene	4.2	5.4	6.6	3.7	7.0	3.6	4.6
Fluoranthene	5.7	9.3	10	6.7	10	7.1	5.9
Pyrene	4.8	7.6	8.5	5.7	9.9	5.8	5.4
Benz[a]anthracene	0.24	0.33	0.19	0.28	0.40	0.33	0.22
Chrysene	0.39	0.40	0.45	0.49	0.44	0.57	0.38
Benzo[b+j+k]fluoranthene	0.06	0.04	0.07	0.35	ND	0.03	ND
Benzo[e]pyrene	0.03	0.04	0.03	ND	ND	0.02	0.02
Benzo[a]pyrene	0.03	0.03	0.02	ND	ND	ND	ND
Oxygenated PAHs							
9–Fluorenone	4.1	8.7	7.7	5.8	7.5	9.0	6.2
9,10–Anthracenedione	1.8	3.0	3.6	2.6	3.3	1.7	1.5

Table A1.1a (cont'd). Atmospheric Vapor Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Alkanes							
Octane	630	570	890	470	1900	530	430
Nonane	510	330	740	290	930	350	270
Decane	180	240	410	230	540	220	170
Undecane	120	130	290	120	300	130	110
Tetradecane	23	29	56	24	61	31	26
Hexadecane	8.9	12	22	9.7	16	ND	ND
Eicosane	3.1	2.2	6.7	3.8	5.4	3.9	3.2
Heneicosane	2.0	0.77	3.2	2.2	1.6	2.3	1.8
Docosane	0.65	ND	ND	0.97	0.66	1.4	ND

[a]ND = not detected at a statistically significant level. [b]Exact concentration
not available due to breakthrough on PUFPs.

Table A1.1b. Atmospheric Vapor Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentration (ng/m^3)					
	2/14– 2/15	3/3– 3/4	3/21– 3/23	3/26– 3/27	4/17– 4/19	4/21– 4/23
Monocyclic Aromatic Compounds						
Toluene	NA[a]	2700	1900	3000	3600	1600
Ethylbenzene	NA	940	830	1900	2100	940
Aldehydes and Ketones						
Methylisobutylketone	NA	19	ND	68	64	17
Furfural	NA	580	220	360	ND[b]	200
2-Heptanone	NA	ND	23	37	150	32
Heptanal	NA	140	ND	ND	ND	ND
Methylfurfurals	NA	130	65	120	ND	18
Benzonitrile	NA	85	96	110	150	94
Salicylaldehyde	NA	330	550	250	290	190
2,4-Dimethylbenzaldehyde	NA	35	32	61	59	28
Chlorinated Compounds						
Tetrachloroethene	NA	400	430	1000	1200	470
α-HCH	ND	0.32	ND	ND	ND	0.12
Phenols						
2-Methylphenol	180	95	68	76	84	50

Table A1.1b (cont'd). Atmospheric Vapor Phase Concentrations of Organic

Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentration (ng/m^3)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/26–3/27	4/17–4/19	4/21–4/23
3+4-Methylphenol	300	160	110	120	120	83
2-Methoxyphenol	NA	190	120	150	130	95
2,6-Dimethylphenol	28	12	7.7	16	22	13
2-Nitrophenol	ND	59	31	50	74	31
2-Ethylphenol	20	11	6.0	7.6	22	6.5
2,4+2,5-Dimethylphenol	83	60	41	54	80	36
2,4-Dichlorophenol	ND	ND	0.54	0.16	ND	0.71
4-Ethyl+3,5-dimethyl phenol	85	58	42	52	89	36
3,4-Dimethylphenol	47	17	7.0	8.5	26	4.0
4-Methyl-2-methoxyphenol	79	120	52	83	160	61
4-Methyl-2-nitrophenol	NA	25	15	19	25	16
1+2-Naphthol	18	6.2	3.8	3.7	4.6	4.4
PAHs and Derivatives						
Naphthalene	>240[c]	350	300	470	420	230
2-Methylnaphthalene	>330	190	170	300	260	140
1-Methylnaphthalene	>160	97	91	150	130	73
2,6-Dimethylnapthalene	63	26	20	36	37	15

Table A1.1b (cont'd). Atmospheric Vapor Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentration (ng/m^3)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/26–3/27	4/17–4/19	4/21–4/23
1,3+1,6-Dimethyl naphthalene	110	51	39	53	67	32
1,4+1,5+2,3-Dimethyl napthalene	38	15	11	20	21	8.9
1,2-Dimethylnaphthalene	18	5.9	3.6	7.2	7.8	3.2
Acenaphthylene	88	25	18	25	19	>3.4
Acenaphthene	15	4.6	3.1	4.3	4.5	2.2
Dibenzofuran	44	21	15	18	13	13
Fluorene	33	11	8.3	11	10	6.6
Dibenzothiophene	4.9	1.7	1.1	1.6	1.7	0.86
Phenanthrene	51	24	18	25	16	13
Anthracene	10	3.7	2.5	4.0	3.1	1.2
2+3-Methylphenanthrene	18	5.6	4.1	6.5	6.6	2.9
1+4+9-Methylphenanthrene	14	4.4	3.6	6.0	6.0	2.9
Fluoranthene	16	7.4	6.0	8.5	5.6	3.8
Pyrene	13	5.8	5.0	7.2	5.2	2.6
Benzo[a]fluorene	3.1	1.7	1.2	1.7	1.1	1.1
Benzo[b]fluorene	2.7	1.5	1.0	1.4	1.1	0.96
Benz[a]anthracene	0.39	0.24	0.20	0.28	0.24	0.41
Chrysene	0.44	0.39	0.33	0.49	0.36	0.55

Table A1.1b (cont'd). Atmospheric Vapor Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentration (ng/m^3)					
	2/14– 2/15	3/3– 3/4	3/21– 3/23	3/26– 3/27	4/17– 4/19	4/21– 4/23
Benzo[b+j+k]fluoranthene	ND	ND	0.13	ND	ND	ND
Oxygenated PAHs						
1-Indanone	35	19	17	29	20	13
Coumarin	11	7.8	14	8.9	11	5.0
9-Fluorenone	13	6.8	5.1	7.1	5.7	3.6
Xanthone	2.8	1.5	1.2	1.4	1.2	1.0
9,10-Anthracenedione	4.7	2.2	2.0	2.4	1.4	1.6
7-Benz[de]anthracenone	0.05	ND	0.05	0.10	ND	ND
Alkanes						
Eicosane	11	2.8	3.3	4.6	7.1	2.5
Heneicosane	ND	ND	3.1	ND	ND	1.9
Phthalate Esters						
Diethylphthalate	8.2	9.9	6.1	3.4	ND	2.3
Dibutylphthalate	ND	13	2.8	5.7	ND	2.3
Butylbenzylphthalate	4.1	5.1	5.7	ND	ND	ND

[a]NA = not available. [b]ND = not detected at a statistically significant level.
[c]Exact concentration not known due to breakthrough on PUFPs.

