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ANALYSIS OF SEASONAL VARIATION AND CORRELATION OF NEUTRAL ORGANIC POLLUTANTS IN NEW YORK CITY PRECIPITATION

BY

AMY YIN ZHANG

A dissertation submitted to the Graduate
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THE CITY UNIVERSITY OF NEW YORK

Abstract

ANALYSIS OF SEASONAL VARIATION AND CORRELATION OF NEUTRAL ORGANIC POLLUTANTS IN NEW YORK CITY PRECIPITATION

By

Amy Yin Zhang

Advisor: Professor David C. Locke

Neutral organic compounds were extracted from rainwater and snow by micro-solvent liquid-liquid extraction or solid phase extraction, and quantitively analyzed for polycyclic aromatic hydrocarbons (PAH), alkanes, and phthalate esters by HPLC or GC and by GC/MS. PAHs are known for their carcinogenicity and mutagenicity. 16 PAHs and 7 n-alkanes were identified in New York City precipitation. 5 PAHs were most frequently detected and are predominant components of total PAH levels. A hump of unresolved hydrocarbons was consistently observed in GC profiles, which indicates significant anthropogenic inputs to the organic content of precipitation. The levels of most compounds varied with season but were mostly at parts-per-billion levels. Seasonal variation of levels of total PAHs and n-alkanes were found in the order: Winter > Fall > Spring > Summer. A correlation between levels of total PAHs and n-alkanes in most of rain events was also identified as an indicator of anthropogenic inputs.

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This thesis is also a gift for my parents and my lovely,cutie daughter, Erica.

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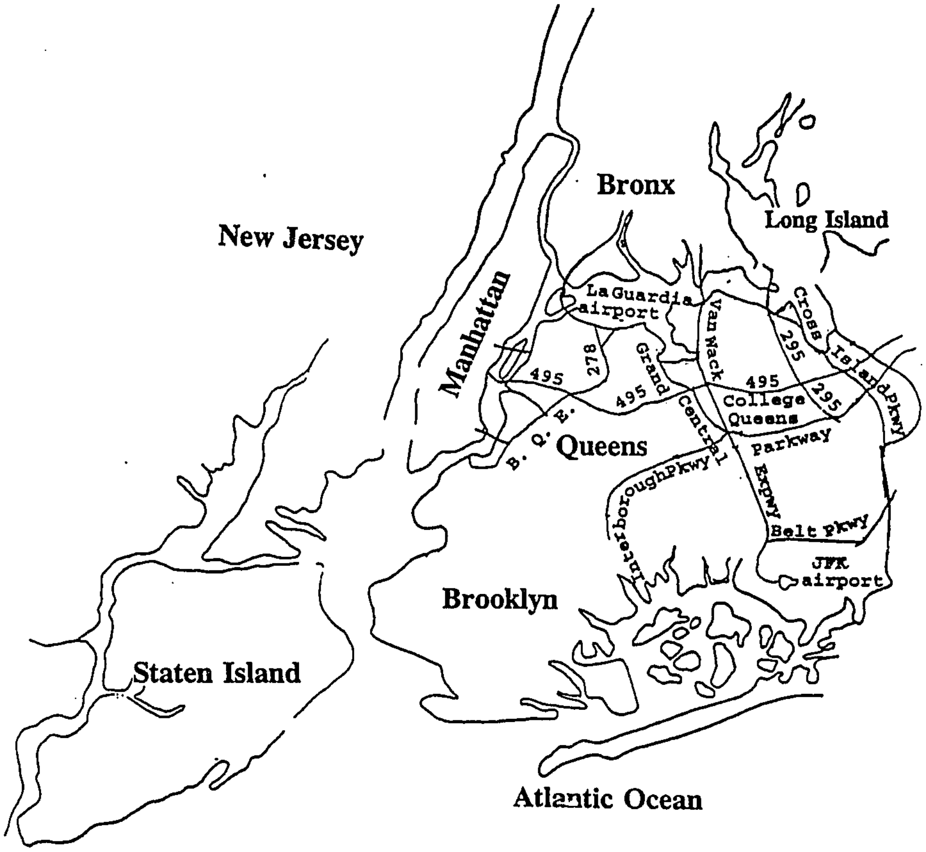


General Introduction

The atmosphere is recognized as an important pathway in the global transport and deposition of anthropogenic and biogenic organic chemicals. Atmospheric organic compounds are present in both the gas and aerosol phases. Anthropogenic compounds, most of which are considered pollutants, originate from various processes such as industrial emissions, energy production/consumption, agricultural/forestry practices, and waste incineration. These chemicals are dispersed in the atmosphere and may be transported by air masses and winds over long distances to finally deposit on land and water during precipitation events. Semivolatile organic chemicals, which are present both in gas phase and adsorbed on particulate matter, are particularly amenable to this type of dispersion mechanism (1).

Trace organic compounds such as phthalate esters, alkanes, and polycyclic aromatic hydrocarbons (PAHs) are relatively inert chemically and are thus expected to persist for long periods of time. These compounds have been found in remote areas thousands of kilometers away from their nearest known sources (2,3).

PAHs are found to be widely distributed in the environment. Many of these compounds have been detected in airborne particles (4), rainwater (5), and river water (6). The concentration of PAH in the New York City atmosphere during the 1970s was reported around 1.2 $\mu g/1000\ m^3$, while the average concentration in US urban atmospheres in 1963 was 5.7 $\mu g/1000\ m^3$ (7). The concentrations of PAHs in precipitation in Germany, Belgium and Norway were reported to be in the range of 10-500 µg/L (8,9). Atmospheric deposition processes and atmospheric inputs of organic pollutants to surface waters have received extensive attention (10). For example, Gschwend and Hites (1981) reported that the average flux of individual PAH (except anthracene) to remote northeastern US surface waters and sediments in 1980 were 5-10 times higher than the 1950 values, and 10-30 times higher than the 1900 values (11). This historical PAH record demonstrated that anthropogenic activities over the last century have resulted in an increased input of PAH to our natural waters. These studies have provided important information to environmental protection agencies to regulate these pollutants from industrial and combustion sources. Many trace organic pollutants, such as PAHs, are known to be carcinogenic and mutagenic (12).

Increased levels of these pollutants in surface water would have a severe impact on the local and global ecological systems, which in turn affect the quality of our living environment.

Distributions of aliphatic hydrocarbons have been measured in air samples collected over the North Atlantic Ocean (13), the Indian Ocean (14), and the Pacific Ocean (15). Aliphatic hydrocarbon and PAH concentrations have been measured in air from Northern Europe (16). These studies show that a wide range of hydrocarbons exist in air in both urban and non-urban regions.

As one of the removal processes for organic compounds and air pollutants to soil and open waters, precipitation has gained widespread attention. It was only in last decade that the atmosphere was identified as a major pathway for the transport of anthropogenic pollutants to surface waters (17). The processes responsible are wet deposition (rain, snow and fog) and dry deposition (particle fallout, air-water exchange). The relative importance of wet versus dry deposition depends on the distribution of the element or compound between the gas and particle phases, particle-size distribution, rain (snow) fall intensity and duration, Henry's law constants, aqueous solubility, etc. (1)

Although analytical studies on neutral organic compounds and other pollutants have been extensive, an evaluation of composition and level of this set of compounds in rainwater in our environment is still of importance. Existing extraction and analysis methods can be improved and simplified So that the evaluation of these compounds can be done in a more efficient and more accurate way. Determination of the composition of PAHs and their derivatives, alkanes, and phthalate esters in New York City rainwater provides valuable information about our local environment situation.

Chapter I: PAHs in New York City precipitation

Introduction

The occurrence of PAHs in the environment is primarily attributed to anthropogenic activities originating mostly from incomplete combustion processes, during which PAHs are pyrosynthesized. Important anthropogenic sources of PAH include combustion of fossil fuel (gasoline, kerosene, coal, diesel fuel), waste incineration, coal gasification and liquefication processes, petroleum cracking, carbon black, coal tar pitch and asphalt (13). Other sources of PAHs include tobacco smoke, coke oven emissions, vapors from barbecued and smoked foods, and industrial effluents(14). They are also found in various petroleum and coal products. There is a small but significant contribution from natural sources, such as forest fires and volcanic activity (18).

Levels of emissions of PAHs from fossil fuel combustion can vary over several orders of magnitude depending upon the particular fuel and combustion conditions. Emissions of PAHs from the burning of coal or wood for residential space heating are several orders of magnitude greater than those from gas or oil burning (18).

PAH vapors emitted from high-temperature sources cool rapidly and may condense on particulate matter (soot and fly ash). PAHs are highly inert chemically and thus persist for long periods of time. The aerosol-adsorbed PAH can be transported by winds for distances which depend on the aerosol diameter. Large airborne aerosol particles (>5 µm) not only have significant gravitational settling velocities, but they are also efficiently removed from the atmosphere by precipitation. Thus large aerosol particles are deposited closer to their sources. Small aerosol particles (<1 µm) are less efficiently removed by wet and dry deposition processes and have longer atmospheric residences times. These account for most of the PAH in remote marine and lacustrine sediments (15). These compounds have been detected in the atmosphere in remote locations such as Enewetak Atoll in the Pacific Ocean (2,3), suggesting that they are globally distributed in the atmosphere. PAHs are subject to the same physical processes that determine the fate of airborne particles, i.e., dispersion by diffusion and turbulence, and removal by sedimentation, impaction, washout and rainout (14).

PAHs of environmental concern

PAHs are the most studied trace hazardous pollutant. Extensive attention and caution has been paid to this widely occuring group of compounds because the PAH-containing fraction from both organic air particulate matter and gasoline engine exhaust condensate (19) are carcinogenic on animal skin or in animal liver (20). Some of the more commonly occurring PAH are given in Table 1.

1. Carcinogenicity and mutagenicity of PAHs

The strong suspicion that PAHs can cause human cancer results from the observation that the binding of diol epoxides of PAH to DNA was correlated with the incidence of mouse skin cancer (21). Adducts of six PAHs metabolites to DNA were recognized using an intensified diode array-optical multichannel analyzer. As for benzo[a]pyrene and many other structurallys similar PAHs, oxidation of these compounds occurs in rat liver microsomes via a lipid peroxidation pathway (22). This pathway has been recognized to be the one that triggers the conversion of potential carcinogens to ultimate carcinogens. Therefore, many members of PAHs are the generic compounds that can cause cancer when metabolized in an animal's body. The diol epoxide metabolites of benzo[a]pyrene, chrysene, and benz[a]anthracene have been investigated. The adduct of benzo[a]pyrene and DNA causes a damage level of 5 bases in 10^6. Allen, *et al.* further found that the mitochondrial DNA of the cell, which accounts for one-tenth of total cell DNA, was 50 to 500 fold more susceptible to modification by PAH than was nuclear DNA (23). Among the PAHs they tested were at least four known animal carcinogens, chrysene, benzo[a]pyrene, 5-methylchrysene and benzo[a]anthracene. Dai has proposed a "diregion theory" to illustrate the mechanism of the direct mutagenic or carcinogenic activity of PAH diol-epoxide upon their adduct to DNA. In short, the "diregion theory" hypothesizes the crucial step in the carcinogenesis of PAH is their ability to cause cross-linking between DNA complementary base pairs (e.g., thymine-adenine or cytosine-guanine base pair). Such a cross-linking phenomena further causes a complementary frameshift mutation in the DNA double helix (24).

2. Phototoxicity of PAHs

Though PAHs are known for their potential as carcinogens, another hazardous aspect of PAHs was recently discovered. Kagan et al (25) found that several noncarcinogenic PAHs were acutely phototoxic. The finding was an anthracene solution that had no effect on tadpoles in the dark became toxic in the presence of sunlight or ultraviolet light. Seven other PAHs were found to become lethal to water fleas at the parts-per-billion level under UV light. Among these, fluoranthene and pyrene, the two most common PAHs, were the most phototoxic. Similar effects were reported for other species (25), for example, the most phototoxic PAH for mosquito larvae is pyrene.

Similar effects were observed in other test species. For mosquito larvae, the most phototoxic PAH was pyrene. Though mildly toxic in the dark it became 1,500 times more so when the larve were also irradiated with ultraviolet light.)

PAH in airborne matter at various environmental sites

1. Airborne PAH from traffic and industrial emissions

Distribution of PAHs in street dust in Tokyo was found by Takada *et al.* in 1990 to be at a level of a few micrograms per gram of dust (26). The abundant level of alkyl-substituted

PAHs was attributed to automobile exhaust in heavy traffic. Mobile sources of atmospheric PAHs were also studied in a roadway tunnel in Japan (27). Analysis of airborne particulate matter collected from the Baltimore Harbor Tunnel showed that the concentrations of PAHs were lower by factors of 5-10 in 1985/1986 in comparison to those measured in 1975 (28). This significant reduction of level of PAH in this heavy traffic site is likely the result of the use of catalytic converters in most of the present automobile fleet. The abundant amount of alkylated phenanthrenes suggests diesel engine sources, while the presence of higher molecular weight PAHs implicates an additional source from gasoline-fueled vehicles.

The level of PAH in air particulate matter from the lightly industrialized urban area of New Zealand was studied in 1985 (29); here the main sources of PAH are considered to be domestic fires and automobiles.

2. Distribution of PAH according to vapor pressure

Measurement of PAH in air in both the particulate and gas phase along the Niagara River was reported between 1982 and 1984 by Hoff and Chan (10). PAH's with three rings or less were found in significant proportions in the gas phase while larger molecules are almost solely in the particulate phase. Furthermore, particulate components of PAH loadings appear to originate locally, while gas-phase PAH components have a more regional character indicating regional or long-range transport. In these studies, 13 PAH were measured in both the gas and particulate phases, including naphthalene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[a]pyrene. Concentrations of the PAH species monitored varied from 3 pgm^{-3} to 40 ngm^{-3}. A second group of PAH which included benzo[a]pyrene was seen only in the particulate phase. A significant gas-phase component exists for PAH of molecular weight less than 252. The highest air concentrations for benz[a]anthracene and chrysene were found in winter samples, which is accompanied by a corresponding highest concentrations of n-C_{22} and n-C_{24}.

3. Seasonal variation of PAH levels in airborne matter

Seasonal variation of PAH in New Jersey was studied in Newark, Elizabeth, Camden and Ringwood during winter and summer of 1981 to 1984. The PAH levels of urban areas were 3-5 times of that of the rural site at Ringwood. The PAH levels generally were 4-6 times higher for the 6-week winter periods than for the 6-week summer periods.

The concentrations of 12 PAH collected on eight different cruises in Lake Michigan between 1975 and 1977 were evaluated (14). Geographically, Lake Michigan lies between an urban and a nonurban range of Michigan State. The PAH concentrations ranged from 0.1 ng/m^3 for several compounds including fluorene, phenanthrene, anthracene and fluoranthene to 4.2 ng/m^3 for pyrene. The values found for benzo[a]pyrene and other PAH compounds over Lake Michigan were found to be 0.3 ng/m^3 to 1.8 ng/m^3. These values fall into the range of the average annual airborne benzo[a]pyrene concentrations from 1966-1970 in urban areas of US, which ranged from 0.2 ng/m^3 over Hawaii to 29.5 ng/m^3 at Altoona, Pennsylvania (14). The same study showed nonurban annual concentrations of 0.1 ng/m^3 - 2.1 ng/m^3.

Ratio of wet and dry deposition of PAH

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment. Upon formation in combustion of fossil fuels, PAHs are subsequently released to the atmosphere, but eventually transported from air to ground as dry and wet deposition.

Studies of the annual average wet, dry, and total PAH deposition to Lake Michigan showed a total combined input of 12 PAH was about 40 x 10^6 g/yr (about 40 tones/yr) with the wet to dry input ratio being approximately 9:1 (14). The average wet to dry deposition ratio of 1:9 showed that dry deposition is the predominant input mechanism for PAHs in Siskiwit Lake (17).

Wet deposition of PAH as the consequence of gas and particulate scavenging

As with many atmospheric organic compounds, PAHs are present in both the gas and aerosol phases. During precipitation, rainwater scavenges from the atmosphere gases as well as aerosols that may contain a large array of organic compounds including PAHs. Thus, both gas and particulate scavenging processes may be important for a given PAH compound.

For non-reactive gas phase pollutants, such as PAHs, the equilibrium distribution of a substance between the gas and aqueous phases is described by Henry's Law for dilute solutions.

$$W_g = C_{rain,dissolved}/C_{air,gas} = RTS/P = RT/H.$$

where W_g is the gas scavenging ratio, R is the gas constant, T is the absolute temperature (K), S is the water solubility, P is the vapor pressure, H is the Henry's constant (atm m^3 mol-1).

Gas scavenging is reversible and depends on the Henry coefficient and air concentration of an organic compound in the gas phase. For PAHs and other compounds of low solubility, the Henry's Law constant is equal to the ratio of the compound's vapor pressure to its solubility. H is a strong function of temperature. For many organic compounds it increases by roughly a factor of two for every 10^0C increase in temperature.

Particle scavenging can occur either by in-cloud processes (nucleating scavenging, rimming) and/or below-cloud processes (scavenging by collision between a hydrometer, e.g. snow flake, rain droplet, fog droplet and a particle). Particle scavenging depends strongly upon the solubility, size and air concentration of the aerosol (30).

Mechanism of scavenging of airborne polycyclic aromatic hydrocarbons by rain

The presence of PAHs in rainwater is the result of both in-cloud and below-cloud scavenging. One of the main differences between these two processes is that the latter can only occur during precipitation events. As PAHs in air are present both in the gas phase and adsorbed on particulate matter (31), the scavenging of PAHs in air by either cloud water or rainwater is the result of dissolving of gas-phase PAHs in water and the result of scavenging of particulate-bound PAHs by cloud or rain drops.

The scavenging of gas-phase PAHs below clouds is the result of gas-water partitioning. The below-cloud scavenging by rain of PAH-containing particulate matter in air is a result of the nature of the particulate matter and not of the PAHs. In general it is believed that aerosol particles are more efficiently removed from within rather than from below clouds (32). Below-cloud aerosol particles are scavenged by gravitational collisions resulting the removal of only giant particles (radius > 1μm) (33,34).

The in-cloud scavenging of particulates is a result of diffusion, interception, and impaction. This scavenging may occur whether precipitation is occurring from a cloud or not.

Measurement of the concentrations of PAHs in wet precipitation in the Frankfurt region of Germany in 1981 demonstrated that local sources of PAH do not contribute significantly to PAH concentrations in rainwater at the various sites, and that concentration profiles do not vary significantly (9).

