POLYCYCLIC AROMATIC HYDROCARBONS IN AIR AND WATER IN THE GREATER MAHONING VALLEY REGION

by

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), which are prone to atmospheric transport because of their low vapor pressures, have been reported in air, water and sediments by a number of researchers all over the globe. Many of these compounds bioaccumulate and exhibit varying degrees of carcinogenicity. Past studies have reported high concentrations of PAHs in the sediment of the Mahoning River. The present study was done to determine concentrations of PAHs in the air and water in the Mahoning Valley and to determine if atmospheric transport was an important source of PAHs to the region. Quantitative analysis was performed using gas chromatography with mass spectrometry and concentrations of twenty-one PAHs were determined in air and water for three sites- Youngstown, OH; Meander, OH and Pennsylvania, PA. Source determination was performed through the combined use of characteristic ratios and principal components analysis (PCA). The Youngstown and Meander sites were found to be similar, exhibiting positive correlations between water samples and Mahoning River sediments but no correlation between the water and corresponding air samples. This is likely due to high levels of PAHs in the sediments of the Mahoning River and its tributaries being the primary source of PAHs to the water column with atmospheric transport providing only a minor contribution. The Pennsylvania site showed a correlation between the air and water samples, probably due to a higher contribution from atmospheric deposition than sediment resuspension to this rural man-made lake. It was also found that Pennsylvania air was correlated to Youngstown air. This may be due to Youngstown being an active urban site located to the west of the Pennsylvania site, making it a source of pollutants through atmospheric transport.

ACKNOWLEDGMENTS

I want to thank all the people who assisted in each facet of my research along the way- and I hope no one has been omitted. First of all, thanks to those people who made the field samples available- Dave Tabak of Mahoning Valley Sanitation Department (Meander Reservoir), Daniel O'Connell of Youngstown State University (press boxes at YSU stadium- not a site for the weak-stomach'ed or acrophobics), Dr. Timothy Wooster and Dr. Clarence Harms of Westminster College (for access to the PA site), and Lou Cimmento of Coca-Cola Bottling Company of Northern Ohio (for the donation of a carbonated pop-dispenser- A.K.A. our water extraction device- "THE pop can").

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INTRODUCTION

SEMIVOLATILE ORGANIC COMPOUNDS

In the 1950's several organic compounds were found to be bioconcentrating in larger fish and their avian predators.[1] Since then, pollution has become an issue of great concern for the general public, as well as scientists and government officials. Many of the problems that have caused concern can be directly linked to man, e.g. photochemical smog in urban air, acid rain, the destruction/depletion of the ozone layer and the threat of global warming.[2] Industrial activities; the burning of fossil fuels, biomass, and vegetation; transportation and agricultural practices are all anthropogenic, or man-made, sources of pollution and have been linked to such problems as the "greenhouse effect" and increased corrosion of materials,[2] as well as biological problems such as impairment of immunity,[3] predisposition to birth defects, reproductive failure[4] and cancer.[5]

One class of pollutants that has aroused much concern over the past 30 years is the group termed the semivolatile organic compounds (SOCs). The compounds in this class vary greatly in chemical structure and reactivity but are grouped together because of similar physico-chemical properties: low water solubility, enhanced lipophilicity, chemical/microbial stability and vapor pressures in the range 10^{-1}-10^{-6} Pa.[1,6,7] These properties allow SOCs to persist in the environment, be transported thousands of kilometers from their point of release and to concentrate in the food chain.[5,8] Persistence and long range atmospheric transport have allowed these compounds to become well dispersed in the environment. Studies have shown SOCs to be present in air, water, soil, sediment and biota throughout the world, including remote regions such as the Arctic and Antarctic.[2,6] There are literally hundreds of thousands of compounds which are classified as SOCs. Some of the more infamous include: polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), DDT, toxaphene, atrazine and the polycyclic aromatic hydrocarbons (PAHs).[7]

POLYCYCLIC AROMATIC HYDROCARBONS

PAHs are an extensive class of organic compounds composed of benzene rings linked in conjugated ring systems. There are 333 possible combinations of a six-ring system, but due to isomeric combinations, differing number of rings and the presence of alkyl sidechains, the class contains about 10,000 compounds.[9,10] PAHs are formed by the incomplete or inefficient combustion of organic matter, and can be derived from both natural and anthropogenic sources.[10-12] Natural sources provide a consistent background level of PAHs and include forest, prairie and brush fires,[13-15] volcanic eruptions,[14,16,17] diagenesis,[18] biosynthesis,[14,18,19] and transformation of plant material.[12,20,21] Natural sources add only a minor amount to the current levels of PAHs in our environment, while a wide variety of anthropogenic sources provide the rest. Some of the man-made sources include: (1) Combustion of fossil fuels and wood;[9,17,22,23] (2) Industrial processes, such as coke production in the steel industry and electric and thermal power plants;[10,14,24,25] (3) Production and spillage of fossil fuels and the leaching of creosote treated items;[10,20,26,27] (4) Urban run-off;[26-28] (5) Atmospheric transport and deposition;[6,22,27,28] and (6) Domestic processes, such as tobacco smoking and various food cooking operations.[9,10,18]

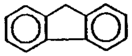
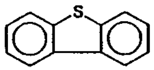
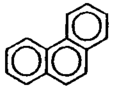
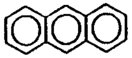
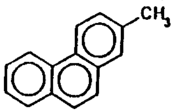
Environmental Concerns

PAHs were first studied as an environmental problem in 1775 when Sir Percival Pott recognized an elevation of scrotal cancer in London chimney sweeps. Upon extraction of chimney soot, he discovered the presence of PAHs, most notably benzo(a)pyrene.[17,29] Since then, PAHs have been studied extensively and are the largest class of chemical carcinogens known today.[29-31] Carcinogenicity varies greatly among the different compounds as well as mutagenicity, toxicity, teratogenicity and genotoxicity.[20,22,32-39] Of the ~10,000 possible PAHs, twenty-four are listed as probable carcinogens and sixteen are on the USEPA's list of priority pollutants.[40] The structures and molecular weights of the 16 priority pollutant PAHs along with several others analyzed in this study are given in Table 1. Many PAHs considered non-toxic are transformed through chemical reactions into carcinogenic or mutagenic compounds.[32,41] Most of the lower molecular weight PAHs, which are abundant in urban air, can react with pollutants such as NO_X to form the carcinogenic nitro-PAHs.[41-43] In a similar situation, some PAHs can undergo "photoinduced toxicity" in which the conjugated ring system absorbs ultraviolet radiation, elevating the ring to an excited state, and increasing its toxicity.[44]

Because PAHs are so widespread in the environment, they have been studied in every imaginable medium. PAHs have been measured in water,[16] sediments[16,45-48] and soils,[14] as well as in innumerable plants and animals.[49-55] They have been found within some natural organic minerals,[16,56] in consumer items such as skin creams,[10] shampoos,[10] mothballs,[10] blacktop,[10] and creosote-preserved wood[10] as well as places of daily exposure such as airborne particulate matter,[16,41,57-60] industrial effluents,[16] workplace atmospheres,[16] tobacco smoke[16] and food.[16] Total daily exposure to PAHs depends on a number of factors which vary from person to person. Gilbert (1994)[9] estimated, for intake through consumption, approximately one-third of the PAHs in the diet of a person from the United Kingdom was from cereals, oils, and fats; and the remaining two-thirds from fruits, sugars, and vegetables. Those foods with the highest PAH levels include charcoal-broiled or smoked meats (as well as other smoked foods),[14,70] leafy vegetables, grains, fats, and oils -all of which may contribute as much as 0.01 mg/kg.[14]

Typical drinking water can contain 0.1-61.6 ng/μL while soils have been found to contain PAHs ranging from 5-100 μg/kg in a forest, 10-100 μg/kg at an agricultural site, to 600-3000 μg/kg in an urban location.[14] Sediments are the most concentrated type of soils with levels ranging from 0.003-232 mg/kg.[14] Urban air[71-73] is more concentrated in PAHs (15-50 ng/m^3) than rural air[74] (about 5.7 ng/m^3) or air over the Great Lakes (0.2-3.0

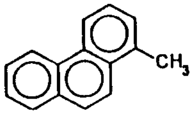
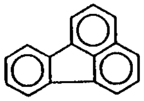
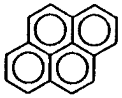
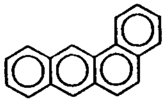
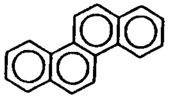
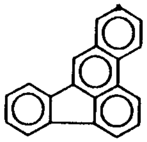
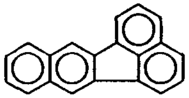
Table 1: PAH Structures, Symbols and Properties

Peak	Symbol	PAH	MW	Structure	Carc. †	Alternative Nomenclature
1	NAP	naphthalene	128			
2	ACY	acenapthylene	152			
3	ACE	acenaphthene	154			ethylenenaphthalene [63] periethylenenaphthalene [63] 1,8 hydroacenaphthylene [63]
4	FLU	fluorene	166		(-)	
5	DBT	dibenzothiophene	184			dibenzo(b,d)thiophene [64] biphenylene sulfide [64] diphenylene sulfide [64] 9-thiafluorene [64]
6	PHEN	phenanthrene	178		(-)	
7	ANT	anthracene	178		(-)	
8	2-MP	2-methylphenanthrene	192			

† References for carcinogenicity include 10, 14, 17, 26, 30, 33, 38, 43, 61, 62, 65-69.

(-) = Carcinogenic; (+) = Non-carcinogenic; (?) = Questionable Carcinogenicity

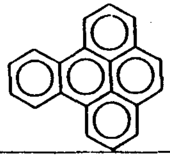
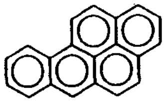
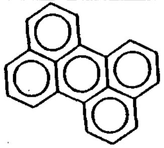
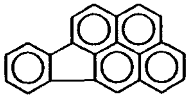
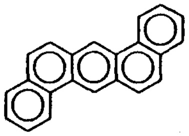
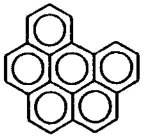
Table 1: PAH Structures, Symbols and Properties (cont.)

Peak	Symbol	PAH	MW	Structure	Carc. †	Alternative Nomenclature
9	1-MP	1-methylphenanthrene	192			
10	FLT	fluoranthene	202		(-)	
11	PYR	pyrene	202		(-)	
12	BAA	benzo(a)anthracene	228		(+)	1,2-benzanthracene[62]
13	CHR	chrysene	228		(+)	1,2-benzophenanthrene[62,63]
14	BBF	benzo(b)fluoranthene	252		(+)	Benz(e)acephenanthrylene[62] 3,4-benzfluoranthene[63] 3,4-benzofluoranthene[62,63]
15	BKF	benzo(k)fluoranthene	252		(?)	11,12-benzofluoranthene[62,63]

† References for carcinogenicity include 10, 14, 17, 26, 30, 33, 38, 43, 61, 62, 65-69

(-) = Carcinogenic; (+) = Non-carcinogenic; (?) = Questionable Carcinogenicity

Table 1: PAH Structures, Symbols and Properties (cont.)