Table A1.2a. Atmospheric Particulate Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
PAHs and Derivatives							
Dibenzofuran	ND[a]	0.35	0.036	0.064	0.23	0.21	ND
Fluorene	ND	0.26	0.012	0.039	0.11	0.13	ND
Dibenzothiophene	ND	0.087	0.010	0.016	0.026	0.12	ND
Phenanthrene+Anthracene	0.10	0.93	0.16	0.35	0.60	0.36	0.077
2+3-Methylphenanthrene	0.086	0.33	0.088	0.16	0.36	0.31	0.036
1+4+9-Methylphenanthrene	0.048	0.28	0.090	0.15	0.23	0.13	0.076
Fluoranthene	0.40	0.63	0.47	0.50	0.79	0.27	0.14
Pyrene	0.65	0.72	0.49	0.51	0.94	0.25	0.17
Benz[a]anthracene	0.95	1.5	1.1	0.82	1.9	0.59	0.44
Chrysene	0.96	1.6	1.7	1.1	2.4	0.73	0.57
Benzo[b+j+k]fluoranthene	2.1	3.0	4.5	2.9	6.5	2.6	2.1
Benzo[e]pyrene	0.76	1.3	1.3	1.0	2.5	0.87	0.64
Benzo[a]pyrene	0.93	1.6	1.3	0.99	2.2	0.88	0.61
Perylene	0.26	0.59	0.17	0.11	0.54	0.25	0.11
Benzo[ghi]perylene	1.1	1.8	3.3	1.2	3.2	1.8	1.3
Coronene	0.24	0.42	1.3	ND	0.65	0.22	0.61

Table A1.2a (cont'd). Atmospheric Particulate Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1984.

Compound	Concentration (ng/m^3)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Oxygenated PAHs							
9–Fluorenone	0.03	0.32	ND	0.07	0.17	0.48	0.020
9,10–Anthracenedione	0.58	0.74	0.65	0.87	0.93	0.44	0.34
7–Benz[de]anthracenone	0.94	0.96	2.3	0.59	2.0	0.44	0.91
Alkanes							
Eicosane	0.58	0.68	0.39	0.19	0.89	ND	0.27
Heneicosane	1.0	1.1	0.59	0.33	2.4	ND	0.73
Docosane	1.1	ND	1.1	0.38	3.8	ND	1.5
Tricosane	0.97	1.4	1.7	0.58	3.4	ND	3.3
Tetracosane	4.0	ND	1.7	ND	5.2	ND	2.5
Pentacosane	1.1	1.3	2.1	0.54	6.2	ND	4.3
Hexacosane	ND	1.3	1.7	ND	2.8	ND	2.3
Phthalate Esters							
Butylbenzylphthalate	3.5	ND	2.7	1.3	NA[b]	9.6	1.7
Bis[2-ethylhexyl]-phthalate	22	ND	9.4	8.1	NA	ND	8.8
Dioctylphthalate	0.45	0.88	0.36	0.15	NA	0.27	0.22

[a]ND = not detected at a statistically significant level. [b]NA = not available.

Table A1.2b. Atmospheric Particulate Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentrations (ng/m^3)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/26–3/27	4/17–4/19	4/21–4/23
PAHs and Derivatives						
Acenaphthylene	0.02	0.038	0.026	0.024	0.014	0.005
Acenaphthene	ND[a]	0.031	ND	ND	ND	ND
Dibenzofuran	0.08	0.065	0.016	0.039	0.020	0.007
Fluorene	0.06	0.050	0.020	0.030	0.015	0.006
Dibenzothiophene	0.015	0.066	ND	ND	0.011	0.004
Phenanthrene	0.34	0.21	0.17	0.24	0.12	0.038
Anthracene	0.06	0.045	0.033	0.049	0.013	0.010
2+3-Methylphenanthrene	0.50	0.28	0.17	0.23	0.11	0.036
1+4+9-Methylphenanthrene	0.40	0.17	0.17	0.20	0.078	0.035
Fluoranthene	1.18	0.48	0.90	0.75	0.32	0.12
Pyrene	1.4	0.54	1.07	0.87	0.37	0.14
Benzo[a]fluorene	0.88	0.33	0.56	0.55	0.17	0.076
Benzo[b]fluorene	0.96	0.34	0.56	0.58	0.19	0.092
Benz[a]anthracene	3.5	1.15	1.3	1.5	0.62	0.56
Chrysene	4.3	1.6	1.5	1.8	0.82	0.77
Benzo[b+j+k]fluoranthene	8.4	2.9	2.7	3.3	2.7	2.9
Benzo[e]pyrene	3.4	1.17	1.06	1.4	0.89	0.94
Benzo[a]pyrene	4.9	1.5	1.5	1.9	1.4	1.3

Table A1.2b (cont'd). Atmospheric Particulate Phase Concentrations of Organic
Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentrations (ng/m^3)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/26–3/27	4/17–4/19	4/21–4/23
Perylene	0.81	0.29	0.25	0.28	0.17	0.16
Indeno[1,2,3-cd]pyrene	3.8	1.14	1.24	1.6	2.4	2.2
Dibenz[a,c]anthracene+ Dibenz[a,h]anthracene	0.72	0.21	0.31	0.38	ND	0.17
Benzo[ghi]perylene	6.0	1.7	1.8	2.6	3.0	2.3
Coronene	2.9	0.63	1.00	1.7	0.91	0.65
Oxygenated PAH						
9-Fluorenone	0.15	0.13	0.14	0.096	0.055	0.035
Xanthone	0.08	0.11	0.081	0.034	0.035	0.021
9,10-Anthracenedione	0.76	0.76	0.59	0.44	0.27	0.27
7-Benz[de]anthracenone	5.0	1.8	1.7	2.1	1.7	1.8
7,12-Benz[a]anthracene dione	0.79	0.32	0.24	0.34	0.28	0.44
Alkanes						
Eicosane	1.8	0.88	0.75	0.93	2.4	0.74
Heneicosane	4.0	1.16	1.3	1.8	2.9	ND
Docosane	9.4	2.9	2.0	2.8	3.8	ND
Tricosane	14	3.1	2.3	2.6	5.0	ND
Tetracosane	15	3.6	2.2	2.3	4.5	ND

Table A1.2b (cont'd). Atmospheric Particulate Phase Concentrations of Organic Compounds during Rain Events in Portland, Oregon in 1985.