The choice of PAHs of environmental importance

The sixteen PAH of my research interest range from 2-membered to 5-membered rings. They are all on the US Environmental Protection Agency (EPA) "Consent Decree" priority pollutant list (35). The recommended analytical procedure has been presented as Method 610 in the Federal Register. The Word Health Organization has recommended that the total concentration of six PAHs, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, fluoranthene, and indeno[1,2,3-cd]pyrene, not exceed 200 ng/L in domestic water (36, 37). These six PAHs are also regulated by the European Commonwealth states for drinking water. The Federal Republic of Germany has legislated a maximum limit for PAHs of 250 ng carbon/L of drinking water (38). These sixteen PAHs are often found in a variety of environmental sources, which range from fly ash wash and factory effluents (39), to ocean and river water, atmospheric dry and wet precipitation.

Modern instrumentation for determination of PAH

HPLC has generally been used to analyze PAHs. Detection of PAH after HPLC separation is usually achieved by UV absorbance, which can be supplemented with a fluorescence detector to achieve greater sensitivity. Excellent sensitivity can be achieved for all PAHs at 255 nm. Good sensitivity and selectivity can be achieved at 280 nm for most of PAHs, except for anthracene. UV at 360 nm gives excellent selectivity for the 5-ring PAHs which are the most biologically active, however, it shows poor sensitivity for 2- to 3-ring PAHs and moderate sensitivity for the higher PAHs (39). A second instrument such as GC/MS should be used as a complementary analytical method, especially when the compounds cannot be easily identified by the HPLC methods.

One limitation of single wavelength UV absorbance or fluorescence detectors is that they do not give qualitative information, other than retention time. A diode array UV absorption detector (DAD) can simultaneously provide qualitative and quantitative information, such that a second method of analysis may not be required. The detection limit for a DAD compares well to that of a single wavelength UV detector. It meets the required detection limits for most compounds. The diode array detector was used here for compound identification.

The rapid scanning capability of the diode array detector allows the recording of all 16 PAH spectra from a single HPLC analysis. The spectra are highly structured and distinctive because of the aromaticity of the PAH structures. In general, the spectra of PAHs show increased absorption at higher wavelengths. Combining the specialty Vydac C_{18} PAH columns with the diode array detector provides for reliable separation and confirmation of compound identity in one fast analysis.

Several techniques can be used to assess individual peak identity and purity, including examining the maximum absorbance wavelength and overlay of sample and standard spectra. The latter technique has been adopted for identification and characterization of PAHs in this work. The exact match of the UV spectrum of an unknown peak and that of a standard with the same retention time offers strong confirmation of solute identity. By searching the on-line PAH library, unknown samples are easily compared with their corresponding standard PAHs.

Solid-phase extraction of neutral organic compounds from rainwater

Sample preparation in modern instrumental analysis is often required for two reasons: cleanup and concentration. The sample matrix frequently interferes with the measurement. In ultraviolet (UV) analysis, for example, absorbing impurities may render the sample opaque. In gas and liquid chromatography, the life of columns may be drastically shortened by impurities. In these cases, sample cleanup is mandatory. In many instances, the analyte concentration falls below the sensitivity range of the analytical method chosen. Only with concentration can the analysis be brought into a practical range. This is the second reason for pretreatment (40).

Traditionally, liquid/liquid extraction has been used for these purposes. However, this manual method using separatory funnels is inefficient, tedious, and costly. Solid-phase extraction (SPE) technology was introduced in the mid-

1980's as an alternative to liquid-liquid extraction for removal of matrix interferences and analyte concentration before analysis (40,41).

In SPE, the matrix containing the analytes is passed through an adsorbent disc or short column which retains the analytes. This is more subtle and selective than liquid/liquid extraction. In liquid/liquid extraction, relative solubility of the analyte in either phase is the only property that can be used.

A wash step may be used prior to elution to remove interferences, resulting in a very clean extract. Finally, the analytes are eluted from the sorbent with a small quantity of appropriate solvent. The benefits of SPE over liquid-liquid methods may include greater recovery for specific analytes, improved selectivity and speed, and reduced solvent and waste volumes. A large number of adsorbent materials are available for performing normal-phase, reversed-phase, ion-exchange, and mixed-phase, extractions.

The most commonly encountered SPE sorbent is based on porous silica, the surface of which has been modified by bonding to a layer of organic molecules. Silica itself is highly polar and water wets it very well. However, by bonding onto this a layer of hydrophobic material, the silica has effectively been water-proofed. In order to use this sorbent to extract a compound from water, it must be prepared (conditioned) to interact with that aqueous sample. This is usually done by passing methanol or a similar solvent through the sorbent bed. The methanol penetrates into the organic bonded layer and permits water molecules and analyte to diffuse into, rather than run over the surface of, the bonded phase (42).

Once conditioned, excess solvent is removed by washing with water or a liquid similar to the sample to be extracted. A sample is applied to a conditioned sorbent and pulled through under vacuum. Those compounds that interact more strongly with the sorbent than with the sample matrix tend to remain on the sorbent. The sorbent can also be eluted with other liquids to flush out potential interferences that can remain on the sorbent. A collection tube is placed in the vacuum manifold and a few milliliters of organic solvent are applied. The solvent that passes through the sorbent is then collected and either injected directly into an analytical instrument or condensed, often under only a stream of dry nitrogen, or reconstituted in a different medium. Extractions may take as little as five minutes from start to finish, and with proper development may lead to recovery exceeding 90% of the analytes of interest from the sample matrix.

The method development process identifies which combination of bonded SPE phase and solvent extraction conditions will yield the cleanest extract with maximal recovery of analytes. Each type of sample may need to be isolated by SPE in a different way, with its own set of rules which must be followed to obtain the best results.

Non-polar extraction columns or discs contain octadecyl, octyl, ethyl, phenyl or other hydrophobic functional groups bonded to silica particles. These sorbents are used to extract hydrophobic compounds from aqueous solutions such as body fluids, wastewater, rainwater, or wine (41).

Experimental approach for this thesis

The rain samples of individual rain/events were subject to liquid-liquid or solid phase extraction followed by condensation. The neutral organic extracts were subjected to HPLC analyses of PAHs and phthalates, or to GC analyses of n-alkanes. GC-MS was used for confirmation of the results of HPLC and GC analyses. An overall experimental scheme is outline in Figure 1.

Sampling site. The precipitation sampling device was situated on the roof of Remsen Hall which is 40 feet above ground at Queens College. The Long Island Expressway is half a mile from the sampling site. The Grand Central Parkway, Van Wyck Expressway, and Interborough Parkway are about 2 miles away. Two major airports, JFK International airport and the LaGuardia airport are 8 and 10 miles away, respectively. Queens College is located in the central north part of Queens area, which is about 20 miles northwest of the nearest coast of Atlantic Ocean and 15 miles east of Manhattan. The neighborhood surrounding of Queens College is a low density residential area with no industrial activities. It is about 30-45 miles east from north eastern New Jersey, which is one of the most heavily industrialized areas in the region and the nation.

Materials. HPLC-grade hexane, dichloromethane, acetonitrile and methanol were purchased from Fisher Scientific, Inc. PAH standards were obtained from Absolute Standards, Inc. Phthalate esters and alkane standards were obtained from Aldrich Chemical Company, Inc. Solid phase extraction discs were purchased from ANSYS, Inc. HPLC columns (25cm x 4.6mm, C_{18} 201TP) specially designed for PAH separations were from Vydac.

Sampling procedure. Rain and snow samples were collected from May 1993 to May 1994 for 36 precipitation events. The rain collector consisted of a 2'2"x 3' rectangular plate made of fiber glass, a Teflon-coated funnel and 5 gallon container made of Teflon-lined polyethylene. Their use eliminated sample cross contamination and interferences that could come from exposing the samples to plastic additives. Rain and snow samples were collected from the rectangular plate. They passed through a funnel that was connected to the top of 5 gallon container. 0.25 inch of precipitation is equivalent to One gallon of rainwater. Each rain/event with at least 0.125 inch of precipitation was subject to analysis.

The collected rainwater was carefully transferred to 4-L brown glass bottles precleaned in the laboratory specifically for trace organic sampling. These rain samples were stored at 4^{0}C in the dark before extraction. During the sampling period, the rain water came in contact only with Teflon and glass. The rain collector was subject to thorough cleaning prior to next sample collection.

Extraction

Liquid-liquid extraction. Neutral organic compounds were extracted using the liquid-liquid extraction method. Hexane solvent is desirable because it floats on top. Liquid-liquid extraction of rainwater was carried out in a 2 liter volumetric flask with magnetic stirring for 24 hours. Two or more liters of rainwater is required to provide sufficient material to analyze. The volume of the extraction solvent used to provide sufficient material to analyses was 15 ml hexane per liter of rainwater. Since the small volume of lighter organic solvent used is the upper layer in the extraction mixture, after the extraction, the hexane layer is moved into the narrow neck of the flask by addition of more of the same rainwater and the thicker layer is then easily transferred out. The hexane layer was dried by passing through a column of Na_2SO_4 and concentrated using a Kuderna-Danish (K-D) concentrator. Acetonitrile was added to the extract in a 2:1 ratio. Solvent exchange to acetonitrile was achieved using a stream of nitrogen, since hexane has lower boiling point and evaporates first. The final volume was adjusted to 500 µl in a 1.8 ml vial using a nitrogen flow.

Solid phase extraction. The solid phase extraction apparatus consists of a 1000 ml filtration flask, a reservoir and a clamp. The SPE discs 47 mm C_{18} were obtained from SPEC ANSYS, Inc. All glassware was cleaned prior to use. The flask, vacuum line and filtration support were assembled, the SPE disc placed in the center, the reservoir carefully placed on top, and the clamp attached so the disc was not subjected to sideways shear. To ensure optimal extraction of the analytes of interest, the disc was conditioned with methanol. Five ml of methanol was added to the disc and a small vacuum applied to draw the solvent through until it almost reached the surface of the disc. Five ml of water was added to the disc and vacuum drawn until the water almost reached the top surface of the disc. The rainwater sample was poured into the apparatus reservoir directly onto the film of water left on the disc from the conditioning step. The vacuum was adjusted to achieve a flow rate of 50-75 ml per minute. After the entire sample was drawn through the disc, the excess water in the disc was dried under vacuum approximately 5 minutes. The elution solvent for the analytes was methylene chloride or hexane. The volume of solvent used was 15 ml for each 1 liter of rainwater. This volume of solvent was chosen as a compromise: it has to be minimized to provide the greatest concentration factor, but sufficient to completely dissolve the analytes. Following elution, the sample solution was passed through anhydrous sodium sulfate to remove all residual water, and concentrated using a K-D condenser to final volume of 1 ml. Acetonitrile was added to the elute for solvent exchange. The final volume was adjusted to 500 µl in a 1.8 ml vial by nitrogen flow.

Analytical methods for separation and identification

HPLC. A Hewlett-Packard/(HP) 1090 liquid chromatograph equipped with autosampler and HP 3392A Diode-Array detector were used along with a 25 cm x 4.6 mm i.d. Vydac 201TP PAH column. Carefully prepared PAH standards were routinely injected to check column performance and to optimize operating conditions. Twenty-five µl of concentrated rainwater extract in acetonitrile was injected. Reference spectra were obtained from PAH standards, phthalate ester standards or from the HP HPLC-Chemstation library.

Optimization of operating conditions for PAHs. The optimum HPLC operating conditions were chosen empirically by adjusting the amount of acetonitrile in the mobile phase, the temperature, and the flow rate singly or in combination to produce the best separation in a reasonable time. The best separation was achieved at ambient temperature, with a 3 min initial 50% acetonitrile, linear gradient over 7 min to 100 % acetonitrile at a flow rate of 1.5 ml/min, a final holding time of 7 min. The theoretical plate number for naphthalene was 15484, which is similar to the efficiency claimed by the manufacturer. The baseline shift accompanying the use of gradient elution is caused by the changing refractive index of the effluent.

GC. A Hewlett-Packard 5880A gas chromatograph with a flame ionization detector (FID) and a 5880 A series GC Integrator were used for determining n-alkanes. A 30 m x 0.32

mm i.d. nonpolar DB-5 (5% phenyl methyl silicone) column was used for the separation.

GC-MS. The identity of neutral organic compounds in rainwater was crosschecked by GC-MS using a Hewlett-Packard 5988A GC/quadrupole mass spectrometer and a HP 1000 data system. Mass spectra of each emerging peak were taken at electron energies of 70 eV. A 30 m x 0.32mm DB-5 GC column was used under conditions similar to the GC analysis indicated above.

Blank. Extraction of a volume of deionized water (MilliQ system) equivalent to the volume of sample using liquid-liquid extraction and solid phase extraction was carried out. Extracts were analyzed using the same HPLC and GC procedures. No PAHs, phthalate esters or n-alkanes were detected.

Results

Extraction recovery and repeatability.

Earlier studies have shown that precipitation samples contain a complex mixture of organic compounds. Extractable neutral organic compounds identified in the present study in urban rain and snow, and the concentration ranges observed are listed in Table 2. These concentrations are based on the assumption of 100% recovery. Experimentally determined recoveries from the spiking experiments are given in Table 3. The recoveries were both compound and concentration dependent. The most volatile species, such as dimethylphthalate and diethylphthalate, have very poor recoveries. but most other compounds are recovered with good efficiencies.

The precision studies were performed at levels around 20 µg/ml. Four determinations were made using liquid-liquid extraction (LLE) and three determinations were made using solid phase extraction (SPE). One hundred microliters of spiking solution of 20 µg/ml was added to 1L of deionized water and carried through the procedure. The spiking solution contained 9-Fluorenone, phenanthrene, chrysene and 1,2,3,4-dibenzanthracene, each at 20 ppm in acetone. The recovery of the four compounds was determined using external standards. A blank consisting of 1L of HPLC grade water (Fisher Scientific) was also carried through each set of extractions. The results for both LLE and SPE are reported in Table 4. The lowest average recovery by LLE was 76.3% for 9-fluorenone, while the highest recovery was 89.4% for chrysene. The lowest average

SPE recovery was 71.7% for chrysene, while the highest recovery was 87.2% for phenanthrene. The relative standard deviations (RSD) varied from 6.13% to 7.65% for LLE, while the RSD varied from 4.85% to 9.63% for SPE.

The reproducibility of the GC peak areas was determined by injecting 2.0 µl of a solution containing approximately 20 µg/ml of 31 compounds (listed in Table 3). Five repetitive injections were made. The RSDs for most compounds varied from 4% to 8%. The reproducibility of the GC retention times for most compounds was 0.06% RSD. The linearity of the GC system was determined with the 7 n-hydrocarbon and 4 phthalate ester standards. The mass of each of the 11 compounds injected ranged from 0.2 to 40 ng. Linear regression analysis of peak area versus mass injected gave correlation coefficients of >0.98 for all compounds.

The reproducibility and linearity of the HPLC system was determined for the 16 PAH standards. The reproducibility of the HPLC peak areas was determined by making 5 repetitive injections of 25 µl of a solution containing 20 µg/ml of each 16 PAH standard. The RSDs for most compounds varied from 4% to 5%. The linearity of the HPLC system was determined by injecting 3 ng to 500 ng of each of the 16 PAH compounds. The correlation coefficients for most compounds were >0.98.

PAHs in precipitation

A total of 16 PAHs and 4 other polycyclic aromatic compounds were detected in 36 precipitation samples from May 1993 to May 1994. These PAHs ranged from 2-ring to 5-ring compounds. All the major PAHs are present in all samples but usually vary in relative proportions. The number of PAHs detected, the concentrations of these PAHs, and the pattern of PAHs in rain varies substantially from one rain event to another. Fig.2 shows the HPLC chromatogram of 16 PAH standards and Fig.3 shows the HPLC chromatogram of a rain sample of May 19, 1993. The overlay spectra of 8 PAHs and their corresponding standard compounds are shown in Figs.4(a-h). The sum of all 2-5 ring PAHs for the calendar year was 20.2 ppb. Frequency of finding PAHs with 2 to 4 rings was for phenanthrene 20 out of 36 events; fluoranthene, 18/36; chrysene, 17/36; pyrene 14 /36; and naphthalene 15/36. Five ring PAHs were occasionally detected.

Seasonal variation of PAH in rainwater

1. PAH profile in winter. The seasonal variation of the occurrence and level of PAHs is shown in Table 5, which gives the concentrations (µg/L) of 16 PAHs in winter rainwater, along with the minimum, median, and maximum concentrations for individual and total PAH. Phenanthrene was detected in almost all the winter rain and snow samples (8 of 9 rain events). Fluoranthene and chrysene were present in most rain events (7/9), and naphthalene and pyrene were frequently detected (5/9). The concentration range of these 5 most abundant and frequently detected PAHs was 0.78-2.6 µg/L in wet precipitation samples from 11/27 to 3/29 (from Table 5). In addition, dibenzothiophene and dibenzofuran were frequently detected, especially during later fall and through most of the winter, with a mean concentration of 0.01 and 0.04 µg/L, respectively. 9-Fluorenone was also frequently detected in the late winter and early spring, with a mean concentration of 0.04 µg/L. In 3 single rain or snow events, a total of 8 of 16 PAHs were detected, and the total concentration was as high as 2.3 µg/L. Acenaphthene, fluorene, anthracene, and benzo(a)anthracene were occasionally detected. Five PAH including acenaphthylene were not detected throughout the winter. Four of these were benzo- or dibenzo- derivatives, i.e. benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, and dibenzo(a,h)anthracene. The total detected PAH levels in winter ranged from 0.02 to 2.3 µg/L with a mean total concentration of 1.0 µg/L.

2. **PAH profile in spring rainwater.** The concentration ranges of individual PAH in spring rain events are also listed in Table 5. Phenanthrene was detected in almost every rain events (8/9), with a concentration range of 0-0.13 µg/L, about the same level as in winter rainwater. Pyrene was detected in most cases (7/9), with a concentration range of 0-0.4 µg/L, which was one-half of the level in winter rainwater. Fluoranthene and chrysene were frequently detected (5/9), with a concentration range of 0-0.15 and 0-0.07 µg/L, respectively, which are one-sixth and one-fourth of the levels of fluoranthene and chrysene, respectively, in winter rainwater. Acenaphthylene was detected in all samples during later spring and early summer with a concentration range of 0 to 0.1 µg/L. Benzo(b)fluoranthene was also frequently detected, especially during later spring with a concentration range from 0-0.1 µg/L. Low levels of naphthalene, benzo(a)anthracene, and

benzo(k)fluoranthene were also detected at certain times in the spring. Only 1,2,3,4-dibenzanthracene and indeno(1,2,3-cd)pyrene were not detected in spring rainwater. The other of 6 PAH, however, were only occasionally detected. The sum of PAH concentrations in spring ranged from 0.06-1.1 µg/L, with the mean concentration of 0.57 µg/L, about half the level in winter rain and snow samples.