Peak	Symbol	PAH	MW	Structure	Carc. †	Alternative Nomenclature
16	BEP	benzo(e)pyrene	252		(?)	1,2-benzopyrene [63]
17	BAP	benzo(a)pyrene	252		(+)	3,4-benzopyrene [63]
18	PERY	perylene	252		(-)	
19	IND	indeno[1,2,3-cd]pyrene	276		(+)	o-phenylenepyrene [63,67]
20	DBA	dibenzo(ah)anthracene	278		(+)	1,2-5,6-dibenzanthracene [63]
21	BGH	benzo(ghi)perylene	276		(?)	11,12-benzoperylene [62,63]

† References for carcinogenicity include 10, 14, 17, 26, 30, 33, 38, 43, 61, 62, 65-69.

(-) = Carcinogenic; (+) = Non-carcinogenic; (?) = Questionable Carcinogenicity

ng/m^3).[1,75] The air in a typical clean office[76] will yield a dose of 1 to 5 μg/day whereas household air ranges anywhere from 8 to 80 ng/m^3, depending on the presence of such things as tobacco smoke and coal or wood combustion.[14] Daily exposure from food, air, soil, water, incidental ingestion of soil, and dermal contact has been estimated at 3.70 μg per person per day in the UK and 5 -17 μg per person per day by the Dutch.[9] A non-smoker in the U.S is estimated to have a daily exposure of 3 μg/day, while for a smoker the value is closer to 15 μg/day.[14]

The importance of anthropogenic sources can be seen by studying ice cores and sediment layers. In these studies, a low, constant level of PAHs- most likely due to natural combustion, i.e. forest fires- is apparent prior to 1900.[12,29] A sharp increase during the onset of the Industrial Revolution occurred in the early 1900's,[12,29,77] with a maximum level of PAHs occurring between 1920 and 1940 due to increased combustion of coal.[77] A slight decrease around 1930 has been attributed to the decreased consumption of energy during the Depression.[29] From 1940 to 1960, studies have shown an overall decline in PAH levels which can be attributed to the substitution of oil and natural gas for coal as home heating fuels as well as increased controls on industrial emissions.[12] Oil and natural gas combustion are more efficient forms of heating, which result in markedly lower production of PAHs.[12,29,77,78] PAH levels have continued to decrease in recent years, possibly due to the extended use of catalytic converters in automobiles, as well as a decrease in coal and open burning.[79] A study of Lake Michigan sediments determined the major anthropogenic source of PAHs to the environment from 1900-1978 was coal combustion, most notably from the production of coke and steel. Coal combustion is still the biggest contributor today, followed by vehicular emissions.[12]

Chemical and Physical Properties

Table 2 gives values for some physical properties for the PAHs studied in this project. The physical properties of PAHs have a direct influence on their behavior and fate in the environment. SOCs exist in the atmosphere in two forms: vapors and adsorbed

TABLE 2: Physico-chemical Properties

	Melting Point § (degree C)		Boiling Point § (degree C)		Aqueous Solubility £ (µmol/L)		BCF ¥	Vapor Pressure p_l(25 C) Pa ¤		Octanol-Water Coeff. log K_{OW} ¤	
NAP	81	*34*	218		249		nr	17.5	*15*	3.37	*18*
ACY	93		270		22.8	*19*	510	nr		4.07	*18*
ACE	96		279	*34, 63*	29		387	1.52		3.92	
FLU	117		294		11		1300	0.72		7.91	
DBT	97	*64*	353	*80*	5.6		nr	nr		nr	
PHEN	101		338		7.2		nr	0.11		4.57	
ANT	216	*34*	340	*34, 63*	0.37		917	0.078		4.54	
2-MP	nr		355		nr		nr	nr		nr	
1-MP	123		359		1.4		nr	nr		5.14	*83*
FLT	111		383		1.2		2702	0.0087		5.22	
PYR	156		393	*34*	0.72		nr	0.012		5.18	
BAA	162		435		0.048		10100	0.00061		5.91	
CHR	256		441		0.013		11000	0.00011		5.86	
BBF	168	*34*	481		0.006		58000	0.000016	‡	5.8	
BJF	166	*34*	480		0.0099		nr	nr		6.44	*83*
BKF	217	*34*	481		0.003		93000	4.1E-06		6	
BEP	179		493		0.025		nr	0.000013	*82*	6.44	*83*
BAP	177		496		0.016		23000	0.000021		6.04	*18*
PERY	278	*34*	503	*34, 63*	0.0012		nr	nr		6.06	*18*
IND	163	*34*	536	*63*	0.00069	†	390000	nr		7.66	*18*
DBA	270		524	*34, 63*	0.002		20000	9E-08		6.75	
BGH	278	*34*	>500	*34*	0.002		180000	0.000023		6.5	

† Outlier

‡ Calculated value.

nr = not reported

§ All from Ref 67 unless noted (in italics to the right).

£ All from Ref 34 unless noted (in italics to the right).

¥ All from Ref 19.

¤ All from Ref 81 unless noted (in italics to the right).

to suspended particles. Partitioning between these phases in air influences their removal mechanisms and thus, their atmospheric lifetimes and fate in the environment. The extent of association with particulate matter depends on the compound's vapor pressure, the amount and type of particulate matter present and the ambient temperature. Compounds with vapor pressures greater than 10^{-2} Pa are found primarily in the vapor phase whereas those with vapor pressures less than 10^{-6} Pa are primarily bound to particles. For compounds in between these values, the amount in each phase varies with temperature and particulate concentration and type.[84] The low molecular weight PAHs (< 178 g/mole) tend to be predominantly in the vapor phase in the atmosphere, as well as the dissolved phase in the water column,[85] due to high volatilities (vapor pressures > 10^{-2} Pa), enhanced water solubilities, and low affinity for organic phases. These compounds are highly reactive photochemically and in the presence of oxidants,[86] and are quickly metabolized in air and water, by both abiotic and biotic degradation.[65] Higher molecular weight PAHs (> 178 g/mole) are predominantly in the particulate phase (vapor pressures < 10^{-6} Pa) in the atmosphere and water column, having lower water solubilities and higher lipophilicity. These properties enhance bioconcentration for higher molecular weight PAHs as compared to the lower molecular weight compounds.

PAHs range from almost completely gaseous to almost completely particulate in the atmosphere, a fact that complicates their atmospheric chemistry. Complicating the determination of fate further is the movement of PAHs between media- from air to water, water to air, air to soil, soil to air, water to sediment, and sediment to water. The direction of flux between media is dependent on many factors including temperature, humidity, particle type, pH, and the chemical and physical properties of each compound. The bioavailability of PAHs also varies, affecting its toxicity and fate. For example, it has been noted that combustion-generated PAHs appear to be less bioavailable than PAHs derived from fresh petroleum products[77,87,88] due to a higher fraction of non-exchangeable compounds which are either embedded within the particle matrix or strongly adsorbed to active sites.[89]

MAHONING VALLEY

The Mahoning River is a 108.3 mile river that runs through Trumbull and Mahoning Counties in Ohio before entering Pennsylvania where it joins Shenango and Beaver Creeks as tributaries to the Ohio River.[90] It has been described as one of the most polluted rivers in the country.[91] Historically, the river has accepted discharges from nine steel plants, a coal-fired power plant, and sanitation waste water from eight municipalities.[91] Although primary and secondary treatment of waste water is no longer the problem it used to be, contamination still occurs from combined sewer overflows (designed to protect against heavy rains)[90] and numerous spills and leaks that have occurred throughout the years.[91] The river at the height of the steel industry contained large amounts of floating oil,[91] averaged 97°F (36°C) during the winter,[91] and was the receptacle for 7,000 gallons of oil each day.[90] There has been improvement in the chemical quality of the river over the past 15 years including a slow decrease in toxin levels[92] due, in large part, to the closing and consolidation of many of the steel mills.[91] The river, which was able to support little or no life twenty years ago,[90] is now the habitat for such species as walleye, carp, catfish and white crappie.[93] However, despite improvements in the biological condition of the Mahoning River, it is still rated "very poor" (the lowest possible category) by the Ohio EPA, although it is now at the upper-most end of this category[92].

Public concern about water quality was substantiated in 1988 when a swimming, wading and fishing advisory[94] was issued by the Ohio EPA for the Mahoning River stretching from Warren to the Pennsylvania border. This advisory was prompted by studies that showed elevated levels of PAHs in the sediments. Although this did not necessarily pose a threat to humans, and no tumor studies were conducted on the fish, a similar situation had occurred in the Black River in Lorain, OH just five years before. The Black River sediment was highly contaminated with PAHs (having endured similar pollution sources as the Mahoning River)[95] and a prevalence of tumors and other abnormalities were found in the brown bullhead fish in the river. Scientific evidence has linked the formation of tumors with exposure to high concentrations of PAHs. Although tumor studies have not been performed on Mahoning River fish, the PAH concentrations in the Mahoning River sediments exceeded those of the Black River.[94] The U.S. EPA concluded "there was a likelihood of an adverse impact on fisheries to the same ... or greater degree than that reported for the Black River."[66]

CHAPTER TWO

BACKGROUND

SOURCE IDENTIFICATION

Atmospheric transport of SOCs over long distances has made them a global problem. For designing control strategies, it is important to determine the sources of these compounds to the atmosphere. Researchers have developed a variety of methods for identifying atmospheric sources of PAHs. For example, one way of differentiating PAH sources is by the presence of specific trace metals. Metallurgical processes and the steel industry tend to release a multitude of elements into the environment including Fe, Cr, Pb, Cd, Zn, and Ni,[23,96] the combustion of oil and other fossil fuels commonly releases vanadium and auto emissions (before the ban on leaded fuel) were linked to increased levels of lead.[23,96-100]

Source-Specific Compounds

Another technique for identifying sources is to analyze for one or two specific PAH compounds (Table 3). Retene is a PAH derived from volatilization of plant residues and the combustion of spruce[101] and coniferous trees[102] and can be used to pinpoint these natural combustion sources.[21,77] Perylene, when found in small quantities, has been linked to coke production[101] and other forms of pyrolysis, but when found at levels greater than 10% of total PAH concentration, often signifies formation of organic compounds under anoxic conditions.[77,103] Others have studied unsubstituted PAHs and oxy-PAHs as possible signs of pyrogenic sources.[102] Cretney (1985)[38] identified methylbenzofluoranthenes, methylbenzopyrenes, dibenzofluoranthenes, and cyclopentabenzo(ghi)perylenes as common elements in domestic soot while cyclopenta[cd]pyrene, benzo(ghi)perylene, and methylenebenzopyrenes were found in automobile emissions. Thiaarenes, the sulfur analogues of PAHs, are commonly found in fossil fuels,[64,105] coal-derived products,[64,104-106] crude oil,[64,104,105,107] shale oil[64,105,106] and