Compound	Concentrations (ng/m^3)					
	2/14– 2/15	3/3– 3/4	3/21– 3/23	3/26– 3/27	4/17– 4/19	4/21– 4/23
Pentacosane	18	3.5	3.2	3.2	7.1	ND
Hexacosane	13	2.8	1.9	2.2	4.3	ND
Heptacosane	NA	NA	NA	NA	4.8	ND
Octacosane	9.7	2.2	1.8	1.3	2.7	ND
Phthalate Esters						
Dibutylphthalate	8.1	ND	2.4	1.8	ND	ND
Butylbenzylphthalate	9.7	2.9	1.5	5.7	4.7	1.7
Dioctylphthalate	0.77	0.70	0.28	0.60	ND	0.62
Naphthols						
1+2-Naphthol	0.11	ND	0.48	0.17	ND	ND

[a]ND = not detected at a statistically significant level.

Table A1.3. Atmospheric Vapor (V) and Particulate (P) Phase Concentrations of Organic Compounds during Rain Events at the Oregon Coast in 1985.

	Concentration (ng/m^3)					
	4/17		4/21		4/25	
Compound	V	P	V	P	V	P
Aromatics						
Toluene	530	NA	980	NA	520	NA
Ethylbenzene	210	NA	290	NA	140	NA
Chlorinated Aliphatics						
Tetrachloroethene	180	NA	320	NA	130	NA
α-HCH	0.39	ND	0.39	ND	0.32	ND
Aldehydes and Ketones						
Methylisobutyl ketone	ND[a]	NA[b]	ND	NA	0.93	NA
Furfural	120	NA	47	NA	71	NA
2-Heptanone	16	NA	ND	NA	ND	NA
Methylfurfural	43	NA	ND	NA		NA
Benzonitrile	ND	NA	35	NA	ND	NA
Salicylcaldehyde	210	NA	190	NA	110	NA
2,4-Dimethylbenzaldehyde	7.4	ND	11	ND	6.5	ND

Table A1.3 (cont'd). Atmospheric Vapor (V) and Particulate (P) Phase
Concentrations of Organic Compounds during Rain Events at the Oregon Coast
in 1985.

	Concentration (ng/m^3)					
	4/17		4/21		4/25	
Compound	V	P	V	P	V	P
Phenols						
2-Methylphenol	31	ND	11	ND	18	ND
3+4-Methylphenol	83	ND	20	ND	29	ND
2-Methoxyphenol	60	ND	29	ND	55	ND
2,6-Dimethylphenol	7.1	ND	1.5	ND	2.9	ND
2-Nitrophenol	9.8	ND	20	ND	8.6	ND
2-Ethylphenol	1.9	ND	0.85	ND	0.80	ND
2,4+2,5-Dimethylphenol	22	ND	6.1	ND	14	ND
2,4-Dichlorophenol	0.32	ND	ND	ND	0.25	ND
4-Ethyl+3,5-Dimethylphenol	28	ND	8.0	ND	16	ND
4-Methyl-2-methoxyphenol	18	ND	NA	ND	19	ND
3,4-Dimethylphenol	5.8	ND	ND	ND	2.7	ND
4-Methyl-2-nitrophenol	0.42	ND	2.0	ND	0.97	ND
PAHs and Alkyl PAHs						
Naphthalene	120	ND	110	ND	63	ND
2-Methylnaphthalene	67	0.04	72	ND	48	ND

Table A1.3 (cont'd). Atmospheric Vapor (V) and Particulate (P) Phase
Concentrations of Organic Compounds during Rain Events at the Oregon Coast
in 1985.

	Concentration (ng/m^3)					
	4/17		4/21		4/25	
Compound	V	P	V	P	V	P
1-Methylnaphthalene	38	ND	37	ND	25	ND
2,6-Dimethylnaphthalene	20	ND	17	ND	14	ND
1,3+1,6-Dimethylnaphthalene	35	ND	29	ND	24	ND
1,4+1,5+2,3-Dimethyl naphthalene	9.6	ND	8.0	ND	6.7	ND
1,2-Dimethylnaphthalene	3.6	ND	2.8	ND	2.4	ND
Acenaphthylene	13	0.015	>4.8	0.005	4.1	0.002
Acenaphthene	1.8	ND	1.1	ND	0.85	ND
Fluorene	6.7	ND	4.3	ND	2.6	0.004
Phenanthrene	17	0.023	9.0	0.055	5.1	0.045
Anthracene	3.4	0.007	1.5	0.011	0.59	0.017
3+2-Methylphenanthrene	3.2	0.040	1.8	0.035	1.4	0.052
1+4+9-Methylphenanthrene	2.5	0.032	1.3	0.033	0.86	0.038
Fluoranthene	8.7	0.13	2.9	0.26	3.1	0.14
Pyrene	7.2	0.13	1.9	0.30	1.8	0.14
Benzo[a]fluorene	1.7	0.090	0.60	0.11	0.41	0.084
Benzo[b]fluorene	1.5	0.082	0.58	0.11	0.35	0.085

Table A1.3 (cont'd). Atmospheric Vapor (V) and Particulate (P) Phase
Concentrations of Organic Compounds during Rain Events at the Oregon Coast
in 1985.

	Concentration (ng/m^3)					
	4/17		4/21		4/25	
Compound	V	P	V	P	V	P
Benz[a]anthracene	0.61	0.39	0.32	0.28	0.19	0.23
Chrysene	0.71	0.53	0.59	0.33	0.29	0.27
Benzo[b+j+k]fluoranthene	ND	3.3	0.08	1.5	ND	0.67
Benzo[e]pyrene	ND	0.88	ND	0.53	ND	0.21
Benzo[a]pyrene	ND	0.97	ND	0.60	ND	0.26
Indeno[1,2,3-cd]pyrene	ND	1.8	ND	0.89	ND	0.22
Benzo[ghi]perylene	ND	1.5	ND	0.84	ND	0.21
Coronene	ND	0.07	ND	0.48	ND	ND
Oxo-PAHs						
1-Indanone	8.7	ND	3.0	ND	3.7	ND
Coumarin	18	ND	NA	ND	6.0	ND
9-Fluorenone	5.1	0.018	2.3	0.030	1.8	0.025
Xanthone	1.3	ND	ND	ND	0.64	0.019
9,10-Anthracenedione	2.2	ND	0.69	0.059	0.87	0.063
7-Benz[de]anthracenone	0.13	1.8	0.12	0.91	0.067	0.39
7,12-Benz[a]anthracene dione	ND	0.16	ND	0.08	ND	0.037

Table A1.3 (cont'd). Atmospheric Vapor (V) and Particulate (P) Phase Concentrations of Organic Compounds during Rain Events at the Oregon Coast in 1985.