3. PAH profile in summer rainwater. Many PAHs were at concentrations below detectable in a total of 9 summer rainwater samples (6/27 to 9/4). None or only 1 or 2 PAH out of the 16 PAHs were detected in every single rain. As listed in Table 5, phenanthrene, fluoranthene and acenaphthylene were the only PAHs that were detected twice in summer rainwater, each of which was at a mean concentration range of 0.02, 0.06, and 0.01 µg/L, respectively. Fluorene, benzo(a)anthracene, and chrysene, were detected only once. The rest of the 11 PAHs were not found in summer rainwater. The concentration of total PAH in summer rainwater ranged from 0 to 0.39 µg/L with a mean total concentration of 0.16 µg/L, about seven time less than that in winter.

4. PAH profile in fall rainwater. The detectable species and levels of PAHs were still relatively low in September.

Naphthalene was the only consistently detectable species, which was also detectable during the entire fall. Its concentration ranged from 0.01 to 0.09 µg/L. The rest of the 15 PAH were not detected with the exception of dibenzothiophene, which was only found once at a concentration of 0.15 µg/L. In later fall, an increased level of PAH was observed through October and November. The rain sample from October 12, 1993 contained the highest PAH concentration in fall. It was also the only event in the entire year that contained a detectable amount of 1,2,3,4-dibenzanthracene (1.3 µg/L). Chrysene and fluoranthene were found in four of the later fall rain events, with concentration ranges of 0.01-0.24, and 0.05-0.23 µg/L, respectively. The concentrations of pyrene and chrysene were a little lower than that found in winter rainwater. The concentration of fluoranthene was only one-fifth that found in winter. Low levels of dibenzothiophene were frequently (5/9 rain events) detected in a range of 0.01-0.27 µg/L. Phenanthrene was detected occasionally. None of the rest of the 11 PAHs was detected in fall rain samples. The concentration of total PAH in the fall rain samples ranged from 0.01 to 1.8 µg/L, with a mean value of 0.5 µg/L.

5. Year-round PAH variations and total PAH. The monthly pattern of total concentration of PAHs from May 1993 to May 1994 is shown in Fig.5. The two months with the highest detectable total PAH levels of the year, with a total concentrations of 1.9 and 2.2 μg/L, respectively were November and January. The levels of total PAH were lowest in the 3 consecutive months of July, August, and September. The total concentrations for these three months were the same, 0.13 μg/L.

The concentrations of phenanthrene in rainwater were found not to vary significantly among winter, spring and summer; these concentrations were three to four times higher than the level in fall. The concentrations of chrysene and pyrene were at the same level in winter and fall, two to three times higher than the respective levels in fall, with none detectable in summer. The concentrations of fluoranthene and naphthalene were maximum in winter, median in fall, low in spring and not detected in summer. The seasonal concentrations of five individual in higher abundance are listed in Table 5. The sum of seasonal concentrations of total PAH in the order of spring, summer, fall, winter and year-round rain events were 0.57, 0.16, 0.50, 1.1 and 2.3 μg/L, with a mean total concentration of PAH wet precipitation was 0.58 µg/L. The winter total PAH level was 2 times, 7 times, and 2 times of the levels in spring, summer, and fall, respectively.

Discussion

The Contributions of the 5 Most Abundant PAHs to Total PAH Levels.

The five most abundant PAH, naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene, account for 10.0%, 8.2%, 27.3%, 20.0%, and 9.1% with a sum of 74.6% of total PAH in winter rain events; and 7.4%, 8.0%, 21.3%, 23.0%, and 8.7% with a sum of 68.4% of total PAH in the annual rain events. Phenanthrene, fluoranthene, and pyrene are often reported to be the major PAH in rain. These most abundant PAHs in rain reported here were also those that were reported to be the most abundant in the atmosphere (43) or in the rain (44) and fog (30). These compounds have been reported in auto-exhausts (45), urban runoff (46) and coastal sediments (47) where they also occur as major components.

Seasonal variation of PAH levels as the seasonally dependent consequence of wet scavenging efficiency.

PAHs represent the compound class most extensively characterized in precipitation both in the USA and in several European countries. In general, seasonal variations have been observed with maximum concentrations during winter. Leuenberger *et al.* (30) demonstrated that snow and, in particular, fog are exceptionally highly contaminated by PAHs; fog preferentially scavenges the high molecular weight PAHs. In Switzerland, the higher molecular weight PAH [phenanthrene, pyrene and benzo(a)pyrene (BaP)] showed strong seasonal patterns (48). Winter rain was higher than spring and summer rain, and winter snow higher than winter rain. Both papers attributed this seasonal variation to differential scavenging efficiency (discussed below).

The seasonal trend of higher PAH in winter versus lower in summer is true for naphthalene, acenaphthene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and the sum of 16 PAHs in the New York City rainwater. In addition, a clear seasonal trend of higher PAH concentrations in spring than in summer was apparent for these PAH. Such a winter > spring > summer seasonal trend suggests the cause is higher emissions of PAH during winter and early spring months due to domestic heating. In addition, the average concentration of total PAH was 1.3 µg/L in 4 snow samples while the concentration was 1.0 µg/L in 5 rain samples. These PAH levels in winter samples agree with the greater efficiency of scavenging by snow (48).

In fall rainwater, naphthalene, fluoranthene, pyrene and chrysene were present at the second highest concentration. Such a clear winter > fall > spring > summer seasonal trend supports is consistent with other reports (5,30,52).

Since scavenging of very slightly water-soluble and semivolatile organic compounds, such as PAHs, is temperature dependent, higher temperatures should result in lower rain scavenging efficiency, based on Henry's law (48). However, the observation that snow contains more organic compounds than rainwater can be attributed to the ability of snow to adsorb the scavenged compounds followed by freezing (48). Fog formation is similar to the formation of rain drops (49). Wet precipitation forms on aerosol nuclei. However, the size of fog droplets is smaller than raindrops, so that the organic content in aerosol will be more diluted in rain than in fog. This is one of the reasons for the observation of a higher organic compounds in fog than in rain. Another reason is that fog usually forms at a lower atmospheric level than rain, where higher concentrations of organic compounds are present. High molecular compounds such as PAHs are found to be more highly concentrated in aerosol and particulate phases than in the gas phase, since they have low vapor pressures and tend to adsorb onto aerosols. The washout process by rain/particulate scavenging thus plays a major role in the wet precipitation of PAH.

In many of the samples, the observed concentrations of PAHs exceed the reported water solubilities (50). This is probably due to phase separation of organic compounds from the bulk water in the raindrop to its surface, when the concentration of these compounds reach the saturation point. This adsorbed organic layer on the raindrop might scavenge more organic compounds during its transport to the ground. Micron sized droplets can have lifetimes of many hours, and can become enriched in both particles and organic compounds (51).

Contribution of anthropogenic activities to the seasonal variation of the PAH levels.

The influence of household heating on the PAH content of rainwater has received most attention during early 1980s (9).

The higher PAH-concentrations during winter, the period of household heating, than that in summer can also be contributed by household heating using oil. Based on the monthly PAH concentrations from May 1993 to May 1994, a tentative approximation of major contributions to the levels of PAH in New York City rainwater is:

1) July, August and September have the lowest detectable PAH level, closer to natural background levels than other seasons; automobile exhaust may be the major anthropogenic PAH source. The level of PAH is 0.13 µg/L and can be regard as the background level for the rest of year.

2) April, May, and October, with a PAH level of 0.5 µg/L, 1.3 µg/L, and 0.68 µg/L, implies a higher influence from industrial activities than in summer, since no household heating during these months. This increased level of PAH exceeds 0.37 µg/L and can be up to 1.17 µg/L.

3) The influence of household heating to the PAH level was observed in November to March. The contribution of household heating exceeded 0.41 µg/L and could be as high as 1.4 µg/L during the winter-months.

Comparison of PAH levels in New York City rainwater to other locations.

A constant annual amount of 140 ng/L PAH was reported in Belgium in 1983, which was about 0.1% of annual total amount of organic carbon in rainwater (9). In Los Angeles during 1986, total concentrations of PAH were reported to be 17 to 261 ng/L, which represented a 0.1-1.2% of the total amounts of n-alkanes, PAHs, unresolved complex mixture, fatty acids, benzoic acids, and phenols measured (44). The mean rural total PAHs in rainwater were 27-80 ng/L, which correspond to 0.2-0.7% of the total of the above organic compounds. The sum of precipitation weighted PAH concentrations in Netherlands rainwater in 1983 was found to be 450 ng/L (52). Comparison of total concentrations in different areas and countries is difficult because different individual and total PAH levels were reported. However, because of the smaller variance in relative concentrations compared with other PAHs, comparison of data for fluoranthene should be sufficient. In Frankfurt the concentrations of fluoranthene in winter and summer are about 900 and 90 ng/L, respectively (53). For the Netherlands these concentrations are 300 and 70 ng/L (52). Our analysis showed that the mean concentrations of fluoranthene was 300 and 60 ng/L in NYC. The seasonal variation of fluoranthene is the same as reported in Netherlands. However, the level of fluoranthene in summer was two-thirds of that reported in Frankfurt. One-third of the level detected in winter Frankfurt was found in New York City.

Seasonal levels of minor PAH species.

The five- and six-membered ring PAH (benzo[b]fluoranthene, benzo[k]fluoranthene, benz[a]pyrene, benzo[ghl]perylene and indeno[1,2,3-cd]pyrene) were not detected during summer and fall. Most of them were detected occasionally in spring or winter, except for benz[a]pyrene, which was frequently detected throughout the spring. The seasonal variation of the total concentrations of these seven PAHs ranged from 0.02 µg/L in fall to 0.08 µg/L in summer, which accounted for a minor portion of the total PAH levels in fall, but a significant portion in summer. The concentration profiles of these seven PAHs were also reported not to vary significantly with either the season or the location in the Netherlands during 1983 (52). Fig.6 shows a monthly series for the total concentrations of these seven PAHs along with fluoranthene in New York City rainwater against that in Witteveen, Netherlands in 1983. A similar variation in the concentration profile of PAH can be observed.

Conclusion

1. An annual level of PAHs in New York City rainwater for the calendar year of May 1993 to May 1994 was 500 μg/m^2, or a total weight of 16.7 kg PAH (Queens area);

2. A clear trend in seasonal variation of the level of PAHs: winter > spring and fall > summer was observed in the New York City rainwater. This seasonal variation of PAHs and n-alkanes was also reported in other cities in both the USA and European countries;

3. High levels of PAHs in later fall, winter, and early spring rain samples can be attributed to both the higher scavenging efficiency according to Henry's law and higher input levels due to household heating;

4. This work is the first to analyze PAHs in rain in New York City.

Chapter II: n-Alkanes in New York City precipitation

Introduction

The sources of alkanes in our environment are both natural and anthropogenic. As a class of compounds, they are chemically inert and bioresistant.

Anthropogenic/biogenic indicators

The n-alkane carbon predominant index (CPI) values are useful indicators for evaluation of anthropogenic/biogenic contributions in aerosols (6, 54). The CPI is defined as:

CPI= sum of weight of odd carbon number n-alkanes/sum of weight of even carbon number n-alkanes

Biogenic n-alkanes which are produced as leaf waxes and in soil biota, generally show a strong odd C-numbered predominance, especially in the C_{29} range. Their CPI values are around 10. Petroleum hydrocarbons have a CPI around 1.0 (55),i.e. no odd/even preference. Thus the greater the anthropogenic contribution, the more closely the CPI approaches unity.

The ratio of the weight of unresolved complex mixture (UCM), to the weight of n-alkanes is also a useful indicator. UCM is associated with incomplete combustion of fossil fuel, mostly in automobiles. The ratio of unresolved-to-resolved (U:R) species has been used as an indication of the relative magnitude of the UCM. Therefore, higher UCM/n-alkanes ratio means greater contribution of anthropogenic sources.

N-Alkanes in the atmosphere

n-Alkanes in the range C_9-C_{18} were regularly found to be present in the gas phase of the atmosphere of Germany by Eichmann, *et al.* (6), even in pure Atlantic air. The total concentrations for this range of C-numbers is about 5×10^{-7} gm^{-3}.

The study of contamination by petroleum residues in the Lake Tahoe air basin was reported by Simoneit, *et al.* (56) Their results showed that vehicular traffic contributed a significant proportion of hydrocarbons to the atmosphere, which was attributable to uncombusted petroleum. The contaminated petroleum residues were at higher levels during the day of the diurnal cycle and during the winter as compared with night and summer. This variation has been attributed to the poorer combustion efficiencies of diesel engines and oil heating furnaces at the elevation of lake Tahoe and at lower seasonal temperatures. N-alkanes of biogenic sources, mainly waxes and resin residues, occur in equal or subordinate amounts to the petroleum residues at the cleanest sites and decrease in relative concentration at more contaminated areas (56).

N-Alkanes in wet precipitation

Removal of n-alkanes from the atmosphere takes place through wet and dry deposition, the same as PAHs. Study of aliphatic hydrocarbons in urban rain, snow and fog in Switzerland was reported by Leuenberger *et al.* (57). n-Alkanes in the range of C_{21}-C_{33} in the particulate phase were characterized by a carbon preference index (CPI) of 7.1 in summer rain compared to 2.1 in winter rain. The n-alkanes in urban rain samples exhibited two speciation types according to their sources. The n-alkanes associated with particulate matter showed a predominance of odd-numbered homologs, indicating plant waxes as the major source for these compounds.

In studies of organic trace compounds and pollutants in Oregon (58), significant levels of plant wax components were found in both rain particles and ambient aerosols, which consisted of n-alkanes and n-alkanols ranging from C_{21} to C_{33} and from C_{22} to C_{30}, respectively. Petroleum and combustion residues are the principal components of the particle-associated organic carbon fraction of rain water. Rain particles are enriched in natural biogenic products. Petroleum residues were detected in all the samples as indicated by the unresolved complex mixture (UCM) of hydrocarbons, n-alkanes with no carbon number predominance from C_{16} to C_{24}.

In southern California wet precipitation, the order of values of the UCM/alkane ratio was: urban (8.6) >> semirural (1.7) >> rural (0.21) (44). n-Alkane patterns typical for biogenic sources were found in rural areas, while patterns of anthropogenic sources of contribution were found in urban areas.

Although organic matter in both dry and wet deposition samples is derived from both biogenic and anthropogenic sources, their relative contributions are quite different depending on sampling locations (44).

Seasonal variation and correlation of N-Alkanes with PAHs

As n-alkanes and PAHs are both released by automobile traffic into the atmosphere, some correlation between the concentrations of PAHs and n-alkanes is expected. This was reported for rainwater in Germany (59).

The n-alkanes in summer rain in Switzerland in 1987 were predominantly homologs with high alkane CPI, whereas winter rain, snow and fog, have low values (58). Similar distributions in summer rain have been observed in rural aerosols (54) and in semi-rural rain and snow (60). The large contribution of combustion-derived n-alkanes in winter rain, snow and fog can be attributed to residential oil burning which is the major heating source in urban areas (54, 60).

Experimental approach for analysis of n-alkanes in rainwater

Optimization of operating conditions for n-Alkanes.

These compounds were determined using GC/FID. The column oven temperature was held initially at 60°C for 2 minutes, programmed to 280°C at 10°C min^{-1} and held at 280°C for 10-15 minutes. Samples were injected in the splitless mode; the split valve opened after 0.75 min. The injection port temperature was 260°C and the detector temperature was 280°C. Helium was used as carrier gas at 13 psi. FID response was calibrated periodically with n-alkane standards as indicated before. Samples were identified and quantified by comparison of retention times and peak areas with those of the n-alkane standards.

Results

N-Alkanes in winter rainwater and snow

Nine winter rain and snow samples (from December 93 to March 94) were analyzed for n-alkanes. All the n-alkanes of interest, ranging from n-$C_{12}H_{26}$ to n-$C_{32}H_{66}$, were observed. Most of the n-alkanes were observed in all samples, except that n-$C_{32}H_{66}$ was detected 5 times out of 9, and n-$C_{18}H_{38}$ was detected 7 times out of 9. The concentration as well as the pattern of the n-alkanes in rain varies substantially from one rain event to the other. Fig.7 shows the GC chromatogram of a sample of 3/8/94. In this sample, the sum of all n-alkanes from n-$C_{12}H_{26}$ to n-$C_{32}H_{66}$ was 15.7 µg/L (ppb). n-$C_{32}H_{66}$ was observed, even in high abundance. In addition, the pronounced hump of branched alkanes indicating predominantly anthropogenic origin is found in the chromatogram. Fig.8 shows the n-alkane pattern in the sample of 3/29/94. The hump of branched pattern was not as significant as that previously observed.

The sum of all n-alkanes in the winter samples varied from 0.45 to 33.7 ppb with a mean level of 4.9 ppb. n-$C_{28}H_{58}$ and n-$C_{32}H_{66}$ were often the two leading alkanes of interest, which ranged 0.14-27.6 and 0.02-5.5 µg/L, respectively. These two compounds were detected at exceptionally high levels in one snow event and in the second highest rainevent, where the total concentration of these two alkanes were 47- and 60- fold higher than the sum of the rest of the alkanes. respectively. C_{14}-C_{24} were consistently found to be present. The detectable concentrations of n-alkanes with higher carbon numbers (C_{28} and C_{32}) were usually higher than those with medium carbon number (C_{12}, C_{14}, C_{16}, C_{18}, and C_{24}).

The total concentrations of n-alkanes in 3 snow events was higher than that of 5 rain events. An average of the total concentration in snow samples was 13.2 µg/L in comparison to a 4.1 µg/L in rain samples, the ratio of the total concentrations was 3:1.

N-Alkanes in spring rainwater

Most of the n-alkanes of interest were frequently detected in 9 spring rain and snow samples, except that n-$C_{32}H_{66}$ was only detected twice in 9 rain events, whereas n-$C_{24}H_{50}$ and n-$C_{28}H_{58}$ were detected in almost all the rain samples. But the concentrations of individual alkanes varied substantially from event to event. The concentrations for the sum of all n-alkane concentrations range from 0.11 to 3.0 µg/L, with a mean total concentration of 0.61 µg/L. All chromatograms showed a pronounced hump indicating anthropogenic activities. The ratio of the sum of n-alkanes with medium carbon number to that with higher carbon number indicates no predominant trend for either subgroup of n-alkanes.

n-Alkanes in summer rainwater

The concentrations as well as the profiles of the n-alkanes in 9 summer samples varied substantially from event to event. Among 4 out of 9 rain events, none of the 7 n-alkanes of interest were detected. n-$C_{12}H_{26}$ was not detected during the entire summer, while n-alkanes with medium carbon number (14, 16, and 18) were occasionally detected. Only n-alkanes with higher carbon number (C_{24}, C_{28}, and C_{32}) were frequently detected. The summed concentrations of all alkanes range from 0 to 1.8 µg/L, with the mean total concentration of 0.29 µg/L.

n-Alkanes in fall rainwater

Apparently abundant patterns of individual and total of n-alkanes of interest were observed in fall rain samples. n-$C_{24}H_{50}$ and n-$C_{28}H_{58}$ were consistently detected in all the fall rain samples. n-Alkanes of medium carbon number, including n-$C_{12}H_{26}$, were more frequently detected approaching late fall. The average concentration of n-alkanes was higher than that in the summer. Highest concentrations of total n-alkanes were found in winter. Total concentration of n-alkanes varied from 0.28 to 7.2 μg/L, with a mean total concentration of 1.3 μg/L. Again, all chromatograms showed the pronounced hump. Similar to that observed for winter rain water, the detectable concentrations of n-alkanes of higher carbon number were generally higher than those with medium carbon number. It is obvious that anthropogenic sources are more important in winter than in summer.