TABLE 3: Characteristic PAHs and Sources

Source	Characteristic PAHs	Reference(s)
Auto Emissions	BAP, BGH, COR, CPP, FLT, PYR,	15, 23, 69, 98, 100, 101
	cyclopenta[cd]pyrene,	38
	methylenebenzopyrenes	38
Diesel Emissions	BNT, S-PAHs	23, 101
Pyrogenic Sources	ANT, BAA, BAP, BBF, BJF, BKF,	85, 102, 104
	DBA, FLT, IND, PYR, oxy-PAHs	85, 102, 104
Incineration	ANT, FLT, PHEN, PYR	23
Coal Combustion	ANT, BAA, BKF, CHR, FLT, PHEN, PYR	23
Coke Production	ANT, BAP, BGH, PHEN,	23, 77
	PERY (if < 10 % Total PAH)	23, 77
Natural Gas Combustion	BAP, BGH, COR	101
Oil Combustion		
(Low Temperature)	FLT, FLU, PYR	23
(High Temperature)	BBF, IND	23
Domestic Soot	methylbenzofluoranthenes,	38
	methylbenzopyrenes,	38
	dibenzofluoranthenes,	38
	cyclopentabenzo(ghi)perylenes	38
Petrogenic Sources		
NAP, ANT, FLT,	Maximum greater than or equal to	85
PHEN, PYR	monomethylated derivative	85
Fossil Fuels	S-PAHs(e.g. DBT, naphtho[2,3-b]thiophene	64, 105
	phenanthro[3,2-b]thiophene	64, 105
Anthropogenic Sources		
low (0.03-0.4)	$\frac{ANT}{ANT + PHEN}$ $\frac{FLT}{FLT + PYR}$	85
	$\frac{IND}{IND + BGH}$	85
Natural Sources	Perylene (if > 10 % Total PAH)	77
Plant Residues	Retene	21, 27, 77, 85, 101

in low temperature pyrolytic emissions.[64] Some common thiaarenes which have been used for source determination include dibenzothiophene, naphtho[2,3-b]thiophene, phenanthro[3,2-b]thiophene and their alkylated derivatives. Although many of these specific PAHs are valuable tracers, they are often found in the environment at levels lower than many of the other compounds in the mixture, making their analysis complicated.

PAH Profiles/Ratios

It is sometimes difficult to distinguish PAH sources by specific compounds alone because different sources often have similar PAH profiles. One solution is to use ratios of specific PAHs. Most emission sources have different characteristic ratios and often these ratios are relative to those PAHs less prone to degradation (e.g. coronene, benzo(e)pyrene). For example, both gasoline and oil combustion produce benzo(ghi)perylene and benzo(a)pyrene at similar ratios to total PAH (~30% and ~10%, respectively). However, gasoline is usually about ten times greater in coronene (~30%) than oil combustion residues (~3%).[100] Some common PAH ratios used for source identification are given in Table 4.

The use of ratios has been expanded to compare the parent PAH to its alkylated derivatives. High temperature processes, such as pyrolysis and combustion, predominantly produce the thermodynamically stable parent PAHs,[13,29,85] while low temperature processes, such as fossil fuel formation (petrogenesis) and petroleum or oil seeps,[29] tend to show a larger number of thermodynamically unstable alkylated derivatives.[13,29,77,108] Some PAHs commonly used for parent-derivative ratios include phenanthrene, anthracene, pyrene, and chrysene.

Principal Components Analysis (PCA)

Often times, one is interested in comparing data sets from different sources or sites instead of comparing compounds within a simple data set. This can be done with the aid of statistical programs such as principal components analysis (PCA). A

Table 4: Characteristic Ratios for Some Specific Sources

	Tunnel/[†] Traffic (PAH/BEP)	Diesel[†] Emissions (PAH/BEP)	Gasoline[†] Emissions (PAH/BEP)	Residential[‡] Coal-Burning (PAH/BEP)	Coke Ovens[‡] Emissions (PAH/BEP)	Wood[¢] Combustion (PAH/BAP)
NAP	213	28	9.8	/	/	2.4
ACY	12(8.33)	9.9	0.33	/	/	12
ACE	3.6	11	0.10	/	/	0.3
FLU	8.7	11	0.59	/	/	1.1
PHEN	5.7	7.4	0.59	/	/	1.2
ANT	3.7	3.3	0.21	0.4	0.3	2.1
FLT	2.2	1.1	0.34	/	/	0.66
PYR	3.9	0.81	0.85	/	/	0.71
BAA	2.0	2.6	0.10	1.4	1.2	0.1
CHR	1.7	1.4	0.12	2.5	1.8	0.25
BBF	0.77	0.91	0.14	1.4	1.3	0.16
BJF	/	/	/	/	/	
BKF	0.79	0.76	0.11	/	/	0.22
BEP	1	1	1	1	1	1
BAP	1.1	1.9	1	0.6	1	1
PERY	/	/	/	0.08	0.3	/
IND	0.24	1.3	bd	0.6	0.6	bd
DBA	0.24	0.51	0.24	/	/	0.1
BGH	0.37	0.6	0.047	0.7	0.6	bd
Coronene	/	0.026	0.046	/	/	0.08

	Diesel Soot[ƒ] Particles	Gas[ƒ] Combustion	Wood[ƒ] Combustion
BGH/COR	2.5	1.5	2
BGH/IND	1.1	3.5	0.8
BKF/IND	0.5	0.4	0.6
CHR/BEP	1.6	2.5	2.4
BAA/BAP	1	0.5	1
BBF/COR	2.9	0.3	/

† Reference 17
‡ Reference 101
¢ Reference 109
ƒ Reference 110

multivariate comparison of data sets can be used to extract information, such as which compounds (variables) have the most impact on a sample and whether or not specific samples are related/correlated. One such multivariate approach, principal components analysis (PCA), has been used previously for statistical analysis of wind patterns and their relationship to pollutant transfer,[111,112] a variety of business (consumer preferences) and scientific applications (samples origins, correlations between specific compounds and biological dysfunction),[113] and more recently, to determine similarities between pollutant concentration at one site to known source profiles and concentrations at other sites.[13,23,85,114-116] There are several benefits to PCA and the use of pattern recognition to extrapolate correlations between samples and data sets.[113] First, PCA can be performed in two manners, supervised and unsupervised. Supervised PCA uses samples that are known to contain specified groupings and results in identification of features used to classify samples in these groupings. Unsupervised PCA analyzes seemingly unrelated data sets and exposes a systematic interrelationship (if any exists).[113] Another benefit of PCA is that variations due to different preprocessing techniques (mid-range normalization, log transformation, and variance and mean scaling) have been shown to produce only minor differences in the observed PCA projections.

SAMPLING AND ANALYSIS TECHNIQUES

The most common method for sampling both particulate and gaseous PAHs in air is with a high volume air sampler with a filter-sorbent sampling head (hi-vol). The particulate phase is collected first on a filter (e.g. glass, quartz fiber, or teflon)[117] then the vapor phase on a sorbent trap such as a polyurethane foam plug (PUF), organic resin (Tenax, XAD, Chromasorb, Bondapak)[118,119] or a combination of the two. This type of sampler provides an experimental estimate of the particle/gas distribution, but is biased by two artifacts: (1) a negative artifact due to volatilization of the compound from the particles on the filter, and (2) a positive artifact due to sorption of gaseous compounds to the particles on the filter or the filter itself. The latter can be approximated and thus accounted for with the use of a second filter. Sampling artifacts can be caused by changing variables during sample collection and include temperature, vapor concentration, particle concentration and particle properties (organic content, weight fraction of aerosol that consists of absorbing liquid film, surface area, and size).[120]

An alternative to the filter-sorbent hi-vol sampler is the diffusion denuder, which removes gaseous SOCs first in the denuder section (a series of parallel tubes coated with an adsorbent such as XAD resin)[121] followed by the particulate-bound species collected on a filter. The biggest drawback to denuder sampling is incomplete removal of vapors. Other air samplers which have been used to collect SOCs include the diffusion separator,[122] which relies on different mobilities of gases and particles for separation, and the low-pressure cascade impactor and centrifugal aerosol collector,[62,104,123-126] which collect only the particulate phase. Although the other methods of sampling overcome some of the problems encountered in the hi-vol sampler, all have problems and limitations, some of which are still under investigation. For this reason, as well as low cost, durability and ease of use, the hi-vol sampler is the most commonly used sampler for SOCs.[86]

Analysis techniques for PAHs include: (1) gas chromatography (GC) with one of the following detectors: mass spectrometer (MS),[6,8,77,87,127] flame ionization detector (FID),[8,28,128,129] electron capture detector (ECD),[16,30,130] or flame photometric detector (FPD)[104,105] and (2) high performance liquid chromatography (HPLC) in combination with one of the following methods of detection: ultraviolet/visible spectroscopy (UV/VIS),[23,124,131,132] fluorescence spectroscopy,[51,133-136] Shpol'skii luminescence spectroscopy (low temperature fluorescence),[67,137] or mass spectrometry (MS).[132,138] Other less common methods include nuclear magnetic resonance (NMR),[139] capillary electrophoresis (CE),[140,141] capillary zone electrophoresis (CZE),[141] phosphorescence[67] and photoluminescence.[67] GC coupled with MS in selected ion monitoring (SIM) mode allows for analysis of trace quantities of semivolatile materials with increased sensitivity and selectivity over other methods.[142]

CHAPTER THREE

STATEMENT OF PURPOSE

Atmospheric deposition has been estimated to yield inputs of polycyclic aromatic hydrocarbons (PAHs) ranging from 38 metric tons/yr for Lake Ontario to 163 metric tons/yr for Lake Superior.[1] Increased public awareness and advances in technology have prompted scientists to monitor not only contaminant levels in the air and their effects, but also to try to determine their sources.[143] Statistical programs can be used to determine the contribution of a given source to a given site (apportionment). The results of source determination and apportionment are used by government agencies when designing regulations to control and minimize pollutant releases and effects.

Previous studies have reported high PAH levels in the sediment and biota of the Mahoning River.[91,144,145] However, very little information is available on concentrations in air or water for the region. PAHs in the atmosphere can be locally derived or transported over a distance from other source centers. PAHs in the water column can come from three general sources: from atmospheric fluxes into the waters, direct input due to dumping, spills or run-off, or re-release from contaminated sediments. The purpose of this study was to obtain concentrations of PAHs in air and water in the Mahoning Valley and to determine possible sources and inputs. Three sites in the greater Mahoning Valley region were studied in an effort to determine if atmospheric transport was an important factor.