	Concentration (ng/m^3)					
	4/17		4/21		4/25	
Compound	V	P	V	P	V	P
Heterocyclic Compounds						
Dibenzofuran	11	0.009	6.2	0.014	4.0	0.009
Dibenzothiophene	0.46	ND	0.50	ND	0.31	ND
Phthalate Esters						
Diethylphthalate	10	ND	2.6	ND	1.5	ND
Dibutylphthalate	2.1	ND	ND	ND	61	ND
Butylbenzylphthalate	ND	1.1	ND	ND	4.4	0.56

[a]ND = not detected. [b]NA = not analyzed in filter samples.

APPENDIX 2 RAIN CONCENTRATION DATA

In this appendix, the meteorological and sampling parameters for the Portland rain events, along with the entire set of rain concentration data for both the dissolved and particulate phases in Portland and at the Oregon coast, are presented. The schematic diagram for the rain sampler valve controller electronics discussed in Section 5.1.1 is also shown.
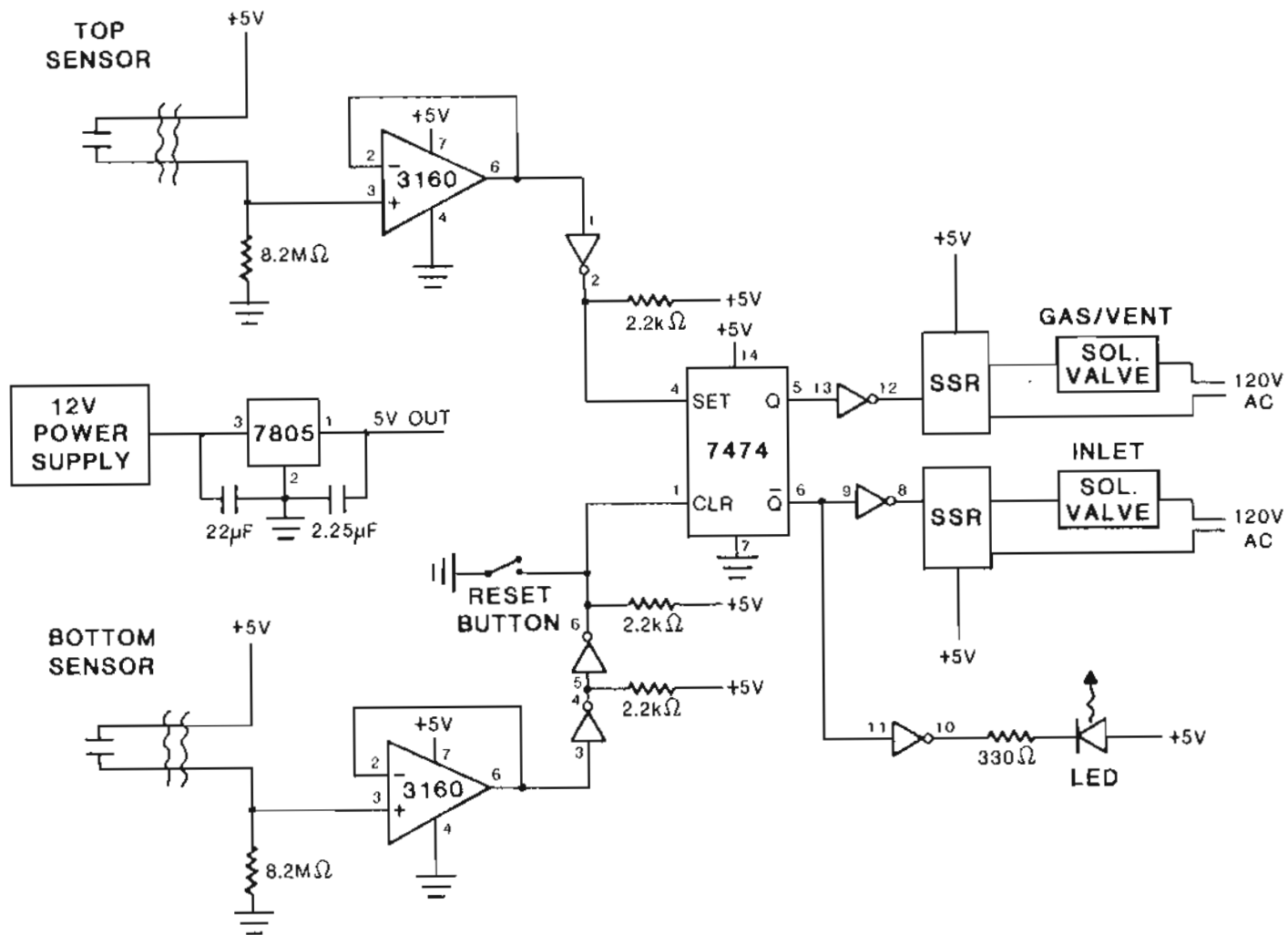
Figure A2.1 Schematic of the rain sampler valve electronics.

Table A2.1a. Meteorological Conditions and Sampling Parameters for Rain Events in Portland, Oregon in 1984.

	Date						
	2/12- 2/13	2/14- 2/15	2/20- 2/21	2/23- 2/24	2/29- 3/1	3/16- 3/20	4/11- 4/12
Storm Type	frontal cyclone	2 weak fronts	showers	cold front	warm front	showers	cold front
Total Rainfall (cm)	4.1	0.58	1.5	1.6	0.90	2.1	0.85
Total rain sample volume (L)	27	4.8	12	15	6.4	12	8.9
Rainfall rate (mm/hr)	2.0	1.2	1.1	0.9	1.9	1.1	0.6
Air sample volume (m^3)	230	53	150	200	50	200	140
Temperature Range (^OC)	5-11	1-13	3-10	4-9	6-18	5-16	7-13
Mean Temperature (^OC)	8	6	5	7	9	9	8
Winds[a]	S-SE:10	S:10	calm	S:20	S-SE:10	SE:15	S:10
NO_x (ppb)[b]	28	14	19	15	41	41	21

[a] Data obtained from the National Weather Service/Portland Airport. [b] Data obtained at the same sampling site by the Oregon Department of Environmental Quality.

Table A2.1b. Meteorological Conditions and Sampling Parameters for Rain Events in Portland, Oregon in 1985.