Year-round variations in n-alkane levels

The monthly pattern of total concentration of n-alkanes from May 1993 to May 1994 is shown in Fig.9. January and March were the months with the highest detectable total n-alkane levels of the year, with a concentration of 8.4 and 5.2 μg/L, respectively. The levels of total n-alkanes were at the lowest ranges in August 1993 and May 1994. The concentrations for the two months were about the same, 0.05 and 0.1 μg/L, respectively.

Discussion

Seasonal variation of N-alkanes in rainwater

Refined petroleum contains n-alkanes ranging from C_1 to about C_{35} with no carbon number predominance (CPI around 1). The absolute concentrations of homologs $< C_{20}$ cannot be accurately determined, since alkanes $< C_{20}$ are probably lost by evaporation in the environment and/or in the experimental procedure according to their boiling points (56).

The year-round mean concentration in NYC rainwater of total N-alkanes was 1.8 μg/L, highest in winter at 4.9 μg/L, and lowest in summer at 0.3 μg/L. The seasonal variation of the total n-alkanes was in the order of winter > fall > spring > summer, with a ratio of 50:13:6:3. Such a seasonal variation indicates that contamination by petroleum residues is greatest during winter. Similar concentration levels of total n-alkanes were found in southern Indiana precipitation, which ranged from 0.4 μg/L to 8.0 μg/L (60). Kawanura, *et al.* reported a mean total concentration of n-alkanes of 2.6 μg/L in summer and 5.1 μg/L in winter rainwater in Los Angeles

(44). In addition, considerably higher n-alkane concentrations were reported by Levsen, *et al*. (59). A mean concentration of total n-alkanes of 15.1 g/L in winter and 40.6 g/L in summer rainwater was found in Germany (59). A higher total concentration of n-alkanes in summer was attributed to higher biogenic activity in the vicinity of the sampling location, since the CPI value was also high during that summer. High concentrations of n-alkane were also found in rain, snow and fog in Switzerland (30). The large contribution of combustion-derived n-alkanes in winter rain and snow was attributed to residential oil burning (30).

Broddin, *et al.* (1980) found that C_{24} to C_{26} hydrocarbons derived from fossil-fuel combustion dominated the n-alkane distribution in aerosols collected in urban areas during winter (7), which explains why n-alkanes with higher carbon number were rich in winter rain samples. The winter concentrations of n-alkanes follow the order fog > snow > rain in Switzerland.

Unresolved complex mixture hump

Unresolved complex mixture (UCM) of n-alkanes, which is composed mainly of branched and cyclic structures (44), is detected as a hump in the GC of neutral organic fractions. These were observed in almost all of the rain events throughout the year, which indicates that anthropogenic activities are predominant in urban areas, such as New York City. A similar profile in rainwater has been reported for other metropolitan areas, including Tokyo (61). Kawamura and Kaplan (44) reported such an n-alkane pattern (similar to Fig.7) in Los Angeles, which revealed the contribution of anthropogenic sources. Petroleum residues were present in all samples in all four seasons as indicated by detectable n-alkanes and the UCM of hydrocarbons. The UCM was generally larger in winter and fall, and smaller in summer. This indicates the anthropogenic contribution is less important in summer than in winter, whereas biogenic sources are more important in summer than in winter.

Relationship of PAHs and n-alkanes

Since both n-alkanes and PAHs in the atmosphere are produced by automobile traffic, it is of interest to check whether there is a correlation between the concentrations of n-alkanes and PAHs. Comparison of the year-round precipitation events (as in Fig.10) that have been analyzed for both compound classes demonstrates that in many instances, there is some correlation between the concentrations of PAHs and n-alkanes. Such a correlation was also observed in the monthly profile (as in figure 11), and the seasonal pattern of n-alkanes and PAHs (Fig.12). Thus in 15 of 36 rain events there are a higher concentration of both PAHs (> 170 μg/L) and n-alkanes (> 450 μg/L) and in 11 of 36 rain events there are a lower concentration of PAHs (< 170 μg/L) and n-alkanes (< 450 μg/L) (59). Five samples have lower PAH and higher n-alkanes while five samples have higher PAH and lower n-alkanes. If the anthropogenic source for PAHs and n-alkanes is the same, samples with a high n-alkane concentration (> 450 μg/L) should also show a high PAH concentration, as generally observed. The deviation from this pattern in 5 samples could result from high biogenic activity. The remaining 5 of 36 samples do not fit into this scheme; there may have been a strong PAH source not producing n-alkanes simultaneously. Such as forest fire and long range transportation.

Conclusion

1. An annual level of n-alkanes in the New York City rainwater for the calendar year May 1993 to May 1994 was 1.64 mg/m^2, or a total weight in precipitation of 55.1 kg n-alkanes (Queens area),

2. A clear trend of seasonal variation of the level of n-alkanes: winter > spring and fall > summer was observed in the New York City rainwater. This seasonal variation of n-alkanes was also reported in other cities in both USA and European countries,

3. Higher levels of n-alkanes in later fall, winter, and early spring rain samples can be attributed to both the higher scavenging efficiency according to Henry's law and higher input levels due to household heating, as found for PAHs ;

4. A correlation of levels of PAHs and n-alkane was also observed in the majority of rainwaters: a high level of PAHs accompanied by a high level of n-alkanes, while a low level of PAHs accompanied by a low level of a-alkanes, which indicates the input of anthropogenic activity to individual rain event;

5. The work is the first to analyze the rain in New York City for n-alkanes.

Chapter III: Phthalate Esters in New York City Precipitation

Introduction

Phthalate esters are widely used as plasticizers in flexible polyvinyl chloride (PVC) and other plastics. Of the phthalates, dioctyl phthalate (bis-(2ethyl-hexyl) phthalate) is the most commonly used, accounting for 26% of the total phthalate plasticizer consumption in the United States (62). Dioctyl and dibutyl phthalate plasticizers in PVC accounts for 60% of total weight in Europe (63). Phthalate esters are found in diverse materials such as children's products, clothing, footwear, flooring, home furnishings, housewares, hardware, sporting goods, cosmetics, tapestry and personal products (62). Furthermore, it is typically used in these PVC products at levels as high as 50% to achieve plasticization. Because dioctyl phthalate is not chemically bound to PVC, significant migration of the plasticizer into the environment is possible. Indeed, dioctyl phthalate has been detected in air, food, and water samples.

Carcinogenicity of phthalate esters

Dioctyl phthalate is reported to be an animal carcinogen. In 1982, the National Toxicology Program found that dioctyl phthalate caused excess liver tumors in bioassays of rats and mice (64). It has also been shown to cause testicular damage in rats. Other evidence showed that dioctyl phthalate and its metabolites can cause birth defects or embryo death in rodents. In 1980, the Environmental Protection Agency suggested not manufacturing dioctyl phthalate under the Toxic Substances Control Act due to its causing liver tumors in rats (65). Furthermore, dioctyl phthalate was detected in blood stored in plastic bags, which produced an increased awareness of the potential for human exposure to dioctyl phthalate from PVC products (62). In addition, migration of dioctyl phthalate from PVC might also lead to human exposure via direct dermal or oral contact. For example, the presence of dioctyl in some baby pacifiers may have exposed infants via direct oral uptake of the compound (62). In addition, both dioctyl and dibutyl phthalate esters are found to be readily accumulated both by animals (66, 67) and by plants (68).

Though several bioassay studies indicated the carcinogenicity of this group of plasticizers, it is still unclear that the results of these studies can be applied to humans. The International Agency for Research on Cancer said there was a risk for using phthalate esters as plasticizers, but the European Union Scientific Committee on Food says they can still be used with an acceptable maximum daily intake of 25 mg/kg for dioctyl and 30 mg/kg for dibutyl (69).

Phthalate esters of environmental concern

As might be expected, phthalates are ubiquitous in the environment. Phthalate ester plasticizers have been detected in the open-ocean environment. Water, sediment, air, and biota from the Gulf of Mexico and North Atlantic were found to contain both dioctyl and dibutyl phthalate esters (70). Since both phthalates were reported to reduce the reproductive rates in aquatic organisms (71), the possibility of reproductive effects along with the high concentrations of both phthalates in the coastal areas where many marine species reproduce could cause an environmentally damaging disruption of marine food webs (70).

Dioctyl phthalate has been detected in surface water,groundwater, and finished drinking water in the United States at concentrations generally in the low ppb range. It was detected in water samples from four of the five Great Lakes at a concentration of 10 ppb (72). Average concentrations of DOP in seawater ranging from 0.005-0.7 ppb have been reported (73). Reported concentrations in drinking water treatment plants in the New Orleans area and from a treatment plant in Philadelphia ranged from 0.05 to 11 ppb (74).

The presence of phthalate esters in atmosphere

Phthalate esters are lipophilic and have low vapor pressures in general. Ubiquitous presence of DOP and DBP in the airborne fallout and in the air of Swedish atmosphere was reported by Thuren and Larsson in 1990. A total deposition of both phthalates to the ground in Sweden was estimated to be 220 tons/per year and was of a similar order of magnitude as the emissions. The fallout rates and the levels of phthalate esters in the air were temperature-dependent. In winter, when the temperature was low, the atmospheric fallout of phthalate esters was high while their levels in the air were low. Higher atmospheric concentration were found in the summer (63).

Phthalate esters in wet precipitation

Few reports of phthalate esters in wet precipitation are available. In 1977, Lunde *et al.* reported detectable but low levels of dibutyl and dioctyl phthalates were present in rain and snow in Norway (13). Kawamural and Kaplan reported that dibutyl and dioctyl phthalates were the most abundant esters in Los Angeles rainwater (75). A concentration range of 3-9 µg/L were detected for total phthalates in that rainwater.

Results

Dioctyl, dibutyl, diethyl and dimethyl phthalates (DOP, DBP, DEP, DMP) were found in NYC precipitation. Among these, DOP was found in almost all rain samples in spring, fall and winter, but not as frequently detected in summer. DBP was often detected in spring and summer, but not as frequently detected in late fall and winter. DMP and DEP were detected only in fall and winter rain events, which accounted 3 and 5 out of 36 year-round rain events, respectively. The average detectable levels of DOP ranged from 2.3 µg/L in summer, 3.0 µg/L in fall, 4.0 µg/L in winter, and 5.1 µg/L in spring. DBP was the second more abundant phthalate, with an average concentration of 1.1 µg/L in summer, 0.7 µg/L in fall, 1.6 µg/L in winter, and 0.7 µg/L in spring. The average of total concentration of total phthalates of interest was 3.4 µg/L in summer, 3.9 µg/L in fall, 6.4 µg/L in winter, and 6.0 µg/L in spring. The individual and total phthalates exhibited a seasonal variation with an order from highest to lowest level: winter > spring > fall > summer, though such a seasonal variation of levels of phthalates have not been statistically distinct for limited samples. A maximum concentration was observed for DOP in spring rainwater with a concentration of 40.1 µg/L and for DBP in summer rainwater with a concentration of 4.3 µg/L. DOP and DBP each account for approximately 75% and 25% of a year-round total concentration of phthalates, respectively. DEP and DMP, both which are the lower molecular weight phthalate components, are depleted in most of rain events as they are more volatile.

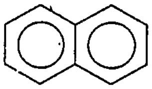
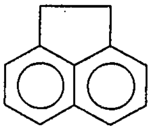
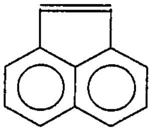
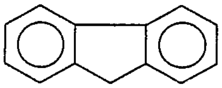
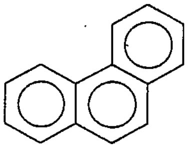
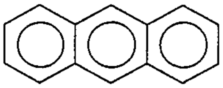
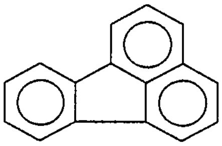
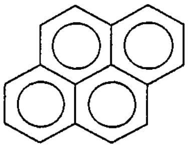
Discussion

Dibutyl and dioctyl phthalates have been reported by Lunde et al (13) in rain in Norway. The levels of DOP, DBP, and total phthalates detected in New York City rainwater are comparable with those reported in Los Angelas rainwater (63). The higher levels of phthalates in our rainwater samples probably results from the local industrialized areas that may emit high level of phthalates into the atmosphere.

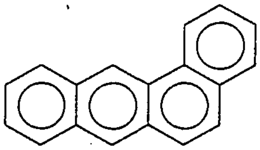
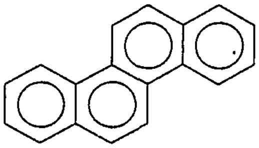
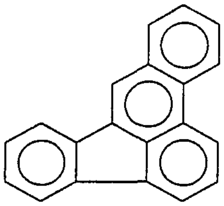
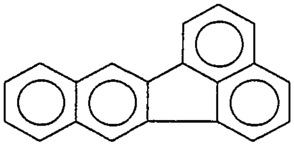
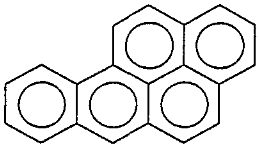
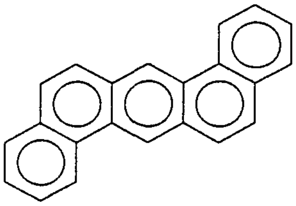
Fig. 13 shows seasonal variations of phthalate concentrations. The highest concentrations for most phthalates appeared in winter, while the lowest concentrations for most of them were in the summer. One of the reasons for such a seasonal variation in the concentration of DOP, DBP and total phthalate may be that the vapor pressure of the gaseous phthalates decreases at low temperature, resulting in a stronger tendency to be adsorbed onto particles and/or partition into water droplets. The rain/particulate scavenging and washout process at lower temperature results in the corresponding rain sample containing more phthalates than at higher temperatures. An higher temperature raises the vapor pressure of the substances and their volatility, so that phthalates tend to build up more in the gaseous phase than the particulate phase. The rain/particulate scavenging and washout process at higher temperature results in lower phthalate concentration than that at lower temperature.

Dioctyl phthalate was found in almost all of the samples with the highest levels of 40.1 ug/L. It may enter the environment in industrial waste waters, air emissions, and solid wastes from manufacturing and processing operations. It can also arise from evaporation of the compound from plastics, from the burning of plastic products, and by leaching of plasticizers in landfills into soil or water.It is expected to stick tightly to soil, sediment, and dust particles once it is released to the environment. If phthalate is released to the atmosphere, the compound may be deposited on dust particles or to surface water in rain. Upon release to surface waters, dioctyl phthalate is expected to partition mainly into sediments and to suspended particulates. The compound strongly adsorb to organic matter contained in soils and sediments; adsorption is probably the most important transport process for the compound in surface waters (72).

Table 1. Structures of 16 Polycyclic Aromatic Hydrocarbons (PAHs)

Structure	Name	Mw
	Naphthalene	128
	Acenaphthylene	152
	Acenaphthene	154
	Fluorene	166
	Phenanthrene	178
	Anthracene	178
	Fluoranthene	202
	Pyrene	202

(Table 1 continued)

Structure	Name	Mw
	Benzo[a]anthracene	228
	Chrysene	228
	Benzo[b]fluoranthene	252
	Benzo[k]fluoranthene	252
	Benzo[a]pyrene	252
	Dibenzo[a,h]anthracene	278

(Table 1 continued)

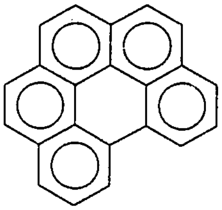
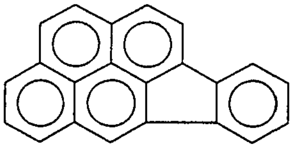
Structure	Name	Mw
	Benzo[g,h,i]perylene	276
	Indeno[1,2,3-cd]pyrene	276

Table 2

Total Weight and Concentration range of neutral organic compounds in New York City Precipitation

Hydrocarbons	Total(mg)	Range(ug/L)
n-Dodecane	1.04	0.01-1.1
n-Tetradecane	0.49	0.01-0.35
n-Hexadecane	0.60	0.006-0.49
n-Octadecane	0.55	0.02-0.39
n-Tetracosane	1.94	0.02-1.5
n-Octacosane	5.22	0.02-5.5
n-Dotriacontane	12.40	0.02-27.6
Hydrocarbon total Weight	22.26	
Polycyclic Aromatic Hydrocarbons		
Naphthalene	0.38	0.009-0.5
Acenaphthylene	0.14	0.02-0.14
Acenaphthene	0.52	0.19-1.2
Fluorene	0.07	0.03-0.15
Phenanthrene	0.44	0.005-0.2
Anthracene	0.09	0.02-0.05
Fluoranthene	1.04	0.05-0.82
Pyrene	1.15	0.02-1.3
Benzo(a)anthracene	0.13	0.03-0.12
Chrysene	0.46	0.01-0.27
Benzo(b)fluoranthene	0.04	0.03-0.12
Benzo(k)fluoranthene	0.07	0.11-0.14
Benzo(a)pyrene	0.22	0.07-0.37
Indeno(1,2,3-cd)pyrene	0.02	0-0.06
Dibenzo(a,h)anthracene	0.02	0-0.07
Benzo(ghi)perylene	0.03	0-0.1
9-Fluorenone	0.08	0.01-0.08
1,2,3,4-Dibenzanthracene	0.44	0.05-1.3
Dibenzofuran	0.10	0.01-0.14
Dibenzothiophene	0.17	0.01-0.29
PAH total Weight	5.49	
Phthalate Esters		
Dimethylphthalate	0.55	0.02-1.6
Diethylphthalate	1.75	0.32-1.8
Dibutylphthalate	10.20	0.04-4.2
Dioctylphthalate	46.20	0.25-40.1
Phthalate total Weight	58.70	

Table 3.
Percent Recoveries of Standard Compounds Spiked in Deionized Water with Liquid-Liquid Extraction(LLE