CHAPTER FOUR

MATERIALS

Solvents were pesticide grade (Fisher Scientific, Fairlawn, NJ). Other reagents include 100-mesh silicic acid (Mallinckrodt Chemical Works, St. Louis, MO), 80-200 mesh alumina, anhydrous sodium sulfate, (Fisher Scientific, Fairlawn, NJ) and sodium chloride (VWR Scientific, Westchester, PA). Analytical standards were purchased from Supelco, Inc. (Bellefonte, PA) or Ultra Scientific (North Kingstown, RI). Isotopically labeled standards were purchased from Cambridge Isotope Laboratories (Andover, MA). Standard Reference Material 1649 (Urban Dust/Organics), SRM 1649, was acquired from National Institute of Standards and Technology, NIST. Helium and nitrogen for chromatographic instruments were ultra pure carrier grade. Nitrogen for sample concentration was dry grade. Type GMF grade filters (47 mm) were used for water filtration (Whatman, Maidstone, England) and type A/E glass fiber filters were used for air filtration (Gelman Science, Ann Arbor, MI). Polyurethane foam plugs were purchased from Graseby Anderson (Cleves, OH).

Air and water filters were precleaned by baking at 450°C for ≥ 20 h in a muffle furnace. After baking, filters were wrapped in clean aluminum foil and sealed in plastic bags. Polyurethane foam plugs (PUF) were cleaned by soxhlet extraction for a minimum of 18 h in acetone, followed by 18 h in petroleum ether (PE). After cleaning, PUF were dried with low heat in a dry seal dessicator. The clean dry PUF plugs were stored in glass jars with teflon-lined lids. Silicic acid (SA) was precleaned by baking at 140°C for a minimum of 24 h. Before use, SA was deactivated with 1.7% water. Adsorption alumina was precleaned by baking over night at 450°C. Before use, alumina was deactivated with 6% water and stored in a glass jar with a teflon-lined lid. Anhydrous sodium sulfate was precleaned by baking overnight at 450°C and stored in a glass jar with a teflon-lined lid. Sodium chloride crystals were precleaned by rinsing with PE, followed by dichloromethane (DCM), and dried at 140°C. Boiling chips were precleaned by soxhlet extraction with PE in a cellulose thimble over-night. The clean boiling chips were dried at 140°C and stored in a glass jar with a teflon-lined lid.

CHAPTER FIVE

EXPERIMENTAL

SAMPLE COLLECTION

Water samples were collected in clean 4-L solvent jugs from three locations (Figure 1): Meander Reservoir, Lake Newport, and Brittain Lake. Water temperature was noted and samples were stored at 4°C until extraction. Duplicate samples were taken two different times at each site. Air samples were taken adjacent to Meander Reservoir, on Youngstown State University campus (~ 3 miles from Lake Newport), and about one mile from Brittain Lake. Sampling conditions are given in Tables 5-7.

Air samples were taken using two hi-vol systems. Concurrent air samples were taken in Youngstown, OH (Y1 air) and at Meander Reservoir (M air) from July 22, 1996 through July 26, 1996; and in Youngstown, OH (Y2 air) and New Wilmington, PA (P air) from July 29, 1996 through August 2, 1996.

A GPS-1 PUF Sampling System (Graseby Anderson, Cleves, OH) was placed on the roof of the Youngstown State University stadium at a height of 160 feet and samples were collected for 12 h intervals. The sampling train consisted of two 102 mm glass fiber filters (GFFs) followed by two 6.5 cm x 5 cm PUF plugs. Filters and PUFs were changed at the site and transported to and from the lab on ice. Filters were placed individually in clean aluminum foil and stored in plastic bags. Front and back PUF were stored separately in glass jars with teflon-lined lids. PUF and filters were stored in the freezer at approximately -10°C until extraction.

The second air sampler, consisting of a Rotron DR-313 brushless pump (Rotron Corp., Woodstock, NY) connected to a stainless steel sampling head, was used at the Meander and Brittain Lake sites, where air samples were collected approximately two feet above the ground for 24 h intervals. For this sampler, two 20.3 cm x 25.4 cm GFFs

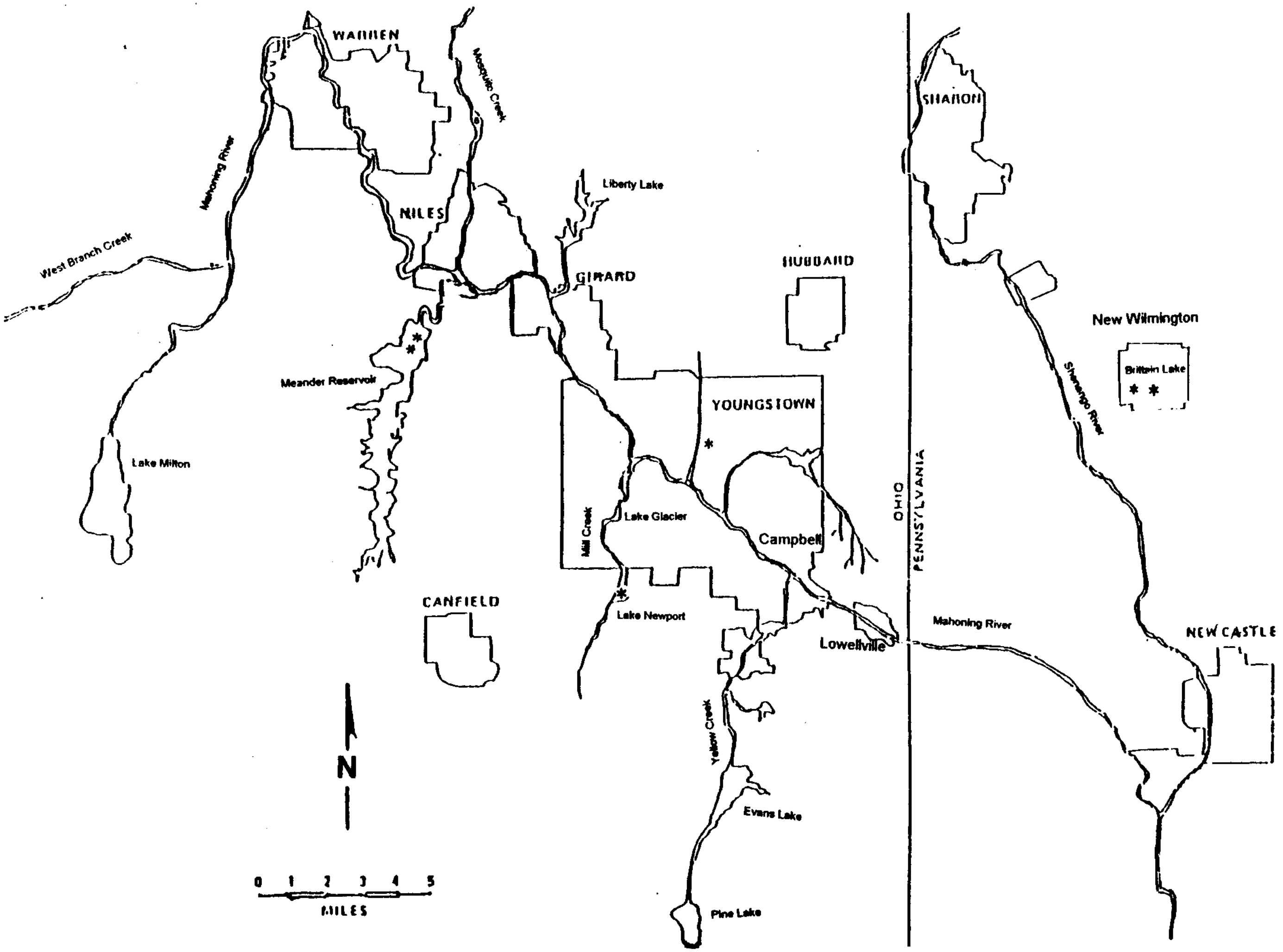


Figure 1. Map of the Greater Mahoning Valley
* Denotes sampling sites.

Table 5: Air Sampling Conditions for Week One

Date	Sample Name	Time Sampled (hr)	Day/ Night	Air Volume (m^3)	Avg. Temp. (^{o}C)	Precipitation (in. rain)	Barom. Pr. (mm Hg)	% Hum	TPC (µg carbon)
7/22/96	YA11	11.77	D	83.17	21.3	0.03	728.2	76.8	NA
7/22-7/23	YA12	12.60	N	149.45	21.0				NA
7/23/96	YA13	12.28	D	125.69	22.8	0.01	728.0	81.6	29.1
7/23-7/24	YA14	11.43	N	115.09	25.0				NA
7/24/96	YA15	12.00	D	123.18	25.5	trace	729.0	72.6	NA
7/24-7/25	YA16	11.30	N	110.34	24.8				41.2
7/25/96	YA17	11.10	D	109.7	23.8	0.1	728.7	85.3	NA
7/25-7/26	YA18	12.50	N	124.08	23.5				NA
7/26/96	YA19	13.30	D	130.21	23.8	0.23	731.3	61.8	NA
7/22-7/23	MA11	23.62	D/N	536.87	27.0	0.03	728.2	76.8	16.9
7/23-7/24	MA12	23.32	D/N	563.1	26.5	0.01	728.0	81.6	< 2.0
7/24-7/25	MA13	23.42	D/N	556.73	26.0	trace	729.0	72.6	NA
7/25-7/26	MA14	23.33	D/N	546	25.5	0.1/0.23	728.7	85.3	12.6

NA: Filter not analyzed for TPC

Table 6: Air Sampling Conditions for Week Two

Date	Sample Name	Time Sampled (hr)	Day/ Night	Air Volume (m^3)	Avg. Temp. (^oC)	Precipitation (in. rain)	Barom. Pr. (mm Hg)	% Hum	TPC (µg carbon)
7/29/96	YA21	11.52	D	128.77	24.0	0.01	732.3	78.5	NA
7/29-7/30	YA22	12.33	N	130.09	25.5				NA
7/30/96	YA23	11.03	D	109.1	24.0	0.3	729.7	88.0	NA
7/30-7/31	YA24	12.53	N	118.15	22.5				NA
7/31/96	YA25	10.90	D	106.93	22.0	0.01	729.5	76.9	NA
7/31-8/1	YA26	13.00	N	122.71	21.5				NA
8/1/96	YA27	10.82	D	103.46	23.5	0.1	729.2	83.3	20.0
8/1-8/2	YA28	12.95	N	128.67	23.5				56.3
8/2/96	YA29	12.33	D	115.02	22.0	0	730.8	82.3	33.9
7/29-7/30	PA11	24.30	D/N	450.16	24	trace	732.3	78.5	11.5
7/30-7/31	PA12	23.28	D/N	562.29	23.0	0.36	729.7	88.0	NA
7/31-8/1	PA13	23.87	D/N	639.03	25.0	0.01	729.5	76.9	13.5
8/1-8/2	PA14	23.93	D/N	586.97	26.3	0.09	729.2	83.3	16.1