	Date					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Storm Type	cold front	cold front	2 cold fronts & showers	weak front	cold front	
Total Rainfall (cm)	0.40	1.10	3.8	2.2	0.80	1.45
Total rain sample volume (L)	2.7	6.7	11.5 (1)[a] 20.6 (2)	7.7 (1) 3.5 (2)	5.1	12
Rainfall rate (mm/hr)	0.53	1.5	2.5	2.0	0.71	0.47
Air sample volume (m^3)	46 (1) 42 (2)	82 (1) 77 (2)	170 (1) 170 (2)	59 (1) 150 (2)	130	350
Temperature Range (^OC)	8-12	1-10	1-14	0-11	8-14	2-16
Mean Temperature (^OC)	9	4	5	3	10	8
Winds[b]	calm	S-SW:15-25	S:10	E-SE:10	W:10-20	

[a] Sampler number.   [b] Data obtained from the National Weather Service/Portland Airport

Table A2.2a. Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12-2/13	2/14-2/15	2/20-2/21	2/23-2/24	2/29-3/1	3/16-3/20	4/11-4/12
Monocyclic Aromatic Compounds							
Toluene	ND[a]	ND	80	40	220	46	55
Ethylbenzene	6.9	29	28	32	72	31	19
m+p-Xylene	34	74	110	130	260	72	97
o-Xylene	12	36	45	49	110	30	35
Styrene	4.0	19	23	25	51	17	19
n-Propylbenzene	1.4	ND	0.50	5.4	6.3	ND	1.2
Mesitylene	2.1	6.3	4.5	3.9	10	5.1	3.8
1,2,4-Trimethylbenzene	16	41	34	29	44	32	25
1,2,3-Trimethylbenzene	7.9	15	4.0	17	21	ND	16
Durene	1.1	2.9	2.8	3.0	5.2	3.2	1.8
1,2,3,5-Tetramethyl benzene	1.8	4.4	4.2	4.1	5.8	4.7	3.1
Halogenated Compounds							
Trichloroethene	0.78	3.2	16	2.6	9.7	4.3	1.9
Tetrachloroethene	0.82	1.6	7.8	2.8	9.2	7.2	2.7
Bromoform	>0.11	ND	ND	ND	4.0	ND	ND
1,4-Dichlorobenzene	4.5	3.3	7.0	ND	4.2	5.2	4.3

Table A2.2a (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
1,2-Dichlorobenzene	0.13	ND	0.17	0.22	0.62	ND	0.17
1,2,4-Trichlorobenzene	0.13	ND	0.18	0.45	ND	ND	ND
α-HCH[*]	12	14	15	11	9.9	14	15
γ-HCH	3.1	0.56	0.51	1.6	1.4	2.8	ND
Phenols							
2-Methylphenol[*]	240	1200	1500	770	2800	>260	>370
3+4-Methylphenol[*]	380	1900	2000	1300	1000	>460	>610
2-Methoxyphenol[*]	790	1900	5400	2300	2300	710	1100
2,6-Dimethylphenol[*]	84	110	280	150	92	91	160
2-Nitrophenol[*]	26	51	130	41	78	43	46
2,4+2,5-Dimethylphenol[*]	300	710	1300	810	750	940	940
2,4-Dichlorophenol	5.0	13	7.4	3.2	2.8	2.9	7.0
4-Ethyl+3,5-dimethyl phenol[*]	160	410	640	440	600	680	500
3,4-Dimethylphenol[*]	54	82	140	160	190	140	140
2,6-Dichlorophenol	0.56	ND	1.1	0.83	1.5	ND	2.5
C_3-Phenols[*]	250	480	1100	1000	790	430	400
2,4,6-Trichlorophenol	0.81	ND	1.9	ND	1.9	0.98	1.2

Table A2.2a (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
2,4,5-Trichlorophenol	0.69	ND	0.92	ND	1.8	1.1	ND
2,3,4,6-Tetrachloro phenol[*]	14	16	34	23	10	21	25
Pentachlorophenol[*]	71	20	54	84	72	44	35

Polycyclic Aromatic Hydrocarbons and Derivatives

Compound							
Naphthalene	46	140	120	91	130	93	86
2-Methylnaphthalene	19	37	54	43	69	53	41
1-Methylnaphthalene	13	23	23	28	48	32	25
Biphenyl	11	7.5	9.7	4.4	6.7	4.2	4.9
2,6-Dimethylnaphthalene	2.4	4.1	5.6	3.1	5.8	3.3	3.5
1,3+1,6-Dimethyl naphthalene	5.8	8.7	12	6.2	12	6.6	7.8
1,4+1,5+2,3-Dimethyl naphthalene	2.1	2.9	7.8	2.7	4.5	2.7	2.4
1,2-Dimethylnaphthalene	1.2	1.5	2.3	1.3	3.1	1.2	1.0
Acenaphthylene	23	59	42	32	43	24	35
Acenaphthene	2.5	5.5	6.6	8.5	4.7	6.6	3.5
Dibenzofuran	9.9	26	22	16	19	11	14
Fluorene	9.1	22	17	11	13	13	11

Table A2.2a (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Dibenzothiophene	1.8	2.4	6.7	3.3	3.1	7.3	3.9
Phenanthrene	61	120	97	61	72	87	67
Anthracene	2.0	7.9	4.2	4.0	6.2	7.0	4.7
2+3-Methylphenanthrene	9.8	20	23	13	14	18	13
1+4+9-Methylphenanthrene	9.1	19	20	11	12	14	12
Fluoranthene	29	66	69	47	36	70	32
Pyrene	24	47	56	40	30	50	26
Benz[a]anthracene	2.7	4.5	4.1	3.7	3.2	3.1	1.6
Chrysene	7.6	8.6	12	7.9	9.5	5.9	3.3
Benzo[b+j+k]fluoranthene	ND	0.26	ND	2.9	ND	ND	ND
Benzo[e]pyrene	ND	0.23	ND	0.51	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	0.18	ND	ND	ND
Oxygenated PAHs							
Benzothiazole	33	63	98	130	110	210	77
9-Fluorenone[*]	46	140	140	100	74	78	75
9,10-Anthracenedione[*]	41	93	130	99	99	62	41

Table A2.2a (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Phthalate Esters							
Diethylphthalate[*]	>22	74	>34	73	97	110	60
Dibutylphthalate	40	59	45	38	34	61	46
Butylbenzylphthalate	20	48	41	64	74	48	61
Bis[2-ethylhexyl]-phthalate	15	74	34	53	33	32	100
Dioctylphthalate	2.0	ND	3.2	1.6	2.3	3.8	2.6

[*]Indicates that breakthrough correction was applied to the concentration.
[a]ND = not detected at a statistically significant level.