Standard Compounds	Efficiency of Recovery		
	7/20/93*	7/12/93*	Concentration(ug/ml)
Hydrocarbons			
n-Dodecane	83.8 %	80.1 %	26.9
n-Tetradecane	88.4 %	90.1 %	24.9
n-Hexadecane	96.1 %	88.9 %	24.7
n-Octadecane	89.8 %	91.5 %	19.6
n-Tetracosane	76.4 %	87.6 %	24.2
n-Octacosane	69.8 %	86.7 %	29.7
n-Dotriacontane	65.7 %	85.3 %	27.7
Polycyclic Aromatic Hydrocarbons			
Naphthalene	85.3 %	82.1 %	20.0
Acenaphthylene	86.4 %	90.0 %	20.0
Acenaphthene	89.4 %	89.9 %	20.0
Fluorene	89.0 %	89.1 %	20.0
Phenanthrene	90.4 %	92.1 %	20.0
Anthracene	88.9 %	92.0 %	20.0
Fluoranthene			20.0
Pyrene	91.9 %	94.4 %	20.0
Benzo(a)anthracene	91.1 %	95.2 %	20.0
Chrysene	90.6 %	87.8 %	20.0
Benzo(b)fluoranthene	92.7 %	91.7 %	20.0
Benzo(k)fluoranthene	85.8 %	86.6 %	20.0
Benzo(a)pyrene	85.8 %	86.1 %	20.0
Indeno(1,2,3-cd)pyrene	81.5 %	85.2 %	20.0
Dibenzo(a,h)anthracene	76.5 %	82.0 %	20.0
Benzo(ghi)perylene	75.1 %	78.0 %	20.0
9-Fluorenone	77.7 %	80.0 %	22.8
1,2,3,4-Dibenzanthracene	75.1 %	82.4 %	24.4
Dibenzofuran	89.6 %	89.9 %	25.6
Dibenzothiophene	89.8 %	91.5 %	25.6
Phthalate Esters			
Dimethylphthalate	19.0 %	15.4 %	31.4
Diethylphthalate	33.1 %	42.8 %	29.2
Dibutylphthalate	82.0 %	82.2 %	27.0
Dioctylphthalate	90.0 %	84.6 %	21.6

* 1ml of Standard spiked in 1.0 L of deionized water with 20 ml hexane stirring 24 h for L-L extraction on 7/20/93 and 7/12/93

Table 4

Precision Study of LLE* (4 Replicates)

		Compound		
	9-Fluorenone	Phenanthrene	Chrysene	1234-Dibenzanthracene
Added(ug)	23	24	23	24
Found	16-18	19-22	19-22	18-22
Mean	17	21	21	21
SD	4.7	5.8	5.7	6.4
%RSD	6.1	6.7	6.3	7.7
%Recovered	76	87	89	84

*Liquid-Liquid Extraction

Precision Study of SPE** (3 Replicates)

		Compound		
	9-Fluorenone	Phenanthrene	Chrysene	1234-Dibenzanthracene
Added(ug)	23	24	23	24
Found	18 -22	19-22	16-18	17-21
Mean	20	21	16	19
SD	6.7	6.7	3.5	7.6
%RSD	7.7	7.5	4.9	9.6
%Recovered	86	87	72	78

**Solid Phase Extraction

Table 5

Seasonal Variations of PAHs in New York City Precipitation

Standard Compounds		Winter		
	(ug/L) mean	(ug/L) min	(ug/L) med	(ug/L) max
Polycyclic Aromatic Hydrocarbons(PAHs)				
Naphthalene	0.1	0	0.05	0.5
Acenaphthylene	0	0	0	0
Acenaphthene	0.2	0	0.5	1
Fluorene	0.003	0	-	0.03
Phenanthrene	0.08	0	0.07	0.2
Anthracene	0.002	0	-	0.02
Fluoranthene	0.3	0	0.3	0.8
Pyrene	0.2	0	0.2	0.8
Benzo(a)anthracene	0.03	0	0.06	0.1
Chrysene	0.1	0	0.1	0.3
Benzo(b)fluoranthene	0.01	0	-	0.1
Benzo(k)fluoranthene	0	0	0	0
Benzo(a)pyrene	0	0	0	0
Indeno(1,2,3-cd)pyrene	0.003	0	-	0.06
Dibenzo(a,h)anthracene	0	0	0	0
Benzo(ghi)perylene	0	0	0	0
9-Fluorenone	0.03	0	0.05	0.08
1,2,3,4-Dibenzanthracene	0.01	0	0.05	0.08
Dibenzofuran	0.04	0	0.07	0.1
Dibenzothiophene	0.01	0	0.01	0.02
Total	1	0	1	4

Table 5 continued

Standard Compounds	Spring			
	(ug/L) mean	(ug/L) min	(ug/L) med	(ug/L) max
Polycyclic Aromatic Hydrocarbons				
Naphthalene	0.01	0	0.03	0.07
Acenaphthylene	0.04	0	0.09	0.1
Acenaphthene	0.02	0	0.1	0.2
Fluorene	0.02	0	0.08	0.2
Phenanthrene	0.07	0	0.06	0.1
Anthracene	0.04	0	0.03	0.3
Fluoranthene	0.04	0	0.06	0.1
Pyrene	0.1	0	0.06	0.4
Benzo(a)anthracene	0.02	0	0.06	0.09
Chrysene	0.03	0	0.05	0.1
Benzo(b)fluoranthene	0.01	0	0.06	0.1
Benzo(k)fluoranthene	0.03	0	0.1	0.1
Benzo(a)pyrene	0.1	0	0.1	0.4
Indeno(1,2,3-cd)pyrene	0	0	0	0
Dibenzo(a,h)anthracene	0.01	0	0.04	0.07
Benzo(ghi)perylene	0.01	0	0.05	0.1
9-Fluorenone	0.003	0	0.01	0.02
1,2,3,4-Dibenzanthracene	0	0	0	0
Dibenzofuran	0.005	0	0.005	0.04
Dibenzothiophene	0	0	0	0
Total	0.6	0	1	2

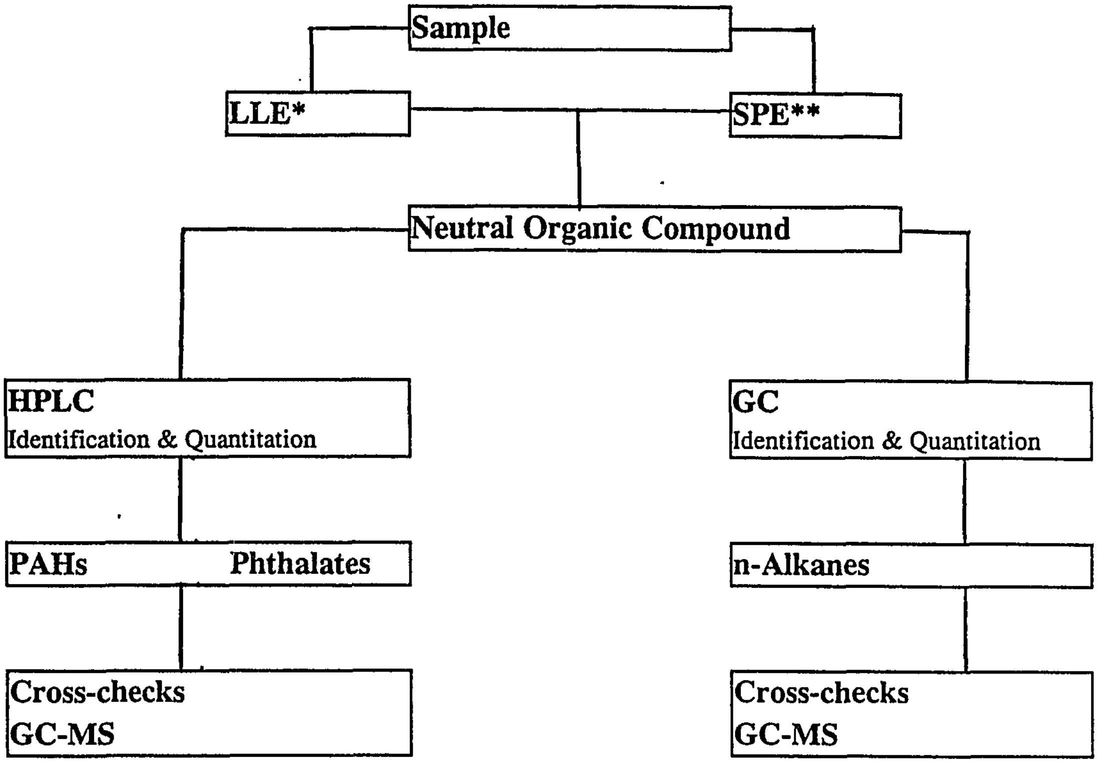
Table 5 continued

Standard Compounds	Summer			
	(ug/L) mean	(ug/L) min	(ug/L) med	(ug/L) max
Polycyclic Aromatic Hydrocarbons				
Naphthalene	0	0	0	0
Acenaphthylene	0.01	0	0.02	0.09
Acenaphthene	0	0	0	0
Fluorene	0.008	0	-	0.07
Phenanthrene	0.02	0	0.04	0.2
Anthracene	0	0	0	0
Fluoranthene	0.05	0	0.05	0.4
Pyrene	0	0	0	0
Benzo(a)anthracene	0.01	0	-	0.1
Chrysene	0.02	0	-	0.2
Benzo(b)fluoranthene	0	0	0	0
Benzo(k)fluoranthene	0	0	0	0
Benzo(a)pyrene	0	0	0	0
Indeno(1,2,3-cd)pyrene	0	0	0	0
Dibenzo(a,h)anthracene	0	0	0	0
Benzo(ghi)perylene	0	0	0	0
9-Fluorenone	0	0	0	0
1,2,3,4-Dibenzanthracene	0.01	0	-	0.1
Dibenzofuran	0	0	0	0
Dibenzothiophene	0.02	0	-	0.2
Total	0.2	0	0.1	1

Table 5 continued

Standard Compounds	Fall			
	(ug/L) mean	(ug/L) min	(ug/L) med	(ug/L) max
Polycyclic Aromatic Hydrocarbons				
Naphthalene	0.04	0	0.03	0.09
Acenaphthylene	0	0	0	0
Acenaphthene	0	0	0	0
Fluorene	0	0	0	0
Phenanthrene	0.003	0	0.005	0.02
Anthracene	0	0	0	0
Fluoranthene	0.05	0	0.1	0.2
Pyrene	0.2	0	0.06	1
Benzo(a)anthracene	0	0	0	0
Chrysene	0.03	0	0.02	0.2
Benzo(b)fluoranthene	0	0	0	0
Benzo(k)fluoranthene	0	0	0	0
Benzo(a)pyrene	0	0	0	0
Indeno(1,2,3-cd)pyrene	0	0	0	0
Dibenzo(a,h)anthracene	0	0	0	0
Benzo(ghi)perylene	0	0	0	0
9-Fluorenone	0	0	0	0
1,2,3,4-Dibenzanthracene	0.1	0	0.7	1
Dibenzofuran	0.001	0	0.005	0.01
Dibenzothiophene	0.05	0	0.02	0.3
Total	0.5	0	0.9	3

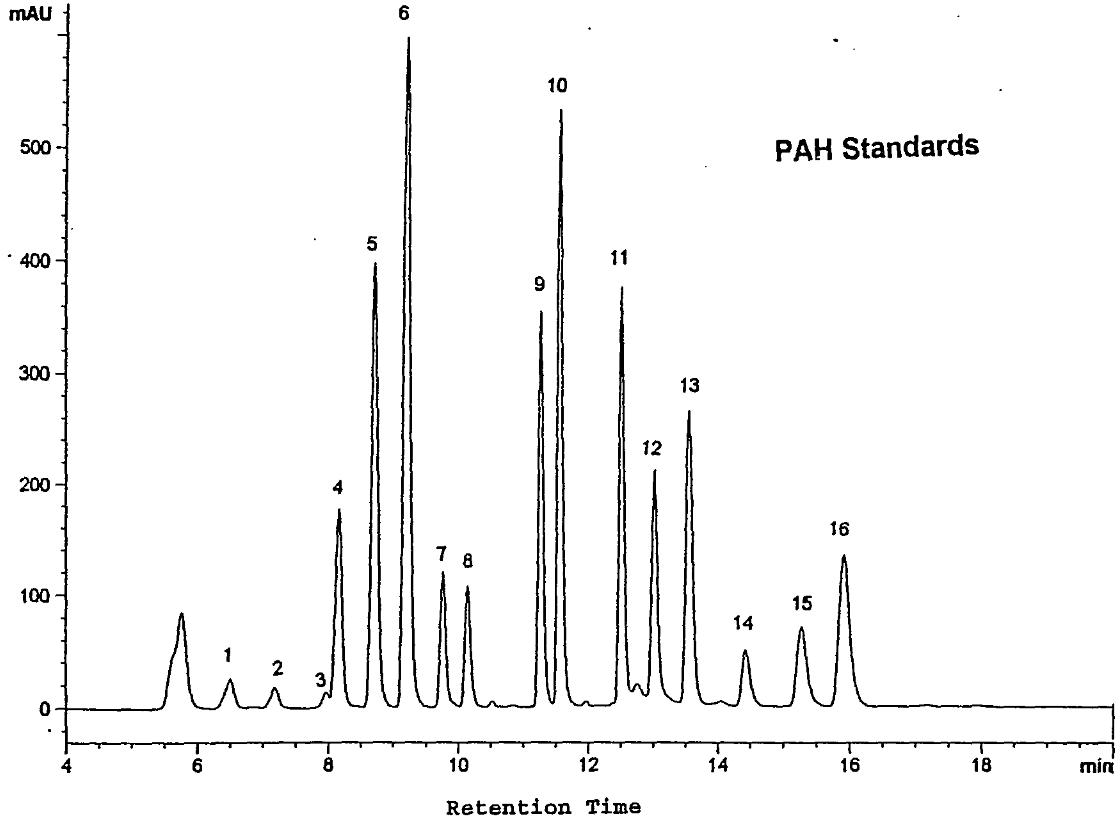
Figure 1. Analytical scheme for the determination of neutral organic compounds in rainwater.



*Liquid-Liquid Extraction

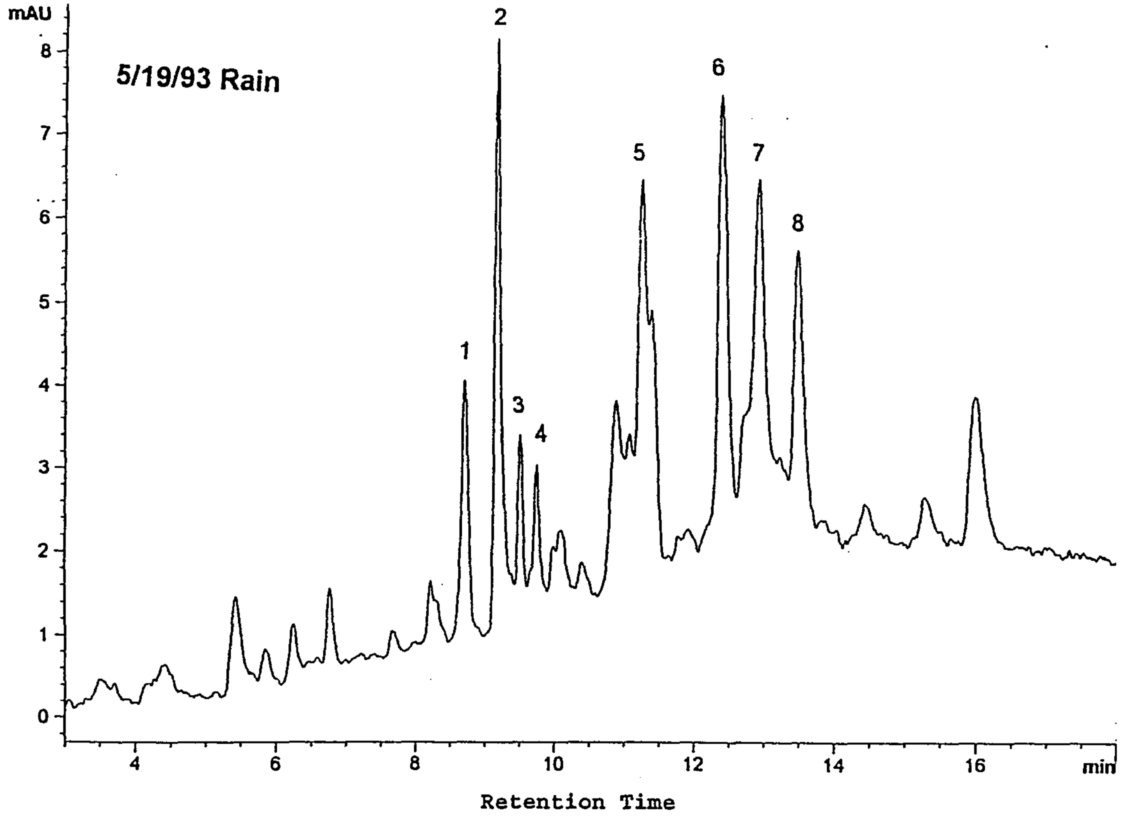
**Solid Phase Extraction

Figure 2. HPLC chromatogram of 16 PAH standards.



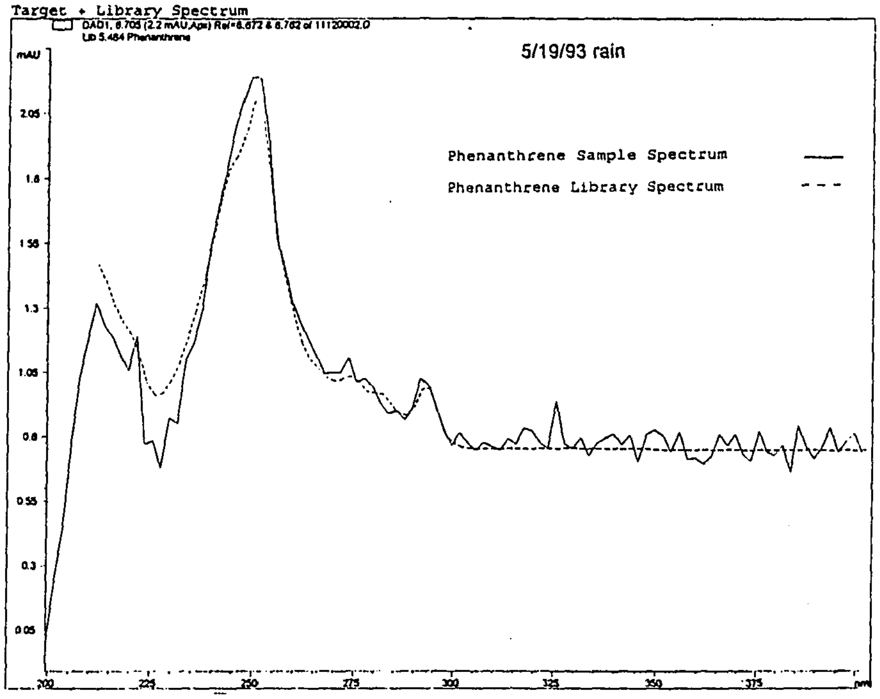
16 PAH Standards
1. Naphthalene 2. Acenaphthylene 3. Acenaphthene 4. Fluorene
5. Phenanthrene 6. Anthracene 7. Fluoranthene 8. Pyrene
9. Benzo(a)anthracene 10. Chrysene 11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthenne 13. Benzo(a)pyrene
14. Dibenzo(a,h)anthracene 15. Benzo(ghi)perylene
16. Indeno(1,2,3-cd)pyrene

Figure 3. HPLC chromatogram of rain sample of May 19, 1993.