NA: Filter not analyzed for TPC

Table 7: Water Sampling Conditions

Date	Sample Name	Avg. Temp. (°C)	Water Volume (L)	pH	No. water filters used
7/22/96	YW11A *	28.0	3.86	8.87	0
	YW11B *	28.0	3.65	8.93	0
7/23/96	YW12	25.5	2.05	8.56	1
7/24/96	YW13	26.0	3.73	8.92	3
7/25/96	YW14	24.0	3.46	8.78	3
7/26/96	YW15A *	24.0	3.41	8.74	2
	YW15B *	24.0	3.20	8.75	2
7/22/96	MW11A *	26.0	3.50	8.33	1
	MW11B *	26.0	3.65	8.39	1
7/23/96	MW12	25.5	3.78	8.18	1
7/24/96	MW13	26.0	3.54	8.17	1
7/25/26	MW14	26.0	3.60	8.33	1
7/26/96	MW15A *	25.0	3.63	8.54	1
	MW15B *	25.0	3.53	8.54	1
7/29/96	YW21	24.0	2.73	8.79	2
7/30/96	YW22	25.0	3.68	8.80	3
7/31/96	YW23	24.0	3.81	8.64	2
8/1/96	YW24	24.0	3.55	8.55	3
8/2/96	YW25	23.0	3.50	8.37	3
7/29/96	PW11A *	28.0	3.68	9.20	1
	PW11B *	28.0	3.45	9.16	2
7/30/96	PW12	26.0	3.46	8.84	1
7/31/96	PW13	27.0	3.58	9.00	1
8/1/96	PW14	28.0	3.68	8.96	1
8/2/96	PW15A *	29.0	3.74	9.13	1
	PW15B *	29.0	3.75	8.94	1

* A, B signify duplicate samples

and two 8 cm x 7.5 cm PUF were used for collection. PUF plugs and filters were changed on site and transported and stored as above.

For most samples, the front PUF plug was spiked with 10 µL of four deuterated PAHs (approximately 100 ng each of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}) before sampling. The air temperature was noted at every sample change, along with the weather conditions and magnehelic reading.

EXTRACTION AND CLEAN-UP

PUF plugs were soxhlet extracted in PE for a minimum of 18 h. For filters, a 1.6 cm diameter circle was taken from the center for TPC analysis and the remaining portion cut into strips and refluxed in DCM for a minimum of 18 h. Before extraction, 10 µL of four deuterated PAHs (approximately 100 ng each of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}) were added to the filters.

The pH of water samples was noted and samples transferred to a stainless steel canister (Coca-Cola Bottling Company of Northern Ohio, Youngstown, OH). 10 µL of the deuterated PAH mix was added to most water samples before samples were pushed with nitrogen pressure through a 47 mm GMF water filter to remove particulate matter. In some cases, more than one filter was needed due to high particulate levels. The water filters were individually wrapped in clean aluminum foil and stored in a plastic bag in the freezer (-10°C). Approximately 400 mL DCM was added to the filtered samples and the samples extracted by rolling on a jar mill (U.S. Stoneware Jar Mill, East Palestine, OH) for 6-12 h. The sample was allowed to settle and the water layer poured off. The organic layer (which still contained a small portion of water) was transferred to a 1-L separatory funnel, the mixture shook and the DCM layer drained off. The sample container was rinsed with 50-100 mL DCM, and this portion was added to the separatory funnel to re-extract the remaining water. The entire rinse and extraction process was repeated two more times with an additional 50-100 mL DCM, and all DCM fractions combined.

Water filters were refluxed in acetone for a minimum of 2.5 h. The acetone fraction was removed and stored in the freezer. The filter was refluxed for another 18 h with DCM. The DCM portion was combined with the acetone extract, along with approximately 500 mL deionized water and 50 mL of a saturated sodium chloride solution (to prevent emulsification). The mixture was placed in a 1-L separatory funnel, mixed and the DCM layer drawn off. The remaining acetone/water mixture was extracted two more times with 50 mL portions of DCM. The DCM portions were combined and rinsed with 50-100 mL of clean deionized water.

All extracts were reduced to 5-10 mL and solvent-exchanged into hexane or iso-octane by rotary evaporation. All samples were reduced to a final volume of 1 mL with a gentle stream of nitrogen. The samples were cleaned up and other organics removed using a silicic acid/alumina column similar to that of Keller & Bidleman (1984).[146] A glass column was dry-packed with three grams of SA (1.7 % water added), overlaid with two grams adsorption alumina (6% water added), followed by 1-2 cm of anhydrous sodium sulfate. The column was cleaned with 30 mL DCM followed by 30 mL PE. The sample was quantitatively transferred to the column and other organic compounds removed by elution with 30 mL PE. The second fraction, 30 mL DCM, contained the PAHs.

Both fractions were solvent-exchanged into iso-octane, reduced to 1.0 mL with a gentle stream of nitrogen and placed in glass vials with teflon-lined caps. Prior to GC analysis, 10 µL perylene-d_{12} (100.038 ng) was added to each 1.0 mL sample as an internal standard.

Blanks and Spikes

Blanks for PUF and filters (air and water) consisted of clean PUF and filters extracted and cleaned-up as for samples. Blank water samples consisted of pure de-ionized water worked up as for samples. All blank samples contained 10 µL of the deuterated PAH mix.

Spike recoveries for all media were obtained by adding a mix of Supelpreme PAHs (approximately 100 ng each of the 16 priority pollutants) to each of the clean media (PUFs, air filters, and deionized water) in addition to 10 μL of the deuterated PAH mix. Spiked media were extracted and cleaned as for samples.

Portions of NIST SRM 1649 Urban dust/organics (~ 0.5 g) was extracted for 24 h in DCM in a pre-cleaned thimble. The extracts were then cleaned-up as for samples.

ANALYSIS

Quantitative analysis was done with a Finnigan MAT GCQ-GC/MS, using a DB5 column (30 m, 0.25 mm id, 0.25 μm film thickness, J&W Scientific, Folsom, CA). Samples were injected splitless (split open after 1.00 minute) at an initial temperature of 90°C. After a 1.00 min hold, the oven was ramped at 6°C min^{-1} to 245°C, held for 0.50 min, ramped again at 3°C min^{-1} to 280°C and held for 6.00 min. Injector, transfer line, and detector temperature were 280°C, 280°C, and 175°C, respectively. The carrier gas was helium at 40 cm s^{-1}. Samples were quantified versus external standards containing each of the compounds analyzed for, including surrogate compounds, which spanned a concentration range of 0.050 to 1.000 ng/μL. Perylene-d_{12} was used as an internal standard at a concentration of 0.100 ng/μL. Chromatographic data were collected and processed using Finnigan MAT GCQ Software (version 2.0). The chromatogram for the most concentrated standard is shown in Figure 2. Figures 3-5 show calibration plots for several PAHs (fluorene, fluoranthene, and indeno[1,2,3-cd]pyrene). Calibration plots for the remaining compounds are given in Figures A-1 to A-22.

Retention times and elution order for compounds were determined by analysis of individual standards. Ions monitored for quantification and retention times for the compounds are listed in order of elution in Table 8. Figure A-23 shows the ion chromatograms for each of the compounds in this study.

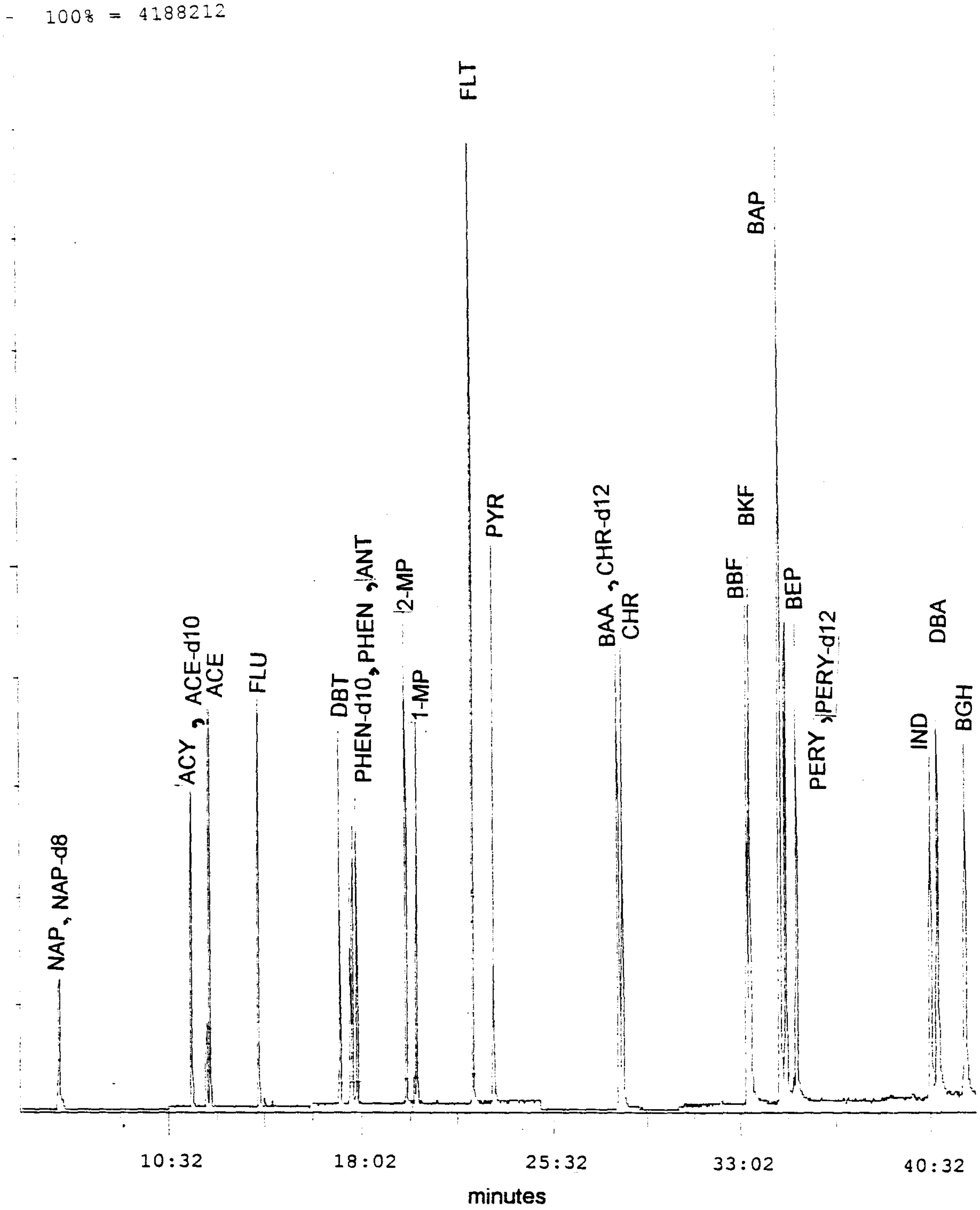


Figure 2. Chromatogram of PAH standard containing 21 PAHs quantified in this study.