Table A2.2b. Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14– 2/15	3/3– 3/4	3/21– 3/23	3/25– 3/27	4/17– 4/19	4/21– 4/23
Monocyclic Aromatic Compounds						
Toluene	190	30	9.0	71	ND	41
Ethylbenzene	45	9.3		31	ND	9.8
Chlorinated Compounds						
Tetrachloroethene	13	ND	0.89	1.6	ND	ND
α-HCH	7.3	6.5	5.3	6.4	10.2	10.1
Aldehydes and Ketones						
Methylisobutylketone[*]	530	>11	>9.3	240	>28	>19
Furfural	>3200	>430	>610	>2000	>510	>170
2-Heptanone[*]	110	33	24	56	22	>22
Heptanal[*]	110	60	37	74	250	>41
Benzaldehyde	3800	930	520	1800	450	960
Methylfurfurals[*]	6800	>3100	1300	5000	920	>1500
Benzonitrile[*]	160	64	51	75	>16	21
Salicylaldehyde[*]	1600	530	490	910	150	310
2+3-Tolualdehyde[*]	1400	340	210	770	260	320
4-Tolualdehyde[*]	900	230	130	530	150	200
2,4-Dimethylbenzaldehyde	140	40	25	84	65	42

Table A2.2b (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Phenols						
2-Methylphenol[*]	10000	2100	830	3500	900	1500
3+4-Methylphenol[*]	24000	3200	960	6100	2500	1800
2-Methoxyphenol[*]	17000	3000	1200	3300	750	1600
2,6-Dimethylphenol[*]	490	220	87	140	58	860
2-Nitrophenol[*]	240	120	42	61	57	82
2-Ethylphenol[*]	490	170	63	200	140	79
2,4+2,5-Dimethylphenol[*]	4100	1600	410	1000	720	900
2,4-Dichlorophenol[*]	13	13	7.4	3.2	15	22
4-Ethyl+3,5-dimethylphenol[*]	5600	1800	460	1200	1400	870
4-Methyl-2-methoxyphenol[*]	6800	3100	880	1900	640	1400
2,6-Dichlorophenol	1.6	ND	ND	ND	ND	ND
3,4-Dimethylphenol[*]	910	310	110	280	150	160
4-Methyl-2-nitrophenol[*]	250	170	83	84	82	190
1+2-Naphthol	440	130	39	150	91	220
2,3,4,6-Tetrachlorophenol	36	19	7.1	8.5	22	18
Pentachlorophenol[*]	97	42	47	36	130	130

Table A2.2b (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
PAHs and Derivatives						
Naphthalene	270	80	57	140	77	56
2-Methylnaphthalene	150	39	30	74	64	28
1-Methylnaphthalene	91	25	20	47	35	18
2,6-Dimethylnaphthalene	15	5.3	3.7	7.6	9.8	3.1
1,3+1,6-Dimethylnaphthalene	36	11	7.9	18	19	6.9
1,4+1,5+2,3-Dimethyl naphthalene	15	6.2	3.1	6.4	7.1	2.9
Acenaphthylene	107	33	17	59	26	23
1,2-Dimethylnaphthalene	5.5	2.5	1.6	3.4	3.0	1.3
Acenaphthene	13	4.2	2.6	7.0	7.7	3.6
Dibenzofuran	44	23	11	22	13	9.7
Fluorene	44	20	11	24	17	10.0
Dibenzothiophene	9.9	3.7	3.1	5.2	3.4	3.4
Phenanthrene	180	81	42	88	40	43
Anthracene	14	11	2.3	11	5.9	3.6
2+3-Methylphenanthrene	34	21	10	26	17	10
1+4+9-Methylphenanthrene	31	20	9.1	25	16	9.6
Fluoranthene	86	59	24	70	29	30
Pyrene	73	51	17	57	20	22

Table A2.2b (cont'd). Dissolved Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14– 2/15	3/3– 3/4	3/21– 3/23	3/25– 3/27	4/17– 4/19	4/21– 4/23
Benzo[a]fluorene	9.6	13	3.6	13	3.2	6.4
Benzo[b]fluorene	13	12	3.9	13	1.8	4.6
Benz[a]anthracene	ND	2.9	1.3	4.5	1.3	3.4
Chrysene	ND	10.8	4.0	10.0	3.9	10.1
Benzo[b+j+k]fluoranthene	ND	ND	2.1	2.2	ND	4.3
Oxygenated PAHs						
1-Indanone[*]	1000	420	160	260	480	400
Coumarin[*]	480	190	61	110	180	160
9-Fluorenone[*]	290	130	50	120	90	97
Xanthone	65	39	14	32	29	28
9,10-Anthracenedione	101	82	46	84	98	93
7-Benz[de]anthracenone	ND	20	6.2	24	16	20
Phthalate Esters						
Diethylphthalate[*]	240	48	19	29	110	120
Dibutylphthalate	250	260	27	40	140	100
Butylbenzylphthalate	110	46	40	120	120	100
Dioctylphthalate	ND	12	ND	ND	ND	ND

[*]Indicates that breakthrough correction was applied to the concentration.

Table A2.3a. Particulate Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
PAHs and Derivatives							
Dibenzofuran	0.15	1.3	0.81	ND[a]	2.1	1.1	0.29
Fluorene	0.15	ND	0.40	ND	0.90	0.32	ND
Phenanthrene+Anthracene	2.0	2.3	6.1	1.9	10.0	5.4	1.3
2+3-Methylphenanthrene	1.1	ND	1.4	ND	ND	ND	ND
1+4+9-Methylphenanthrene	0.76	ND	0.90	0.11	ND	ND	ND
Fluoranthene	1.8	1.5	7.2	1.7	9.6	6.3	2.5
Pyrene	1.7	1.2	6.6	1.8	9.7	5.1	2.3
Benz[a]anthracene	0.61	0.60	2.2	0.45	4.5	1.5	0.49
Chrysene	1.6	1.5	6.0	1.4	11	2.7	1.3
Benzo[b+j+k]fluoranthene	2.7	1.3	12	9.0	32	5.3	1.9
Benzo[e]pyrene	1.0	0.56	3.9	2.9	11	1.5	0.18
Benzo[a]pyrene	0.54	0.28	3.4	1.1	8.5	ND	ND
Perylene	0.16	ND	0.45	0.10	1.6	ND	ND
Benzo[ghi]perylene	1.4	ND	5.7	4.6	18	ND	0.36
Coronene	0.49	ND	2.4	1.1	9.4	ND	ND
Phenols							
Pentachlorophenol	2.1	ND	ND	ND	ND	ND	ND

Table A2.3a (cont'd). Particulate Rain Concentrations of Organic Compounds in Portland, Oregon in 1984.