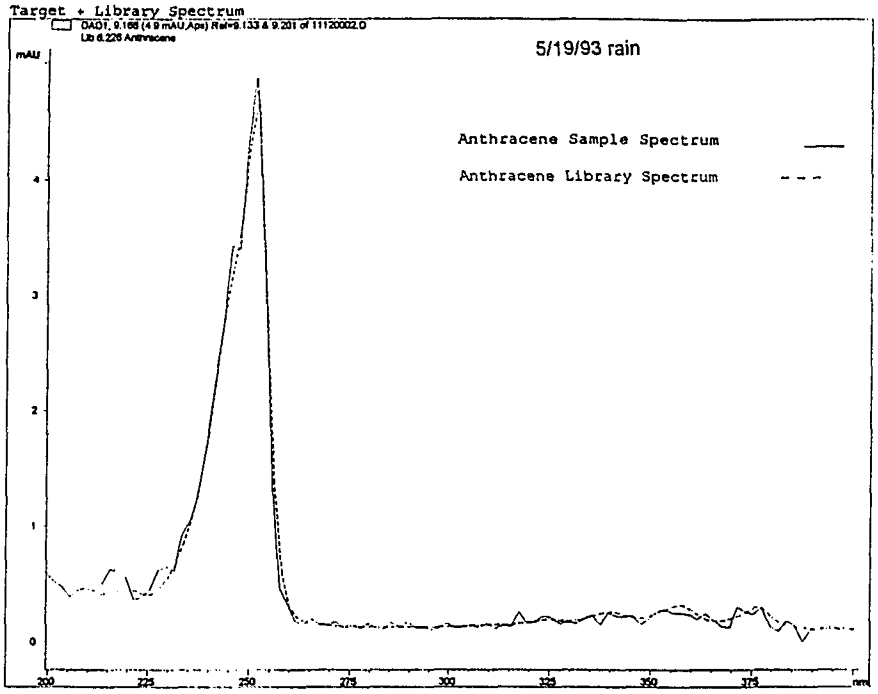
Sample: 5/19/1993 Rain
Peak: 1. Phenanthrene 2. Anthracene 3. Fluoranthene
4. Pyrene 5. Chrysene 6. Benzo(b)fluoranthene
7. Benzo(k)fluoranthene 8. Benzo(a)pyrene

Figure 4(a-h). UV overlay spectras of phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene.



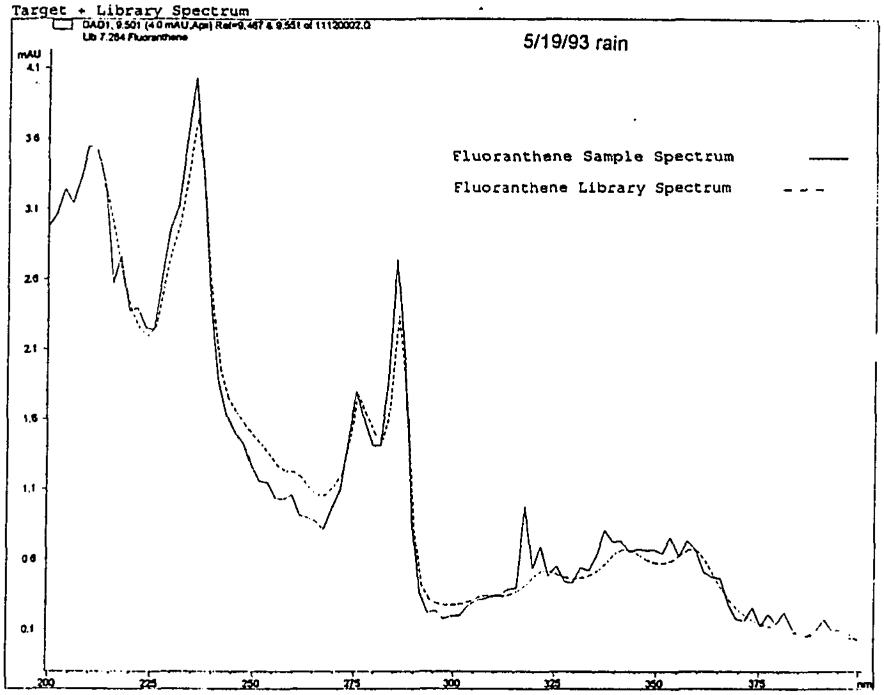
Phenanthrene Spectral Overlay

```
Search result of : DAD1, 8.705 (2.2 mAU,Apx) Ref=8.672 & 8.762
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
________________________________________________________________
             Library search results

 #     Match    Entry  Time [min]  Name
-----------------------------------------------------------------
 1  946.0235    11       5.484    Phenanthrene
 2  818.7006     9       6.226    Anthracene
 3  675.8900     5      10.014    Indeno[1,2,3-cd]pyrene
 4  672.4657     8       4.727    Triphenylene
 5  665.4754    20       6.321    Benzo[b]naphtho[2,1-cd]thiophene
 6  663.2313    29      10.116    Benzo[b]fluorene
 7  590.9281    23      12.077    Perylene
 8  487.3721    16       7.198    Benzo[b]fluoranthene
 9  425.7015    28      10.272    Benzo[a]fluorene
10  425.5162    10       4.544    Fluorene
-----------------------------------------------------------------
________________________________________________________________
```



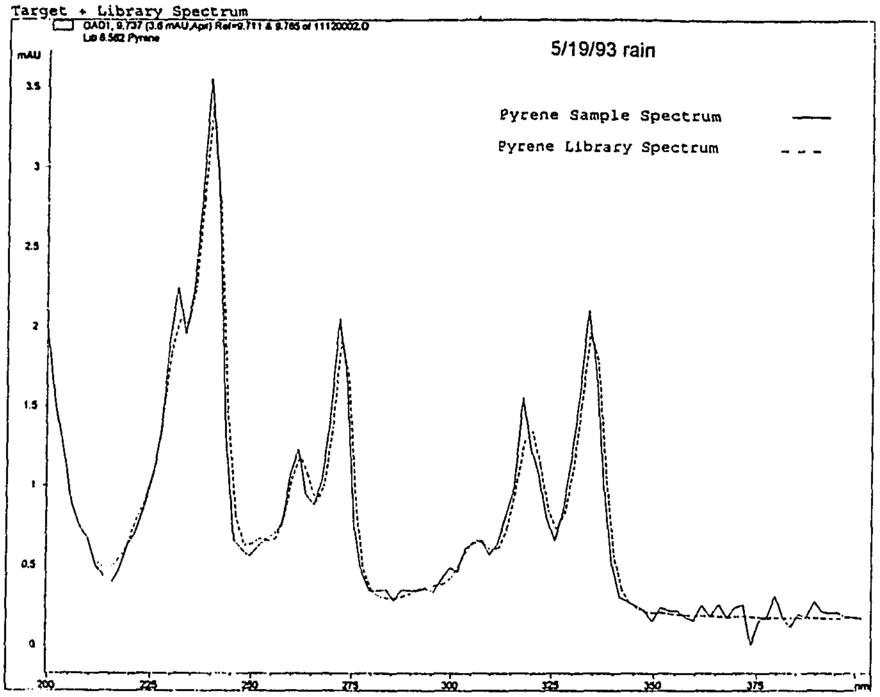
Anthracene Spectral Overlay

```
Search result of : DAD1, 9.166 (4.9 mAU,Apx) Ref=9.133 & 9.201
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
__________________________________________________________________
            Library search results

  #    Match    Entry  Time [min]  Name
---------------------------------------------------------------
  1  990.4378     9       6.226    Anthracene
  2  778.6306    11       5.484    Phenanthrene
  3  590.5015     5      10.014    Indeno[1,2,3-cd]pyrene
  4  441.4485    20       6.321    Benzo[b]naphtho[2,1-cd]thiophene
  5  419.5166     8       4.727    Triphenylene
  6  386.3840    23      12.077    Perylene
  7  340.6961    29      10.116    Benzo[b]fluorene
  8  299.3391    26       7.900    Benzo[k]fluoranthene
  9  275.0387    16       7.198    Benzo[b]fluoranthene
 10  196.8875    31       1.570    Biphenyl
---------------------------------------------------------------
__________________________________________________________________
```



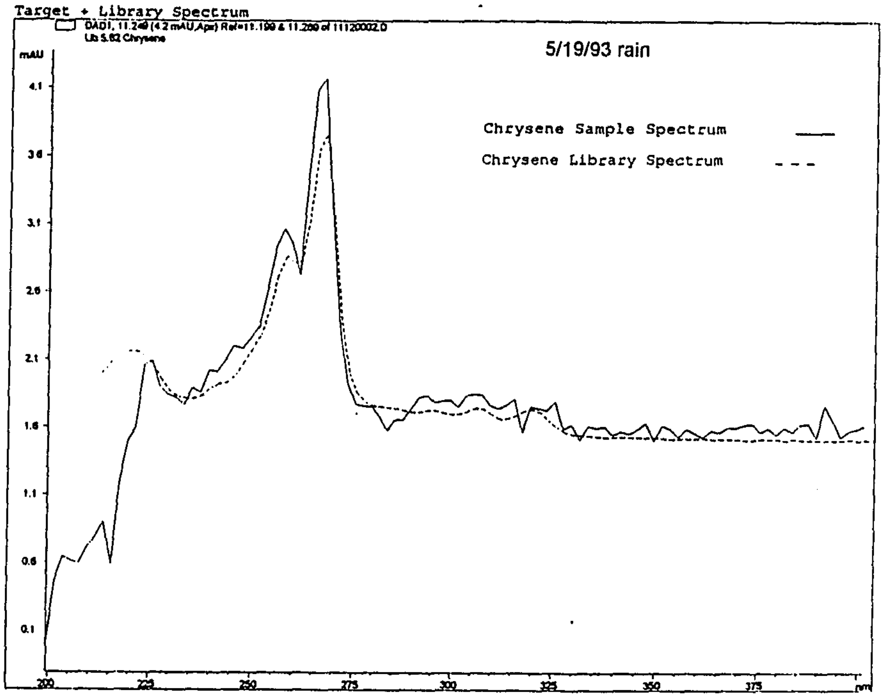
Fluoranthene Spectral Overlay

```
Search result of : DAD1, 9.501 (4.0 mAU,Apx) Ref=9.467 & 9.551
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
-------------------------------------------------------------------
            Library search results

 #    Match    Entry  Time [min] Name
-------------------------------------------------------
 1  971.5846    14       7.284   Fluoranthene
 2  689.7231     7       5.211   Cyclopenta[c,d]pyrene
 3  544.8457    18       6.795   Benzo[j]fluoranthene
 4  526.0646    16       7.198   Benzo[b]fluoranthene
 5  523.7704    23      12.077   Perylene
 6  518.9272    17       6.732   Benzo[e]pyrene
 7  483.6186    31       1.570   Biphenyl
 8  456.0482    20       6.321   Benzo[b]naphtho[2,1-cd]thiophene
 9  398.3712     5      10.014   Indeno[1,2,3-cd]pyrene
10  383.9996     2       5.632   Benz[a]anthracene
-------------------------------------------------------
-------------------------------------------------------------------
```



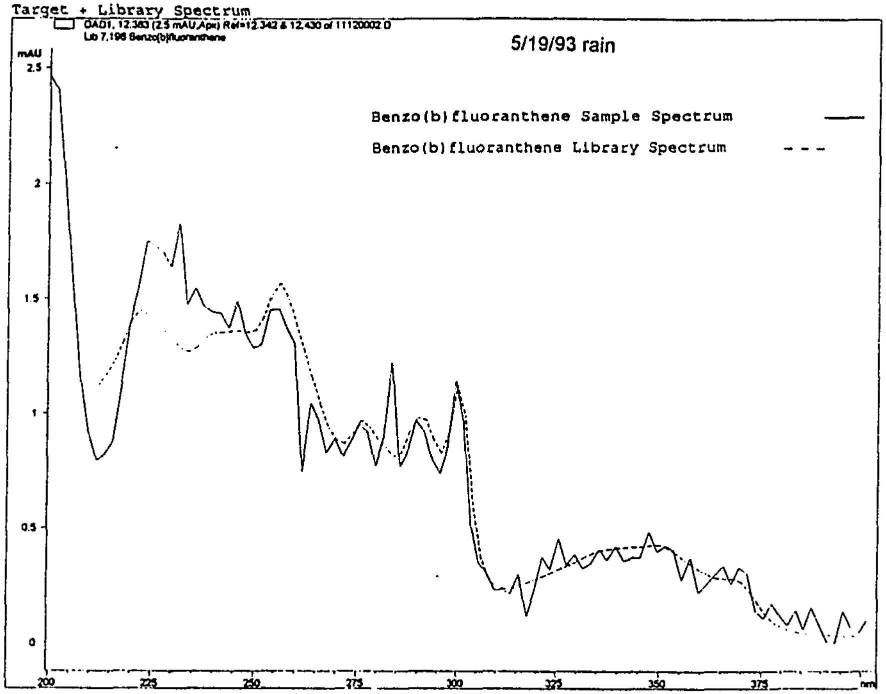
Pyrene Spectral Overlay

```
Search result of : DAD1, 9.737 (3.6 mAU,Apx) Ref=9.711 & 9.765
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
_____________________________________________________________________
            Library search results

 #     Match    Entry  Time [min]  Name
-------------------------------------------------------
 1   969.6424    13       8.562    Pyrene
 2   302.5401    18       6.795    Benzo[j]fluoranthene
 3   295.6738    20       6.321    Benzo[b]naphtho[2,1-cd]thiophene
 4   289.1363    14       7.284    Fluoranthene
 5   203.1514    16       7.198    Benzo[b]fluoranthene
 6   192.0685    26       7.900    Benzo[k]fluoranthene
 7   178.1639    17       6.732    Benzo[e]pyrene
 8   147.0286     1      11.313    Anthanthrene
 9   140.2402     7       5.211    Cyclopenta[c,d]pyrene
10   119.9444    11       5.484    Phenanthrene
-------------------------------------------------------
_____________________________________________________________________
```



Chrysene Spectral Overlay

```
Search result of : DAD1, 11.249 (4.2 mAU,Apx) Ref=11.199 & 11.289
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
__________________________________________________________________
            Library search results

 #     Match    Entry  Time [min]  Name
-------------------------------------------------------------------
 1   752.3992     6       5.820    Chrysene
 2   356.1097     8       4.727    Triphenylene
 3   341.3497    28      10.272    Benzo[a]fluorene
 4   310.0739    29      10.116    Benzo[b]fluorene
 5  .266.4728     3       8.220    Benzo[a]pyrene
 6   262.5372    10       4.544    Fluorene
 7   259.6357    20       6.321    Benzo[b]naphtho[2,1-cd]thiophene
 8   216.8612    30      11.416    Picene
 9   188.0163    16       7.198    Benzo[b]fluoranthene
10   149.3051    11       5.484    Phenanthrene
-------------------------------------------------------------------
__________________________________________________________________
```



Benzo(b)fluoranthene Spectral Overlay

```
Search result of : DAD1, 12.383 (2.5 mAU,Apx) Ref=12.342 & 12.430
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    Library Name : PAH
      Parameters : None
-------------------------------------------------------------------
            Library search results

  #     Match    Entry  Time [min]  Name
-----------------------------------------------------
  1  921.7790    16        7.198   Benzo[b]fluoranthene
  2  786.2222    20        6.321   Benzo[b]naphtho[2,1-cd]thiophene
  3  674.0872    14        7.284   Fluoranthene
  4  657.9241    23       12.077   Perylene
  5  657.3501     5       10.014   Indeno[1,2,3-cd]pyrene
  6  618.0532     7        5.211   Cyclopenta[c,d]pyrene
  7  542.5075    26        7.900   Benzo[k]fluoranthene
  8  534.1565    11        5.484   Phenanthrene
  9  525.2241    17        6.732   Benzo[e]pyrene
 10  521.8580    18        6.795   Benzo[j]fluoranthene
-----------------------------------------------------
-------------------------------------------------------------------
```
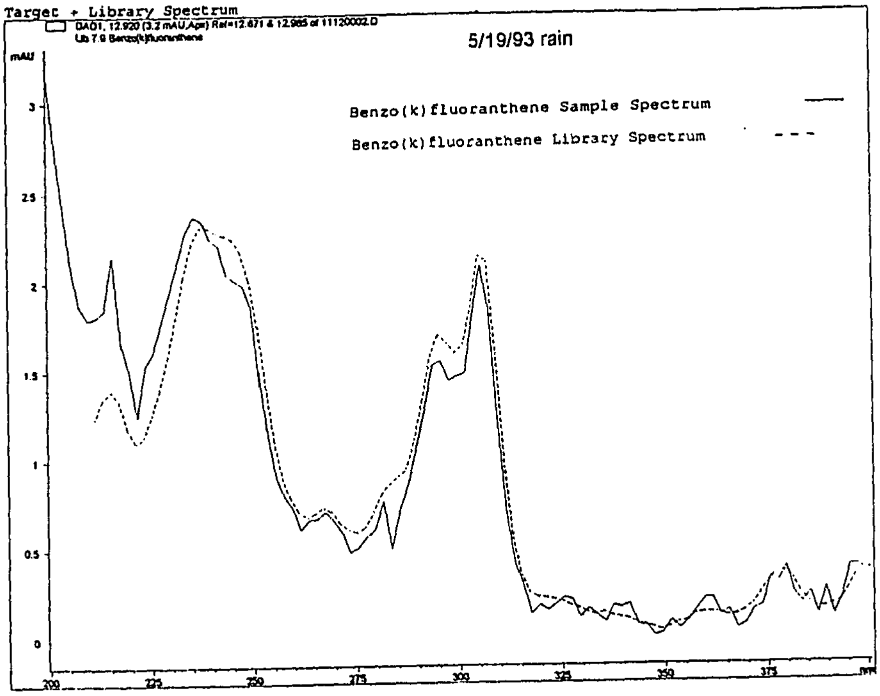
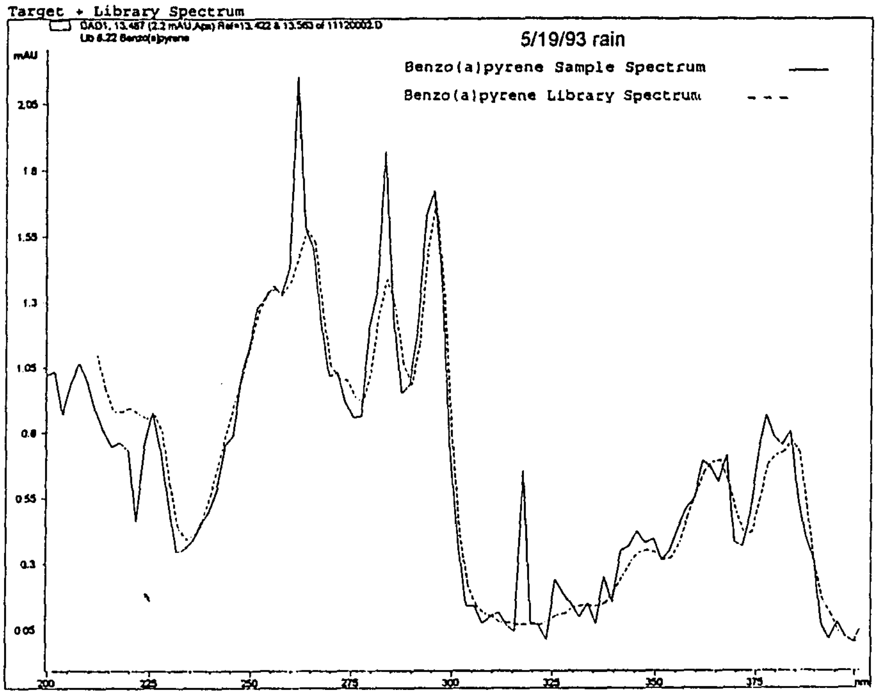