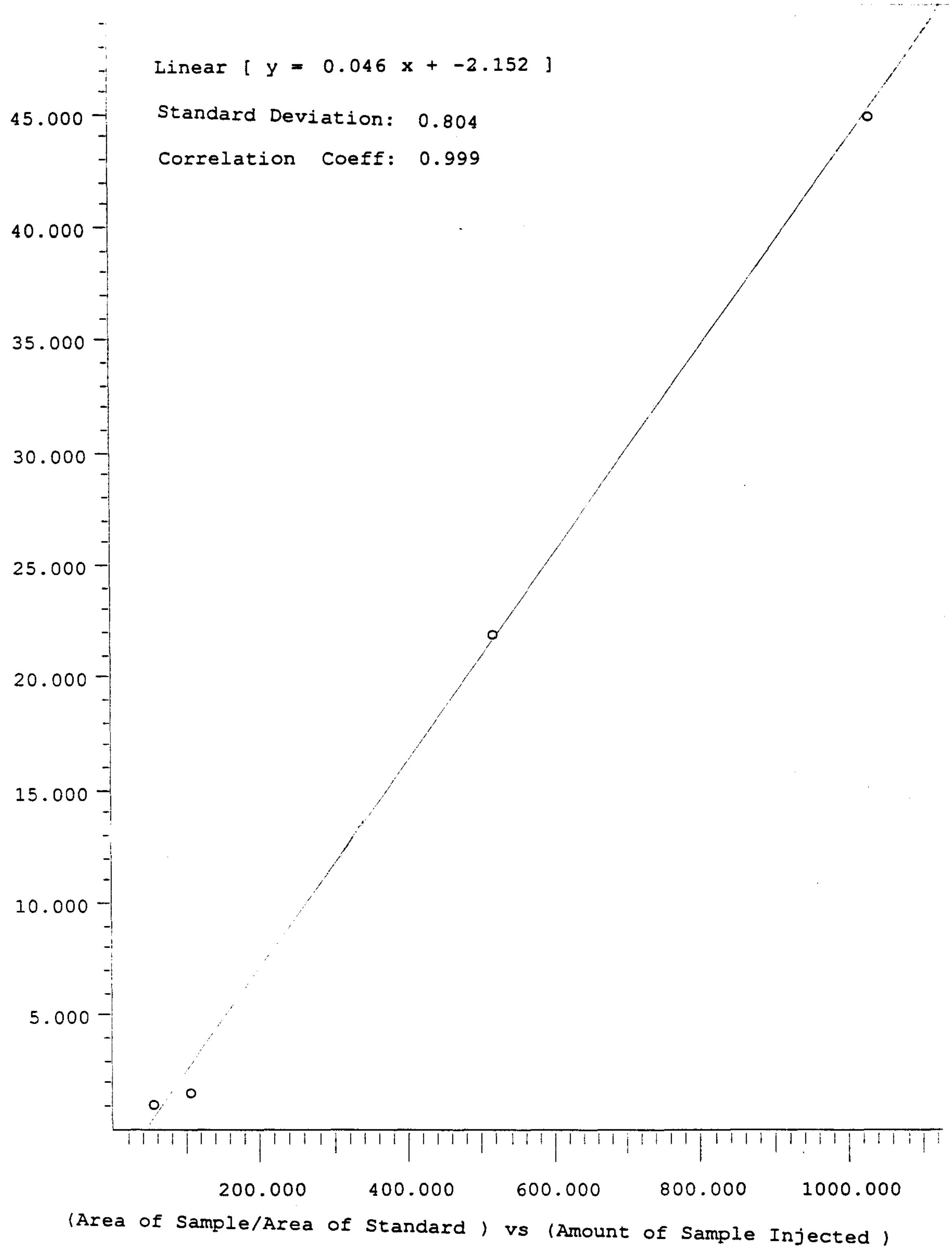


Figure 3. Standard Calibration Plot of fluorene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

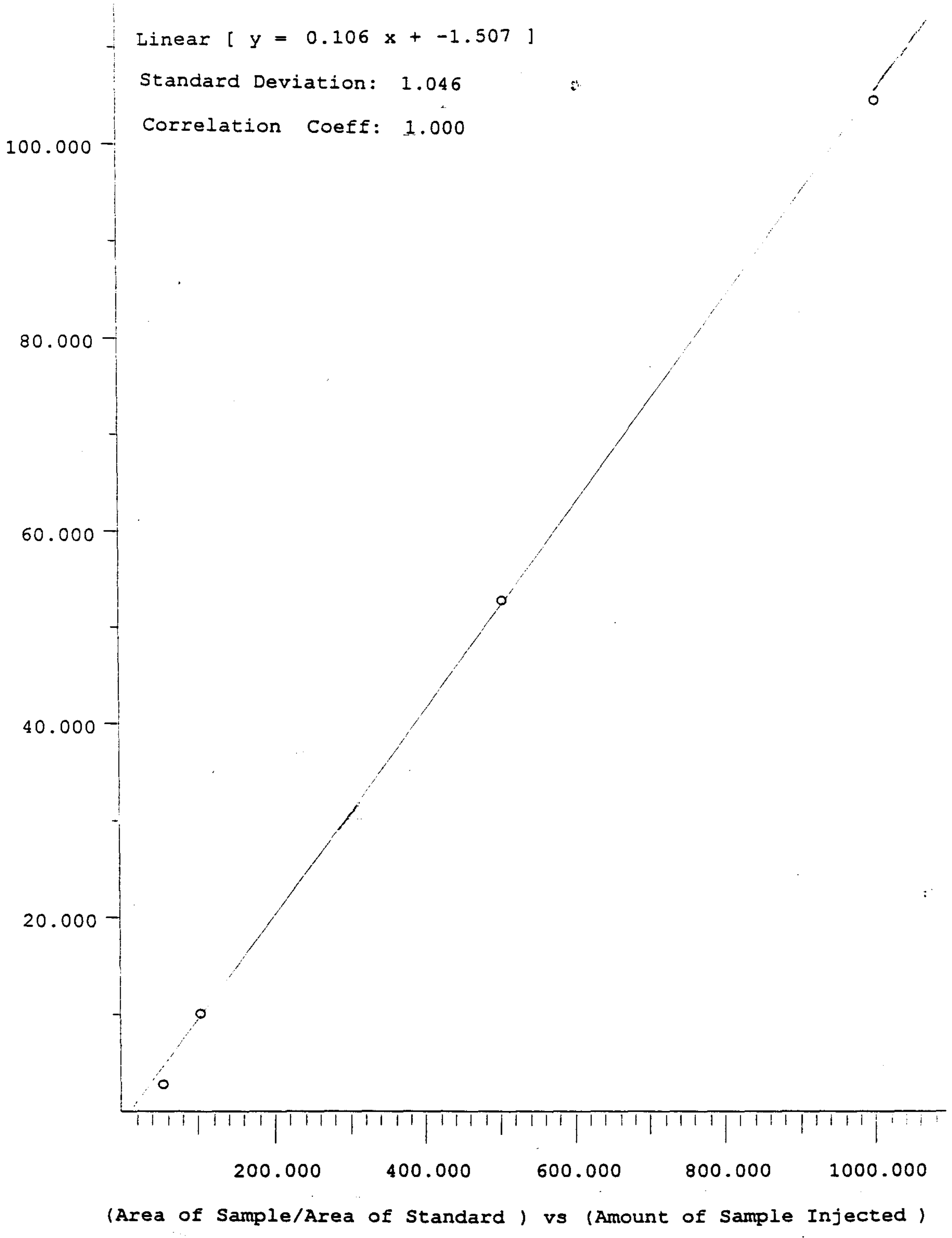


Figure 4. Standard Calibration Plot of fluoranthene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