Compound	Concentration (ng/L)						
	2/12–2/13	2/14–2/15	2/20–2/21	2/23–2/24	2/29–3/1	3/16–3/20	4/11–4/12
Oxygenated PAHs							
9-Fluorenone	0.78	ND	1.2	0.65	2.8	0.92	0.36
9,10-Anthracenedione	0.99	ND	1.9	1.2	3.7	ND	ND
7-Benz[de]anthracenone	0.53	ND	2.5	0.53	5.4	ND	ND
Alkanes							
Eicosane	12	ND	5.7	17	39	4.5	8.7
Heneicosane	14	ND	9.5	25	110	16	8.6
Docosane	17	ND	13	24	130	10	9.4
Tricosane	26	5.4	27	17	150	20	44
Tetracosane	40	5.6	30	16	140	27	16
Pentacosane	52	6.5	24	14	180	31	93
Hexacosane	40	4.3	24	9.6	100	19	16
Phthalate Esters							
Butylbenzylphthalate	3.5	ND	35	13	13	ND	ND
Bis[2-ethylhexyl]-phthalate	200	ND	350	120	680	60	ND
Dioctylphthalate	13	ND	5.5	9.9	10	9.5	5.5

[a]ND = not detected at a statistically significant level.

Table A2.3b. Particulate Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Polycyclic Aromatic Hydrocarbons and Derivatives						
Acenaphthylene	1.2	1.2	0.61	0.30	1.2	0.66
Acenaphthene	0.44	ND[a]	ND	ND	0.68	0.20
Dibenzofuran	1.6	1.4	0.61	0.43	2.2	0.79
Fluorene	1.9	0.56	0.22	0.18	1.4	0.35
Dibenzothiophene	0.62	0.29	0.19	0.073	1.2	0.20
Phenanthrene	15	5.8	5.3	2.8	12	4.1
Anthracene	1.5	0.75	0.62	0.30	ND	0.56
2+3-Methylphenanthrene	10	2.3	4.3	1.9	8.4	2.6
1+4+9-Methylphenanthrene	8.4	1.9	3.2	1.5	6.2	1.9
Fluoranthene	28	9.6	9.3	6.8	25	7.3
Pyrene	27	8.0	8.4	6.2	21	7.0
Benzo[a]fluorene	8.6	2.4	3.1	2.7	8.5	2.4
Benzo[b]fluorene	7.5	2.1	3.0	2.3	8.0	1.9
Benz[a]anthracene	5.0	2.7	2.2	3.0	5.7	3.2
Chrysene	13	5.9	6.7	6.6	32	8.1
Benzo[b+j+k]fluoranthene	11	7.2	8.5	9.7	69	17
Benzo[e]pyrene	5.2	2.9	3.2	3.8	21	5.8

Table A2.3b (cont'd). Particulate Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Benzo[a]pyrene	4.8	2.4	3.5	2.8	26	6.2
Perylene	0.85	0.48	0.75	1.1	3.6	0.84
Indeno[1,2,3-cd]pyrene	3.6	1.5	3.9	4.4	49	16
Dibenz[a,c]anthracene+ Dibenz[a,h]anthracene	0.30	ND	0.77	0.74	7.4	ND
Benzo[ghi]perylene	8.1	3.4	6.2	6.2	49	15
Coronene	1.4	ND	3.1	2.2	30	9.8
Oxygenated PAHs						
9-Fluorenone	2.1	2.4	1.0	0.61	2.6	1.2
Xanthone	ND	0.12	ND	ND	1.3	0.34
9,10-Anthracenedione	6.0	2.2	2.9	1.7	11	4.4
7-Benz[de]anthracenone	2.4	2.1	2.5	3.1	18	4.3
7,12-Benz[a]anthracenedione	4.4	ND	ND	0.51	10	ND
Alkanes						
Eicosane	41	ND	7.5	ND	66	14
Heneicosane	38	ND	34	ND	160	28
Docosane	ND	ND	25	16	190	29
Tricosane	ND	ND	90	34	370	84

Table A2.3b (cont'd). Particulate Rain Concentrations of Organic Compounds in Portland, Oregon in 1985.

Compound	Concentration (ng/L)					
	2/14–2/15	3/3–3/4	3/21–3/23	3/25–3/27	4/17–4/19	4/21–4/23
Tetracosane	ND	24	54	ND	330	55
Pentacosane	110	47	170	48	520	260
Hexacosane	ND	29	53	18	310	60
Heptacosane	NA	NA	NA	48	600	360
Octacosane	ND	40	65	24	180	53
Nonacosane	NA	NA	NA	NA	NA	470
Phthalate Esters						
Dibutylphthalate	ND	ND	ND	ND	310	ND
Butylbenzylphthalate	71	16	9.6	110	82	29
Bis(2-ethylhexyl)phthalate	ND	ND	110	ND	440	ND
Dioctylphthalate	40	12	19	7.7	60	25
Pesticides						
p,p'-DDT	ND	0.50	ND	ND	ND	ND

[a]ND = not detected at a statistically significant level.

Table A2.4. Rain Dissolved (D) and Particulate (P) Phase Concentra-
tions of Organic Compounds at the Oregon Coast in 1985.

	Concentration (ng/L)					
	4/17		4/21		4/25	
Compound	D	P	D	P	D	P
Monocyclic Aromatic Compounds						
Toluene	16	NA	ND	NA	19	NA
Ethylbenzene	3.6	NA	13	NA	16	NA
Chlorinated Compounds						
Tetrachloroethene	ND	NA	ND	NA	0.44	NA
α-HCH	12	ND	14	ND	18	ND
Aldehydes and Ketones						
Methylisobutyl ketone*	29	NA[a]	ND[b]	NA	>2.5	NA
Furfural*	590	NA	ND	NA	>63	NA
2-Heptanone*	33	NA	40	NA	13	NA
Methylfurfural*	760	NA	75	NA	1400	NA
Benzonitrile*	22	NA	29	NA	22	NA
Salicylaldehyde	120	NA	51	NA	>140	NA
2+3-Tolualdehyde*	59	ND	72	ND	55	ND
2,4-Dimethyl benzaldehyde	29	ND	4.6	ND	9.1	ND

Table A2.4 (cont'd). Rain Dissolved (D) and Particulate (P) Phase Concentrations of Organic Compounds at the Oregon Coast in 1985.

| | Concentration (ng/L) | | | | | |
| | 4/17 | | 4/21 | | 4/25 | |
Compound	D	P	D	P	D	P
Phenols						
2-Methylphenol*	1200	ND	220	ND	260	ND
3+4-Methylphenol*	2500	ND	510	ND	410	ND
2-Methoxyphenol*	1300	ND	190	ND	1200	ND
2,6-Dimethylphenol*	45	ND	5.7	ND	28	ND
2-Nitrophenol*	28	ND	31	ND	11	ND
2-Ethylphenol*	79	ND	29	ND	22	ND
2,4+2,5-Dimethylphenol*	460	ND	110	ND	230	ND
2,4-Dichlorophenol*	5.6	ND	6.5	ND	5.6	ND
4-Ethyl+3,5-Dimethyl phenol*	710	ND	300	ND	200	ND
4-Methyl-2-methoxy phenol*	540	ND	81	ND	860	ND
3,4-Dimethylphenol*	120	ND	32	ND	49	ND
4-Methyl-2-nitrophenol*	10	ND	14	ND	12	ND
2,3,4,6-Tetrachloro phenol*	34	ND	9.5	ND	32	ND
Pentachlorophenol*	94	ND	39	ND	59	ND

Table A2.4 (cont'd). Rain Dissolved (D) and Particulate (P) Phase Concentrations of Organic Compounds at the Oregon Coast in 1985.