Benzo(k)fluoranthene Spectral Overlay

```
Search result of : DAD1, 12.920 (3.2 mAU,Apx) Ref=12.871 & 12.985
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
----------------------------------------------------------------------
            Library search results

 #     Match     Entry  Time [min]  Name
-------------------------------------------------------
 1   945.4591    26       7.900    Benzo[k]fluoranthene
 2   823.0647     1      11.313    Anthanthrene
 3   721.5050     5      10.014    Indeno[1,2,3-cd]pyrene
 4   703.5852    18       6.795    Benzo[j]fluoranthene
 5   562.5474    20       6.321    Benzo[b]naphtho[2,1-cd]thiophene
 6   562.4815    16       7.198    Benzo[b]fluoranthene
 7   540.5502    23      12.077    Perylene
 8   535.7468     7       5.211    Cyclopenta[c,d]pyrene
 9   492.2715    14       7.284    Fluoranthene
10   465.3826    31       1.570    Biphenyl
-------------------------------------------------------
----------------------------------------------------------------------
```



Benzo(a)pyrene Spectral Overlay

```
Search result of : DAD1, 13.487 (2.2 mAU,Apx) Ref=13.422 & 13.563
    Library used : C:\HPCHEM\SPECLIBS\DEMODAD.UVL
    Library Name : PAH
      Parameters : None
__________________________________________________________________
            Library search results

 #    Match    Entry  Time (min) Name
-----------------------------------------------------------
 1  908.2215     3       8.220   Benzo[a]pyrene
 2  435.0700    30      11.416   Picene
 3  432.8785    10       4.544   Fluorene
 4  417.8200    29      10.116   Benzo[b]fluorene
 5  393.8217    19       7.702   Dibenz[a,c]anthracene
 6  392.1716    22      14.688   Benzo[b]chrysene
 7  377.9812     2       5.632   Benz[a]anthracene
 8  356.0117     6       5.820   Chrysene
 9  345.6457    28      10.272   Benzo[a]fluorene
10  335.0631    16       7.198   Benzo[b]fluoranthene
-----------------------------------------------------------
__________________________________________________________________
```

Figure 5. The monthly PAH total concentration distribution in New York City precipitation.

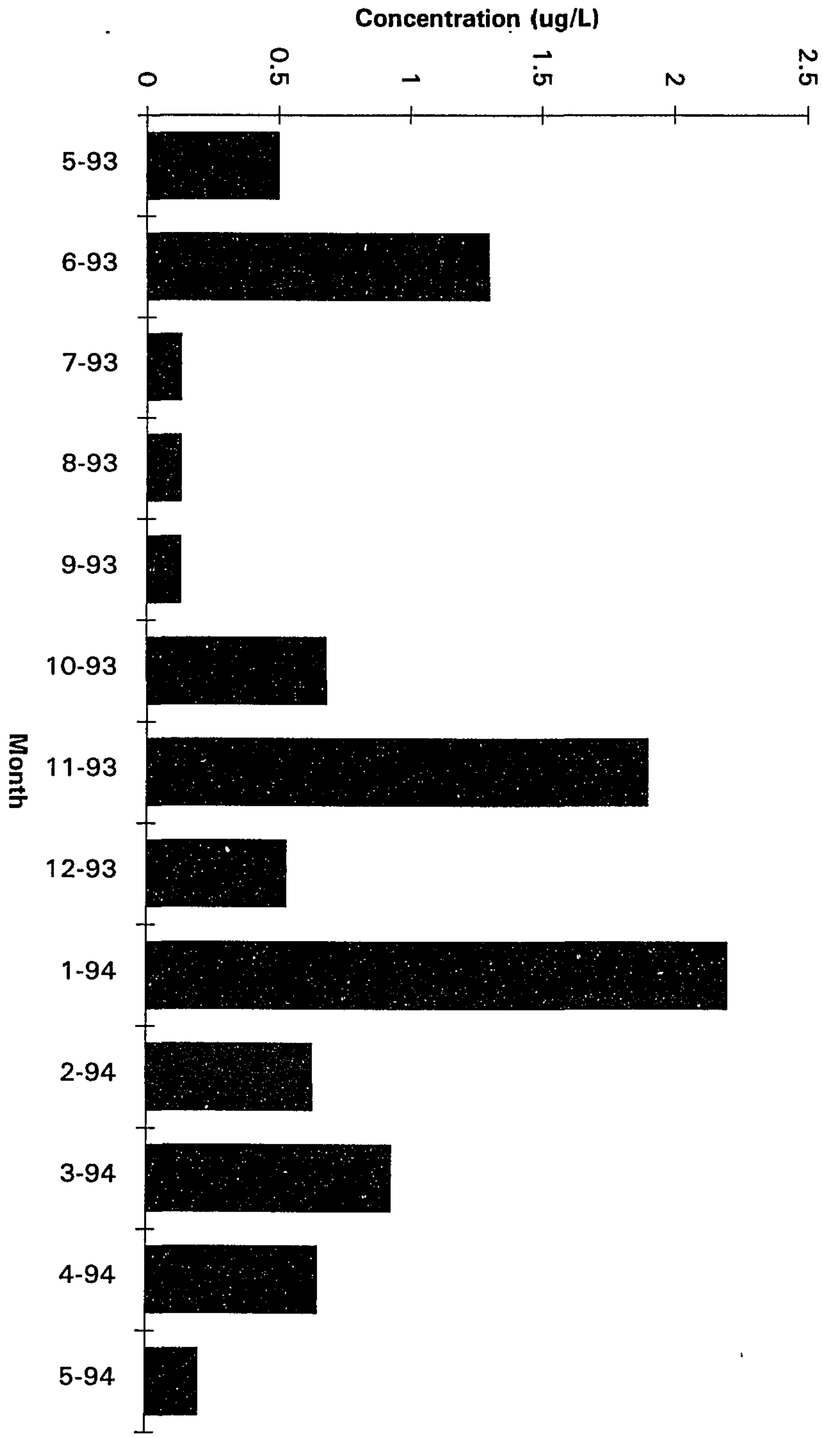

Concentration (ug/L)
0
0.5
1
1.5
2
2.5
Month
5-93
6-93
7-93
8-93
9-93
10-93
11-93
12-93
1-94
2-94
3-94
4-94
5-94

Figure 6. Comparison of the sum of 8 PAH concentration in New York City with that in the Netherlands(1983).

The sum of the concentration of fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[123-cd]pyrene in New York City and in Netherlands.

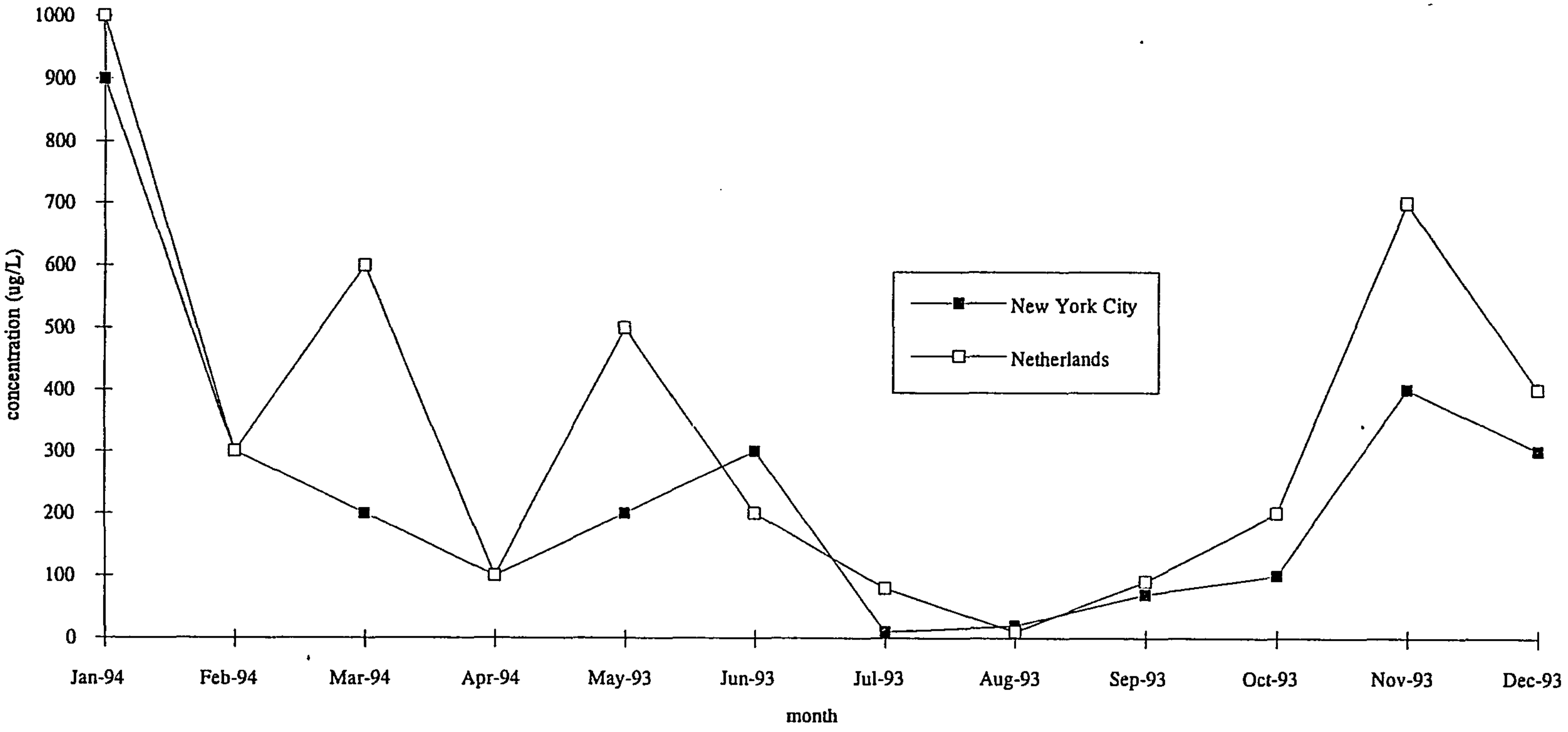
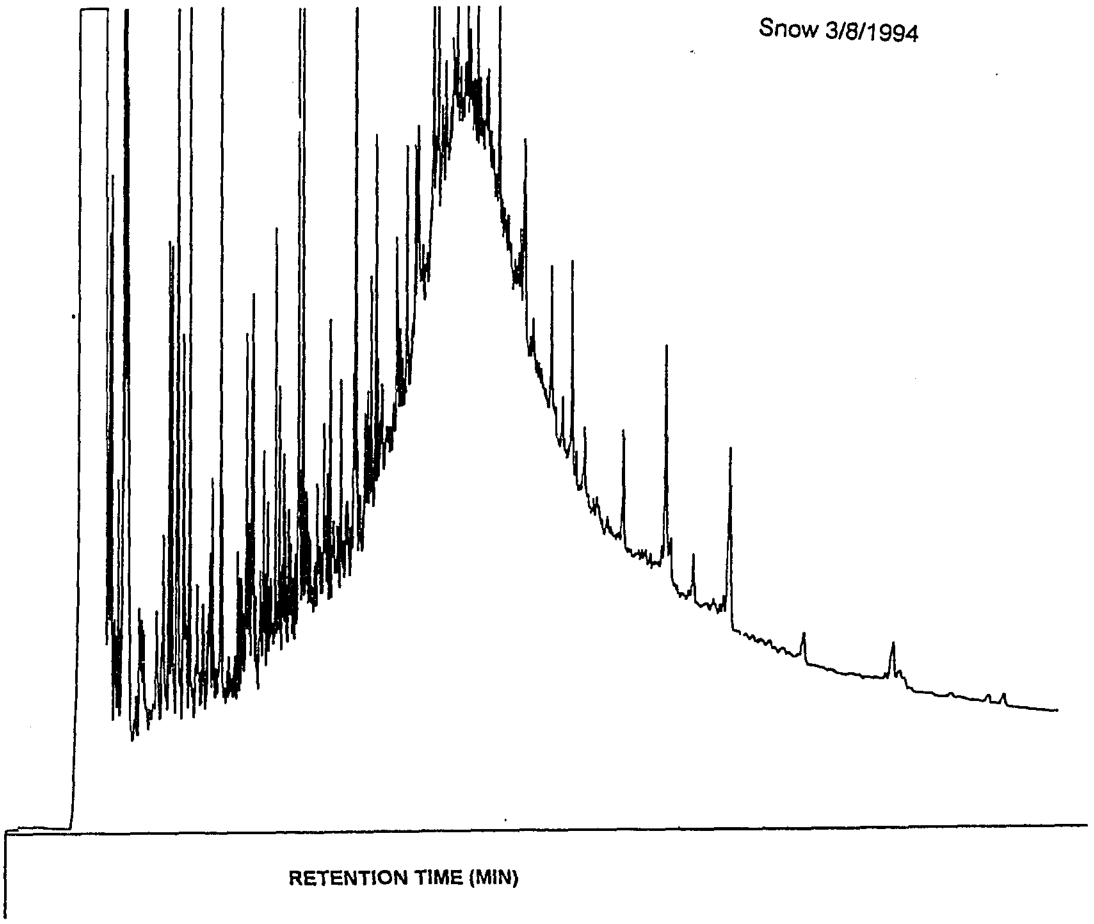
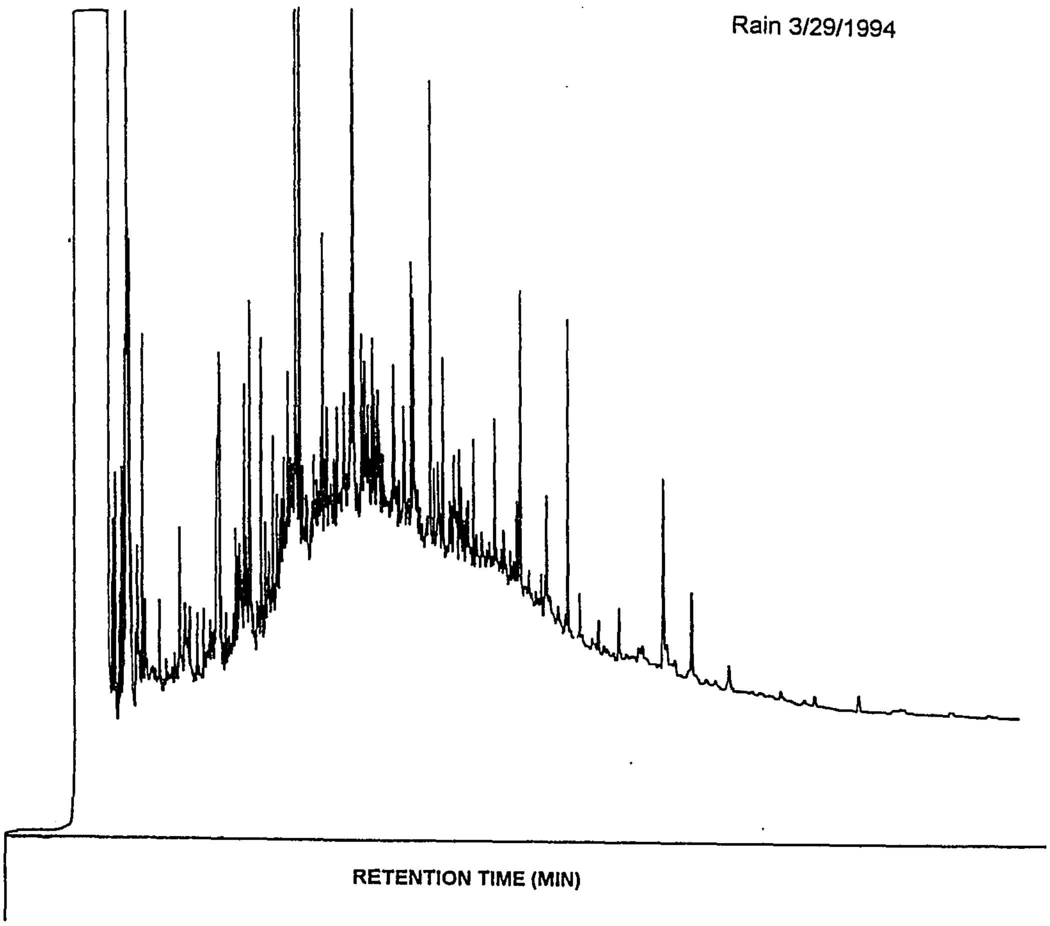


Figure 7. GC chromatogram of extract of snow of 3/8/1994.



Snow sample of 3/8/1994.
GC conditions: 2 ul splitless injection, 50^0-280^0C at 10^0C/min.
32mx0.32 mm ID DB-5, flame ionization detector (attenuation x1).

Figure 8. GC chromatogram of extract of rain of 3/29/1994.



Rain sample of 3/29/1994.
GC conditions: 2 ul splitless injection, 50°-280°C at 10°C/min. 32mx0.32 mm ID DB-5, flame ionization detector (attenuation x1).

Figure 9. The monthly n-alkane total concentration distribution in New York City precipitation.