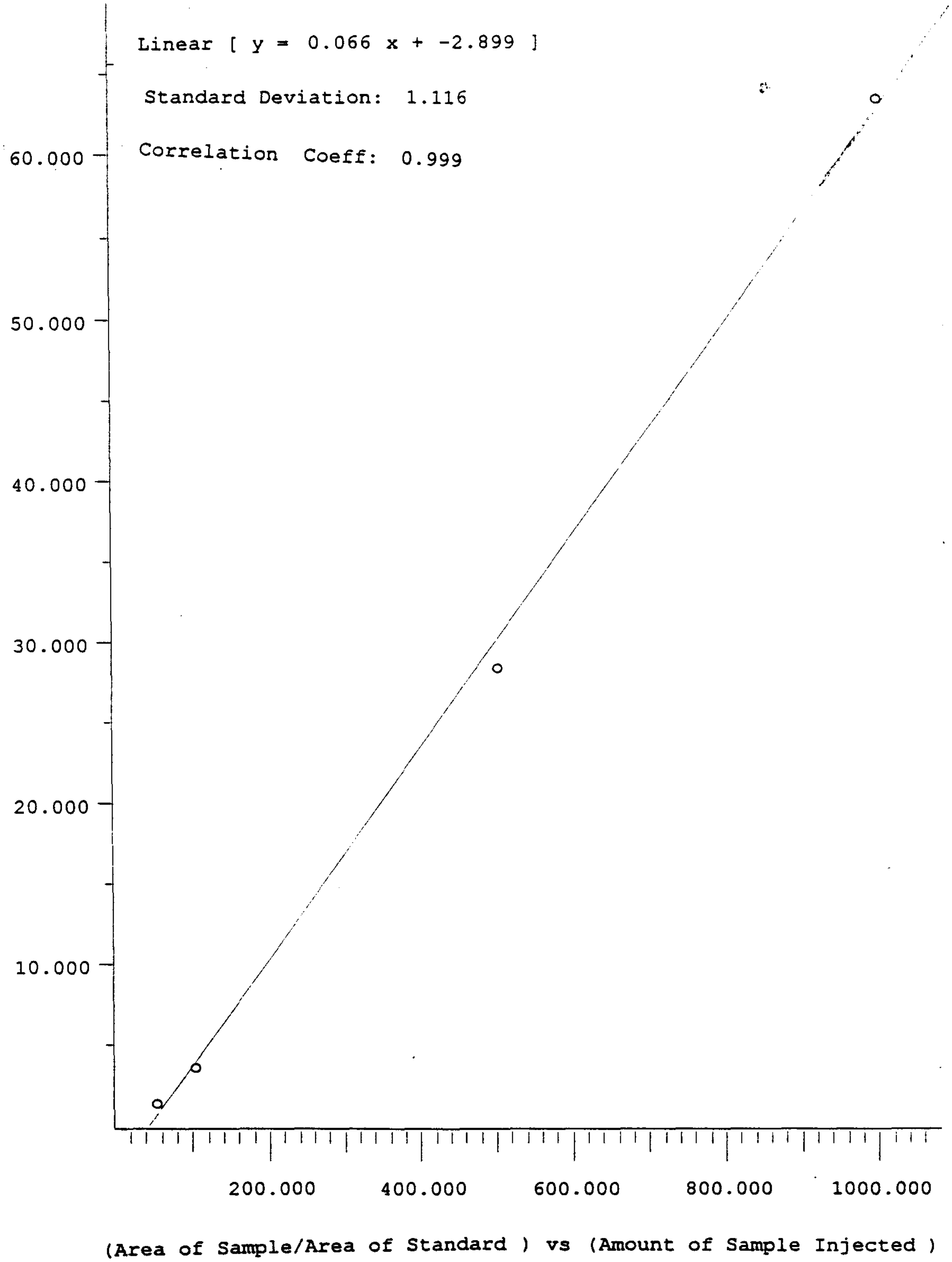


Figure 5. Standard Calibration Plot of indeno[1,2,3-cd]pyrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

Table 8: Retention Times (min.) and SIM Ions

	Type	Retention Time (min)	Quantifying Ion	Qualifying Ion(s)
NAP-d8	**S**	6:15	**136**	
NAP	A	6:19	**128**	126, 127
ACY	A	11:31	**152**	150
ACE-d10	**S**	12:05	**164**	
ACE	A	12:13	**152**	150, 151, 154
FLU	A	14:08	**165**	164, 166
DBT	A	17:17	**184**	185
PHEN-d10	**S**	17:41	**188**	
PHEN	A	17:47	**178**	176
ANT	A	17:57	**178**	176
2-MP	A	19:52	**192**	191
1-MP	A	20:17	**192**	191
FLT	A	22:29	**202**	200
PYR	A	23:18	**202**	200
BAA	A	28:15	**228**	226
CHR-d12	**S**	28:19	**240**	
CHR	A	28:25	**228**	226
BBF	A	33:25	**252**	250, 251
BKF	A	33:34	**252**	250, 251
BEP	A	34:44	**252**	250, 251
BAP	A	34:58	**252**	250, 251
PERY-d12	**IS**	35:17	**264**	
PERY	A	35:24	**252**	250, 251
IND	A	40:44	**276**	138, 274
DBA	A	41:02	**278**	274, 276, 277
BGH	A	42:06	**276**	138, 274

S = Surrogate compound
A = Analyte
IS = Internal Standard

The 1.6 cm circles cut from air filters were sent for Total Particulate Carbon (TPC) analysis to Desert Analytics Laboratories in Tucson, AZ. In addition, three circles (1.6 cm) cut from blank air filters were sent to the lab for blanks and Standard Reference Material 1649 (Urban Dust/Organics, from National Institute of Standards and Technology, NIST) for a standard. Results of TPC analysis are given in Tables 5 and 6.

Principal Components Analysis (PCA) was performed on a 286 IBM personal computer AT, equipped with DOS (version 3.20, 1986) and an 80(2)87 math coprocessor, using Einsight Pattern Recognition Software (version 2.0, 1987; Infometrix, Inc., Seattle, Washington, 98121).

CHAPTER SIX

RESULTS

QUALITY CONTROL

Tables 9 and 10 give the limit of detection (LOD = mean blank + 3 x SD), mean blank values (+/- standard deviation), and spike recoveries for the different media. For each of the media, a more comprehensive listing of blank values (Tables A-1 to A-6, ng) and spike recoveries (Tables A-7 to A-9, ng detected/ng added in spike x 100 = %) are given in the Appendix.

Blanks

In general, all blank media tended to have higher blank values for the lower molecular weight compounds (naphthalene to pyrene). Both size PUF yielded low blank values for most of the compounds analyzed (Table 9, Tables A-1 and A-2). The highest values found in the small and large PUF blanks were for naphthalene and phenanthrene. Phenanthrene has been reported as having high blank values in previous studies.[6,147,148] Figure 6 shows a chromatogram for a typical PUF blank.

Blank air filters also had low values for most compounds (Table 9, Tables A-3 and A-4). Pyrene showed the highest values in small and large filter blanks while large filters also showed a high blank value for benzo(a)anthracene. Figure 7 shows a chromatogram for a typical air filter blank. Fellin et al. (1996)[6] also reported high blank values for pyrene on filters.

Water blanks (Figure 8) for the dissolved fraction yielded low values for most compounds (Table 10, Table A-5). Compounds with higher values included naphthalene, pyrene, phenanthrene and chrysene. Water filter blanks (Figure 9, Table A-6) were similar to the dissolved fraction blanks, yielding low values for most compounds except pyrene, phenanthrene and naphthalene. All samples were blank corrected with the values from Tables 9 and 10 as described later.

Table 9: Quality Control Information for Air Samples

		YA PUF (small)					MA/PA PUF (large)		
		(n = 9)		(n = 5)			(n = 9)		(n = 5)
PAH	LOD (ng)	Mean Blank (ng)	(+/-) S.D	Recovery (%)		LOD (ng)	Mean Blank (ng)	(+/-) S.D	Recovery (%)
NAP-d8	2.29	0.24	0.68	19.97		0.75	0.08	0.23	27.28
NAP	262.53	67.91	64.87	9.03		1062.06	164.50	299.19	64.30
ACY	1.26	0.13	0.38	35.81		8.98	1.13	2.62	52.81
ACE-d10	200.22	43.97	52.08	bd		256.46	53.00	67.82	bd
ACE	55.87	15.13	13.58	35.84		118.58	27.71	30.29	103.82
FLU	60.57	16.57	14.67	45.31		126.89	27.59	33.10	121.36
DBT	10.25	1.25	3.00	NA		13.10	3.15	3.32	NA
PHEN-d10	0.00	0.00	0.00	57.09		1.04	0.10	0.31	74.81
PHEN	151.25	35.15	38.70	46.63		200.15	63.81	45.45	137.35
ANT	9.42	2.41	2.34	58.90		8.55	3.35	1.73	78.10
2-MP	32.61	7.12	8.50	NA		46.42	17.67	9.58	NA
1-MP	20.15	4.03	5.37	NA		20.30	6.45	4.62	NA
FLT	1.95	0.72	0.41	32.45		28.75	7.80	6.98	32.29
PYR	18.52	8.31	3.40	83.46		53.82	14.81	13.00	56.40
BAA	1.76	0.23	0.51	79.04		4.50	0.86	1.21	96.07
CHR-d12	1.28	0.15	0.38	134.23		17.02	2.10	4.97	157.11
CHR	3.23	0.37	0.96	71.61		2.63	0.56	0.69	88.72
BBF	11.58	1.67	3.30	47.33		15.63	2.89	4.25	34.18
BKF	0.66	0.10	0.19	66.66		1.87	0.30	0.52	76.11
BEP	2.44	0.33	0.70	NA		0.88	0.26	0.21	NA
BAP	11.55	2.56	3.00	55.22		3.41	1.26	0.72	79.05
PERY	3.29	0.82	0.83	NA		5.32	2.36	0.99	NA
IND	2.38	0.40	0.66	65.89		8.92	1.28	2.55	89.49
DBA	8.96	1.69	2.42	74.61		16.37	2.61	4.59	94.03
BGH	0.13	0.01	0.04	66.60		10.10	1.12	2.99	81.57

LOD = Limit of Detection; bd = below LOD; S.D. = Standard Deviation; n = Number of Samples; NA = Not Analyzed

Table 9: Quality Control Information for Air Samples (cont.)

		YA Filter (small)					MA/PA Filter (large)		
		(n = 5)		(n = 4)			(n = 3)		(n = 5)
PAH	LOD (ng)	Mean Blank (ng)	(+/-) S.D	Recovery (%)		LOD (ng)	Mean Blank (ng)	(+/-) S.D	Recovery (%)
NAP-d8	0.46	0.07	0.13	21.14		0.07	0.07	5.94	8.11
NAP	16.05	5.65	3.47	32.20		5.65	11.60	2.56	11.41
ACY	0.00	0.00	0.00	34.37		0.00	0.58	0.63	18.58
ACE-d10	10.25	2.40	2.61	32.39		2.40	2.40	18.58	16.66
ACE	8.03	1.84	2.06	35.51		1.84	1.76	1.53	18.54
FLU	3.09	0.59	0.83	45.16		0.59	2.60	4.51	26.19
DBT	0.79	0.13	0.22	NA		0.13	0.30	0.52	NA
PHEN-d10	0.00	0.00	0.00	62.98		0.00	0.00	14.42	45.27
PHEN	8.09	2.85	1.75	74.07		2.85	11.58	8.98	32.76
ANT	2.85	0.96	0.63	45.30		0.96	4.72	8.17	37.79
2-MP	6.92	2.04	1.63	NA		2.04	5.47	1.43	NA
1-MP	9.40	1.80	2.53	NA		1.80	5.35	5.69	NA
FLT	5.64	1.53	1.37	42.64		1.53	6.02	10.42	24.82
PYR	108.57	23.71	28.29	68.44		23.71	27.08	34.21	51.34
BAA	3.77	0.79	0.99	114.22		0.79	20.66	18.74	70.97
CHR-d12	7.57	0.98	2.20	186.59		0.98	0.98	39.46	143.43
CHR	2.62	0.54	0.69	96.33		0.54	9.35	14.20	81.56
BBF	0.50	0.10	0.14	103.31		0.10	0.21	0.36	64.65
BKF	0.62	0.09	0.18	90.77		0.09	1.54	2.44	68.78
BEP	26.47	3.73	7.58	NA		3.73	0.00	0.00	NA
BAP	12.61	2.38	3.41	89.84		2.38	0.84	1.09	64.84
PERY	6.05	1.25	1.60	NA		1.25	1.80	1.30	NA
IND	1.30	0.17	0.38	104.51		0.17	0.00	0.00	92.71
DBA	0.49	0.06	0.14	112.00		0.06	0.00	0.00	94.56
BGH	1.24	0.16	0.36	131.15		0.16	0.00	0.00	83.11