	Concentration (ng/L)					
	4/17		4/21		4/25	
Compound	D	P	D	P	D	P
PAHs and Derivatives						
Naphthalene	47	ND	29	ND	19	ND
2-Methylnaphthalene	18	ND	19	ND	16	ND
1-Methylnaphthalene	12	ND	12	ND	11	ND
2,6-Dimethylnaphthalene	4.6	ND	4.2	ND	3.3	ND
1,3+1,6-Dimethyl naphthalene	9.3	ND	9.0	ND	6.1	ND
1,4+1,5+2,3-Dimethyl naphthalene	3.1	ND	3.1	ND	2.9	ND
1,2-Dimethylnaphthalene	1.5	ND	1.6	ND	1.2	ND
Acenaphthylene	11	0.19	19	1.25	7.0	0.21
Acenaphthene	2.6	ND	1.1	0.11	1.3	0.06
Dibenzofuran	13	0.52	5.7	1.5	6.0	0.46
Fluorene	11	0.07	6.5	0.51	4.7	0.20
Dibenzothiophene	1.7	ND	1.4	0.14	1.1	0.08
Phenanthrene	48	2.3	26	4.5	16	1.7
Anthracene	9.1	0.39	ND	0.44	0.95	0.36
3+2-Methylphenanthrene	9.6	2.3	4.4	1.2	4.0	1.3
1+4+9-Methyl phenanthrene	8.6	1.9	3.4	1.1	3.1	1.3

Table A2.4 (cont'd). Rain Dissolved (D) and Particulate (P) Phase
Concentrations of Organic Compounds at the Oregon Coast in 1985.

| | | | Concentration (ng/L) | | | |
| | | 4/17 | | 4/21 | | 4/25 |
Compound	D	P	D	P	D	P
PAHs and Derivatives						
Naphthalene	47	ND	29	ND	19	ND
2-Methylnaphthalene	18	ND	19	ND	16	ND
1-Methylnaphthalene	12	ND	12	ND	11	ND
2,6-Dimethylnaphthalene	4.6	ND	4.2	ND	3.3	ND
1,3+1,6-Dimethyl naphthalene	9.3	ND	9.0	ND	6.1	ND
1,4+1,5+2,3-Dimethyl naphthalene	3.1	ND	3.1	ND	2.9	ND
1,2-Dimethylnaphthalene	1.5	ND	1.6	ND	1.2	ND
Acenaphthylene	11	0.19	19	1.25	7.0	0.21
Acenaphthene	2.6	ND	1.1	0.11	1.3	0.06
Dibenzofuran	13	0.52	5.7	1.5	6.0	0.46
Fluorene	11	0.07	6.5	0.51	4.7	0.20
Dibenzothiophene	1.7	ND	1.4	0.14	1.1	0.08
Phenanthrene	48	2.3	26	4.5	16	1.7
Anthracene	9.1	0.39	ND	0.44	0.95	0.36
3+2-Methylphenanthrene	9.6	2.3	4.4	1.2	4.0	1.3
1+4+9-Methyl phenanthrene	8.6	1.9	3.4	1.1	3.1	1.3

Table A2.4 (cont'd). Rain Dissolved (D) and Particulate (P) Phase

Concentrations of Organic Compounds at the Oregon Coast in 1985.

Compound	4/17 D	4/17 P	4/21 D	4/21 P	4/25 D	4/25 P
Fluoranthene	41	6.3	9.3	3.3	35	2.0
Pyrene	29	3.9	6.3	2.9	28	2.2
Benzo[a]fluorene	2.7	0.70	1.1	0.30	1.2	0.30
Benzo[b]fluorene	NA	0.78	1.1	0.25	0.80	0.38
Benz[a]anthracene	1.4	1.3	0.51	0.51	2.0	0.37
Chrysene	2.8	3.7	0.95	1.4	2.4	1.1
Benzo[b+j+k]fluoranthene	ND	5.0	ND	2.3	ND	1.9
Benzo[e]pyrene	ND	1.4	ND	1.2	ND	0.57
Benzo[a]pyrene	ND	1.1	ND	1.2	ND	0.59
Indeno[1,2,3-cd]pyrene	ND	4.7	ND	0.89	ND	0.49
Benzo[ghi]perylene	ND	4.5	ND	1.5	ND	0.53
Coronene	ND	0.57	ND	ND	ND	0.09
Oxygenated PAHs						
1-Indanone*	230	ND	71	ND	58	ND
Coumarin*	102	ND	55	ND	23	ND
9-Fluorenone	84	0.85	24	1.9	17	0.98
Xanthone	5.8	ND	5.8	0.41	3.0	ND
9,10-Anthracenedione	37	2.8	17	1.1	6.1	ND

Concentration (ng/L)

Table A2.4 (cont'd). Rain Dissolved (D) and Particulate (P) Phase Concentrations of Organic Compounds at the Oregon Coast in 1985.

Compound	Concentration (ng/L)					
	4/17		4/21		4/25	
	D	P	D	P	D	P
7-Benz[de]anthracenone	ND	1.6	1.0	1.2	0.43	1.7
7,12-Benz[a]anthracene dione	ND	ND	ND	ND	ND	0.31
Phthalate Esters						
Diethylphthalate*	100	ND	15	ND	56	ND
Dibutylphthalate	81	ND	18	ND	48	ND
Butylbenzylphthalate	100	ND	ND	ND	20	16
Dioctylphthalate	ND	28	ND	11	ND	14
Alkanes						
Heneicosane	ND	18	ND	ND	ND	34
Docosane	ND	21	ND	ND	ND	78
Tricosane	ND	33	ND	10	ND	150
Tetracosane	ND	28	ND	36	ND	170
Pentacosane	ND	50	ND	47	ND	210
Hexacosane	ND	41	ND	ND	ND	180
Heptacosane	ND	150	ND	60	ND	250
Octacosane	ND	35	ND	8.8	ND	170

[a]NA = not available. [b]ND = not detected at a significant level.