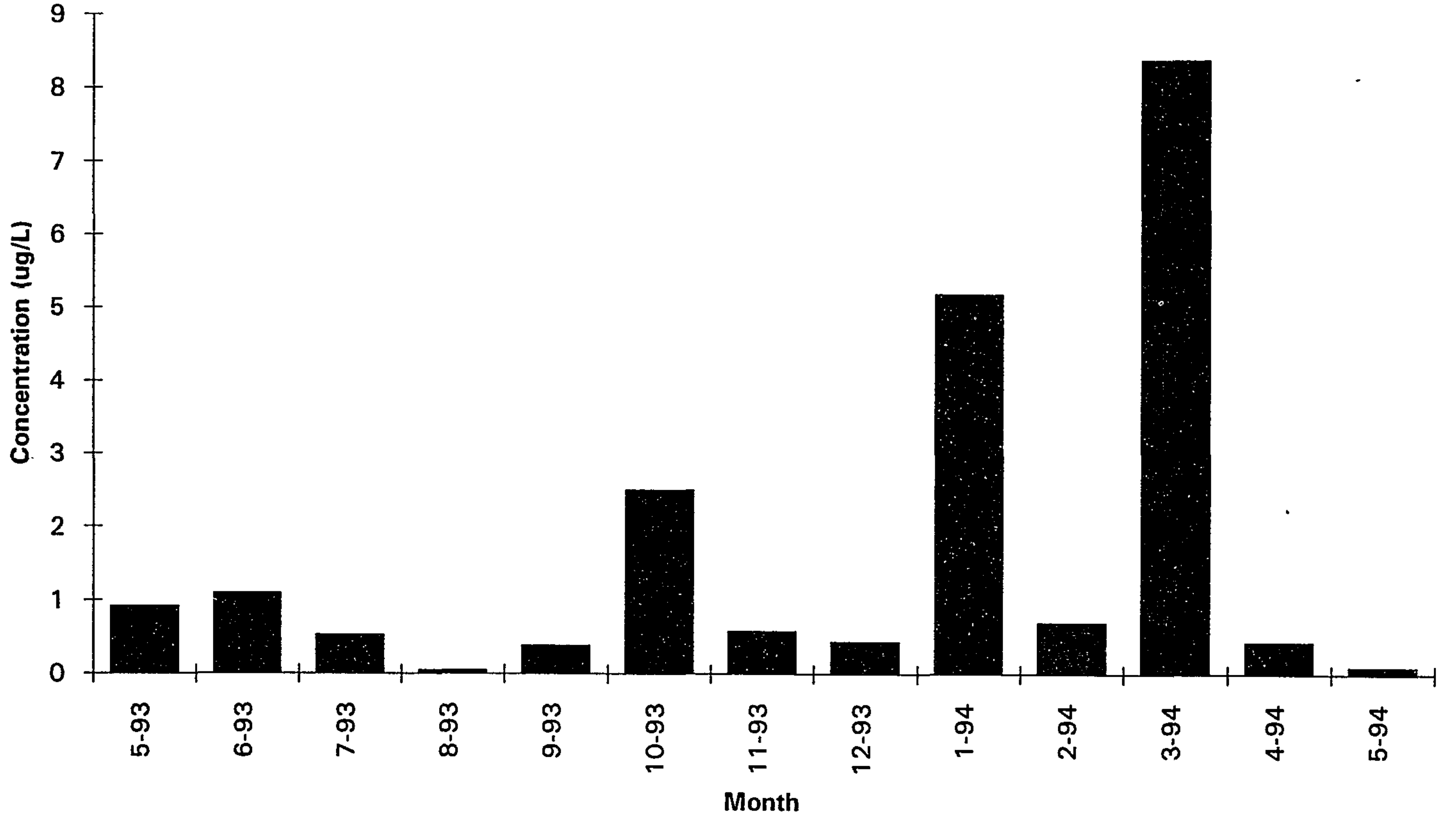

Concentration (ug/L)
0
1
2
3
4
5
6
7
8
9
5-93
6-93
7-93
8-93
9-93
10-93
11-93
12-93
1-94
2-94
3-94
4-94
5-94
Month

Figure 10. The total concentration difference of n-alkanes and PAHs in 36 precipitation events.

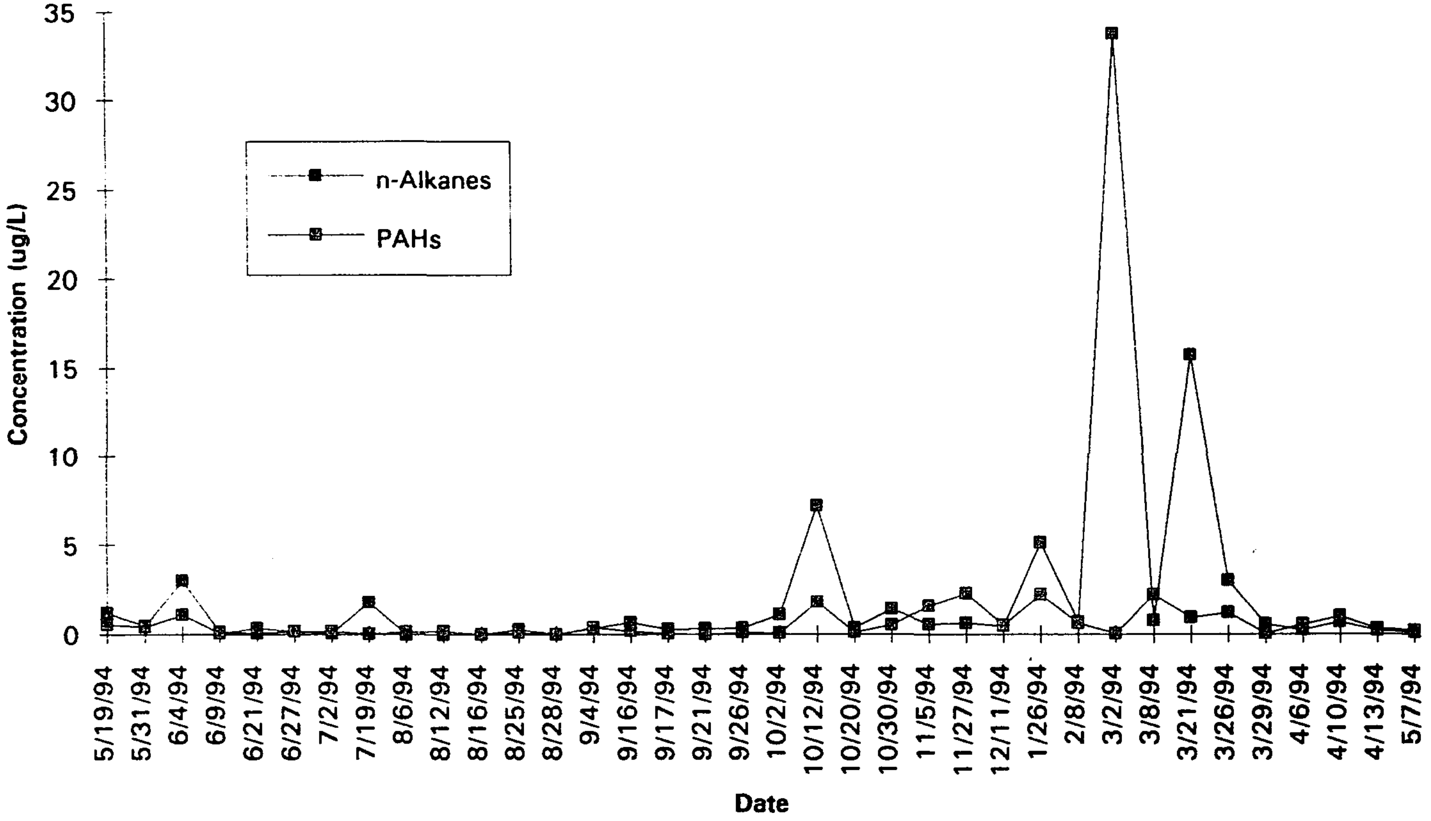

Concentration (ug/L)
35
30
25
20
15
10
5
0
n-Alkanes
PAHs
5/19/94
5/31/94
6/4/94
6/9/94
6/21/94
6/27/94
7/2/94
7/19/94
8/6/94
8/12/94
8/16/94
8/25/94
8/28/94
9/4/94
9/16/94
9/17/94
9/21/94
9/26/94
10/2/94
10/12/94
10/20/94
10/30/94
11/5/94
11/27/94
12/11/94
1/26/94
2/8/94
3/2/94
3/8/94
3/21/94
3/26/94
3/29/94
4/6/94
4/10/94
4/13/94
5/7/94
Date

Figure 11. The monthly n-alkane and PAH total concentration distribution.

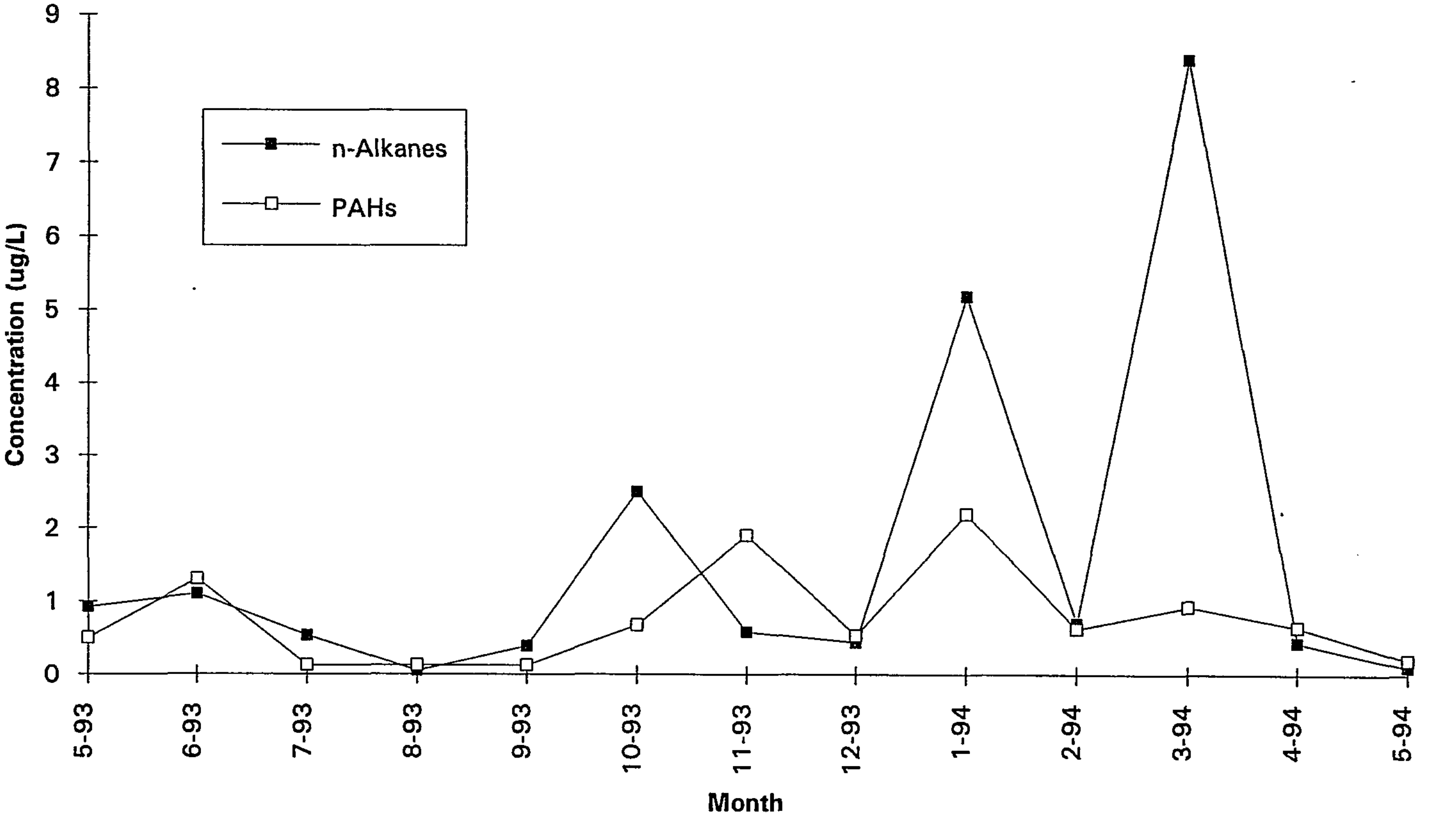
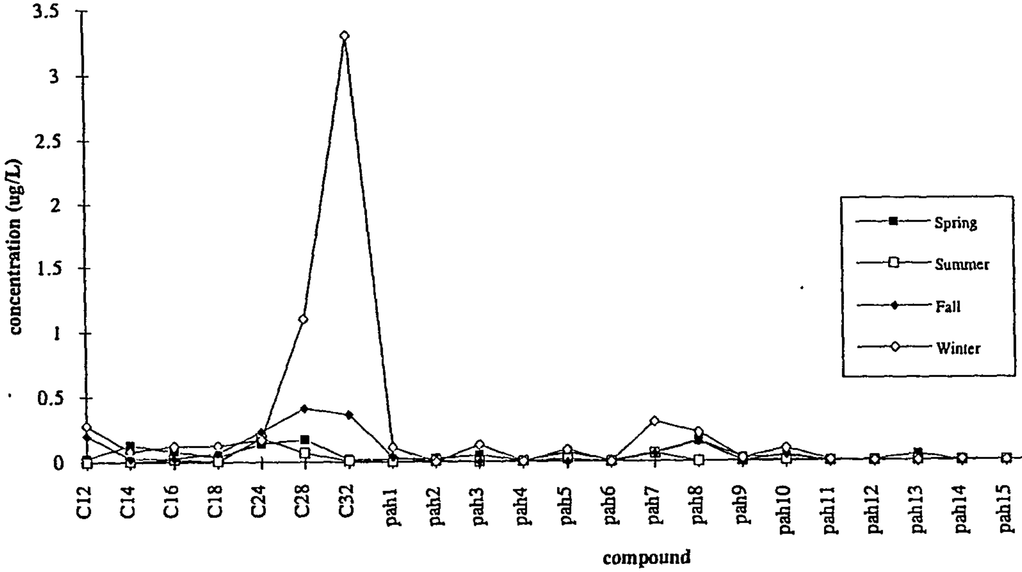

Concentration (ug/L)
0
1
2
3
4
5
6
7
8
9
n-Alkanes
PAHs
5-93
6-93
7-93
8-93
9-93
10-93
11-93
12-93
1-94
2-94
3-94
4-94
5-94
Month

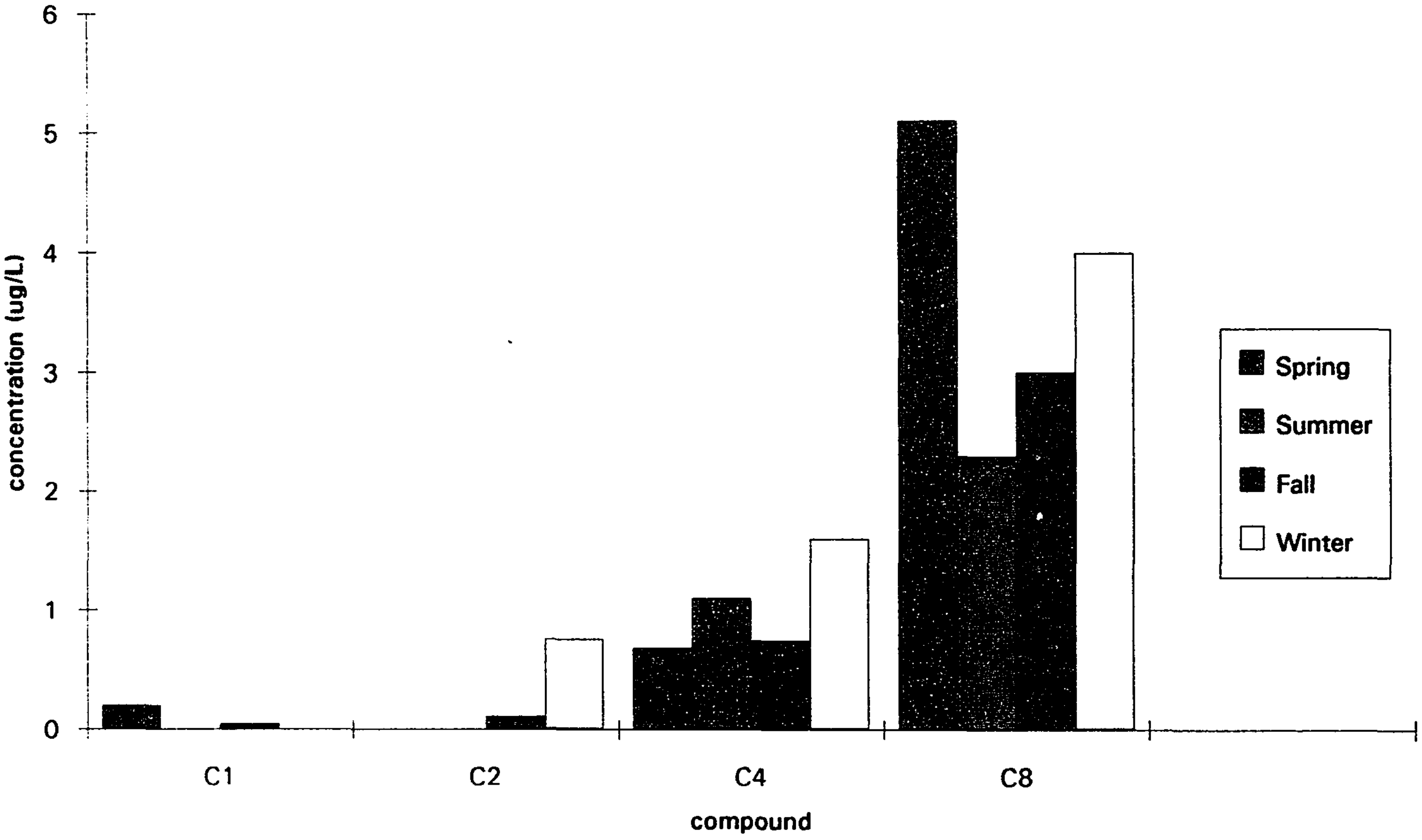
Figure 12. The seasonal mean concentration variations of n-alkanes and PAHs.



pah1. Naphthalene pah2. Acenaphthylene pah3. Acenaphthene pah4 4. Fluorene
pah 5. Phenanthrene pah 6. Anthracene pah7. Fluoranthene pah8. Pyrene
pah9. Benzo(a)anthracene pa 10. Chrysene pah11. Benzo(b)fluoranthene
pah12. Benzo(k)fluoranthene pah13. Benzo(a)pyrene pah14. Dibenzo(a,h)anthracene
pah15. Benzo(ghi)perylene pah16. Indeno(1,2,3-cd)pyrene
P17. 9-fluorenone P18. 1,2,3,4-dibenzanthracene
P19. Dibenzofuran P20. Dibenzothiophene

Figure 13. Seasonal variations of total concentration of phthalate esters.

C1-dimethyl phthalate
C2-diethyl phthalate
C4-dibutyl phthalate
C8-dioctyl phthalate


6
5
4
3
2
1
0
concentration (ug/L)
C1
C2
C4
C8
compound
Spring
Summer
Fall
Winter

Chapter IV: Literature cited

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