LOD = Limit of Detection; bd = below LOD; S.D. = Standard Deviation; n = Number of Samples; NA = Not Analyzed

Table 10: Quality Control Information for Water

		Water					**Water Filter**				
		(n=5)		(n=5)			(n=5)		(n=5)		WATER
PAH	LOD (ng)	Mean Blank (ng)	(+/-) S.D.	Recovery (%)		LOD (ng)	Mean Blank (ng)	(+/-) S.D.	Recovery (%)		TOTAL %
NAP-d8	NA	0.00	30.71	31.55		NA	0.00	0.48	0.00		31.55
NAP	159.64	69.89	29.92	bd		18.89	10.12	2.92	4.52		2.19
ACY	6.07	1.19	1.63	31.19		1.76	0.40	0.45	0.19		31.38
ACE-d10	NA	0.00	34.68	32.05		NA	0.00	1.83	0.10		32.14
ACE	14.15	7.16	2.33	28.89		7.08	2.32	1.59	0.09		28.98
FLU	22.25	10.14	4.04	27.94		5.28	2.55	0.91	bd		27.85
DBT	4.23	1.45	0.93	NA		1.53	0.95	0.19	NA		NA
PHEN-d10	NA	0.00	39.26	49.87		NA	0.00	0.00	0.00		49.87
PHEN	58.54	20.96	12.53	53.60		34.09	16.19	5.97	bd		49.59
ANT	4.17	1.43	0.91	43.20		3.03	1.32	0.57	bd		43.07
2-MP	26.85	7.14	6.57	NA		11.75	4.17	2.53	NA		NA
1-MP	9.49	5.67	1.27	NA		4.98	2.20	0.93	NA		NA
FLT	6.22	3.09	1.04	29.70		15.26	8.40	2.29	bd		27.76
PYR	63.62	23.05	13.52	69.08		66.67	25.99	13.56	bd		63.02
BAA	59.67	20.01	13.22	60.90		2.49	0.91	0.53	4.47		65.36
CHR-d12	NA	0.00	66.85	177.17		NA	0.00	0.94	2.18		179.34
CHR	77.95	20.86	19.03	51.76		1.60	0.77	0.28	2.30		54.06
BBF	1.21	0.41	0.27	50.97		1.14	0.15	0.33	7.85		58.82
BKF	0.73	0.24	0.16	44.66		0.34	0.05	0.10	4.68		49.34
BEP	0.60	0.20	0.13	NA		0.71	0.15	0.19	NA		NA
BAP	1.75	0.87	0.29	40.62		3.14	1.17	0.66	2.50		43.12
PERY	3.75	1.09	0.89	NA		3.82	1.18	0.88	NA		NA
IND	0.91	0.27	0.22	42.71		3.06	0.76	0.77	23.47		66.18
DBA	1.15	0.20	0.32	41.03		1.52	0.28	0.41	16.50		57.53
BGH	1.97	0.43	0.51	45.93		2.40	0.44	0.65	16.06		61.99

LOD = Limit of Detection; bd = below LOD; S.D. = Standard Deviation; n = Number of Samples; NA = Not Analyzed

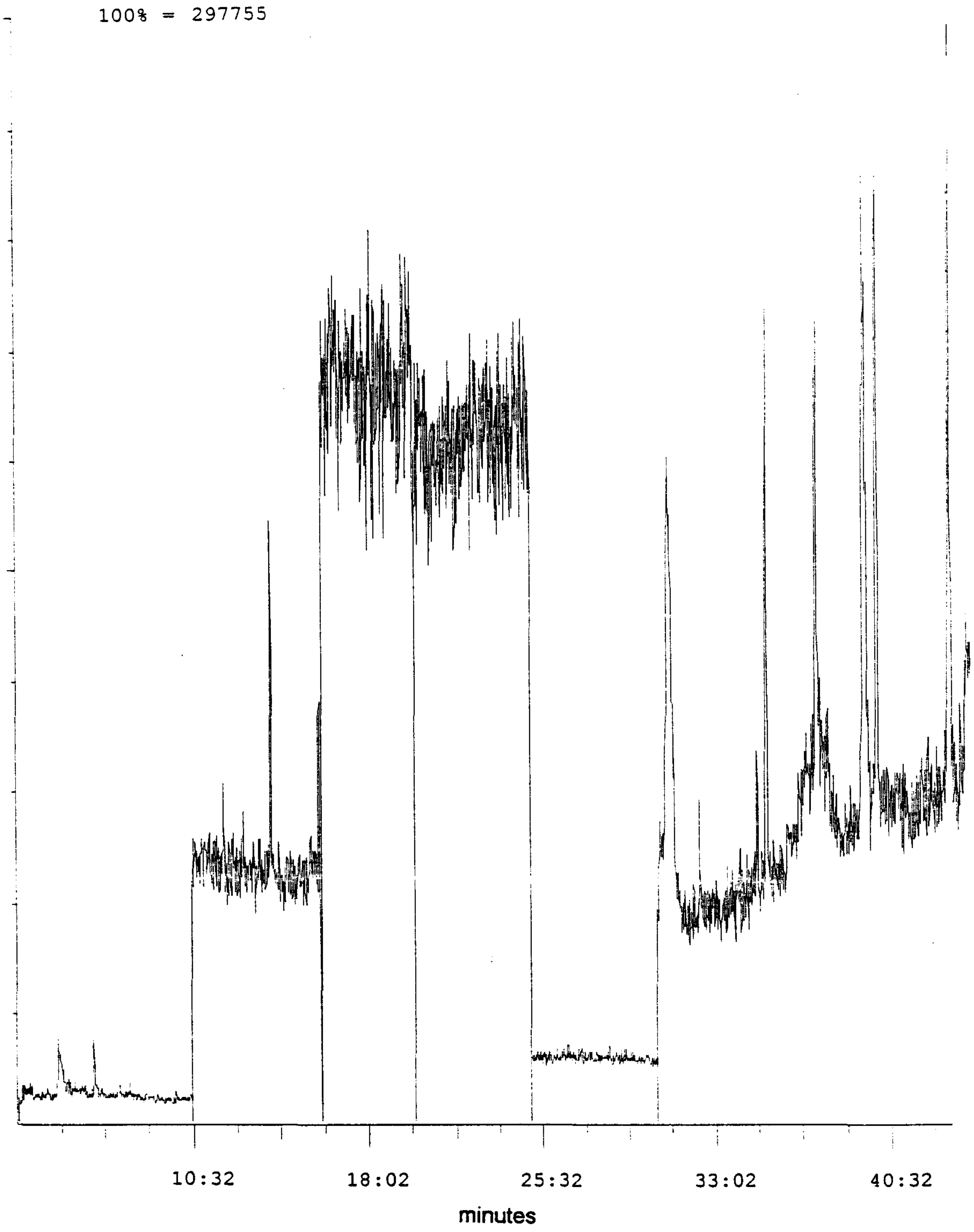


Figure 6. Example Chromatogram of PUF blank.

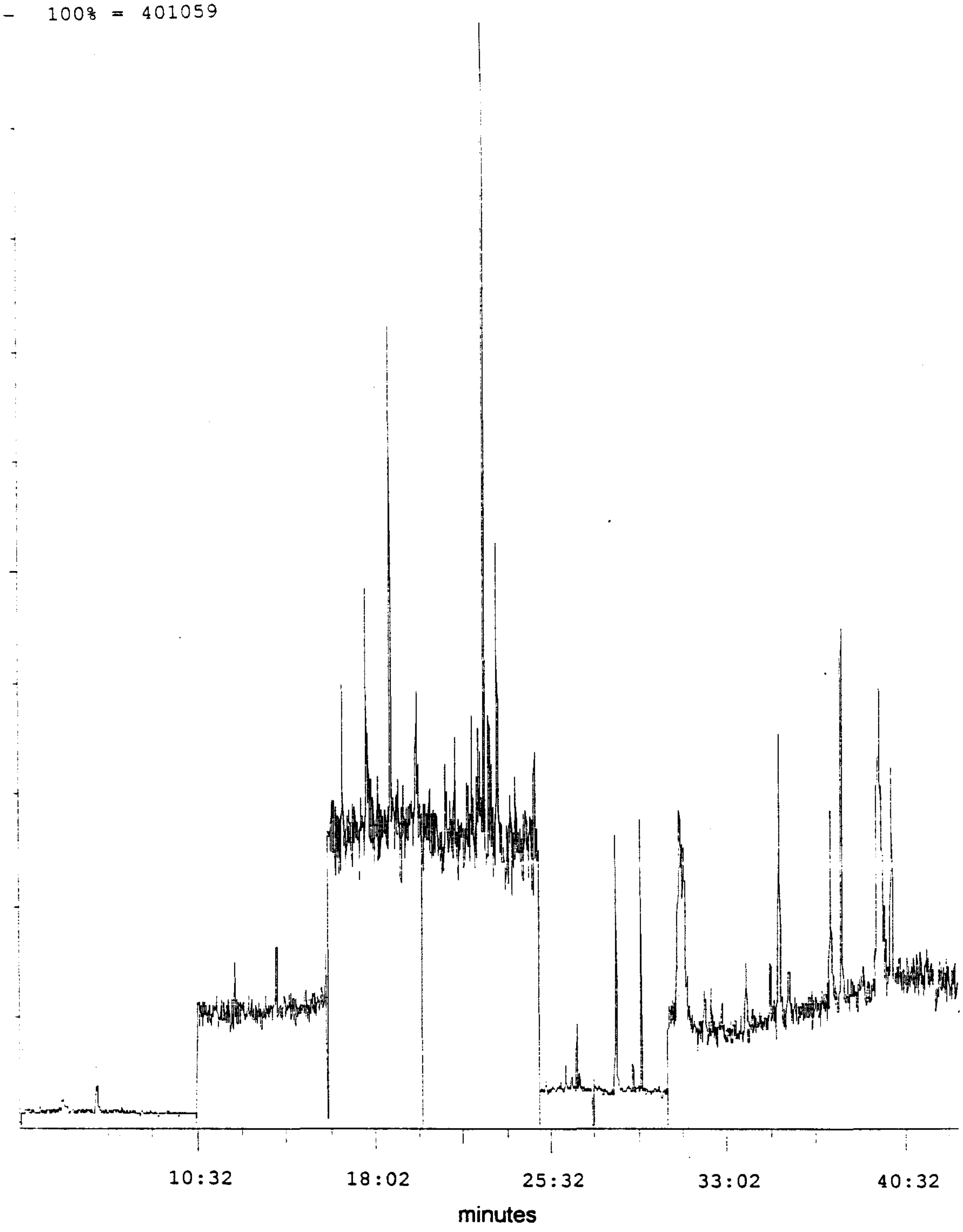


Figure 7. Example Chromatogram of air filter blank.

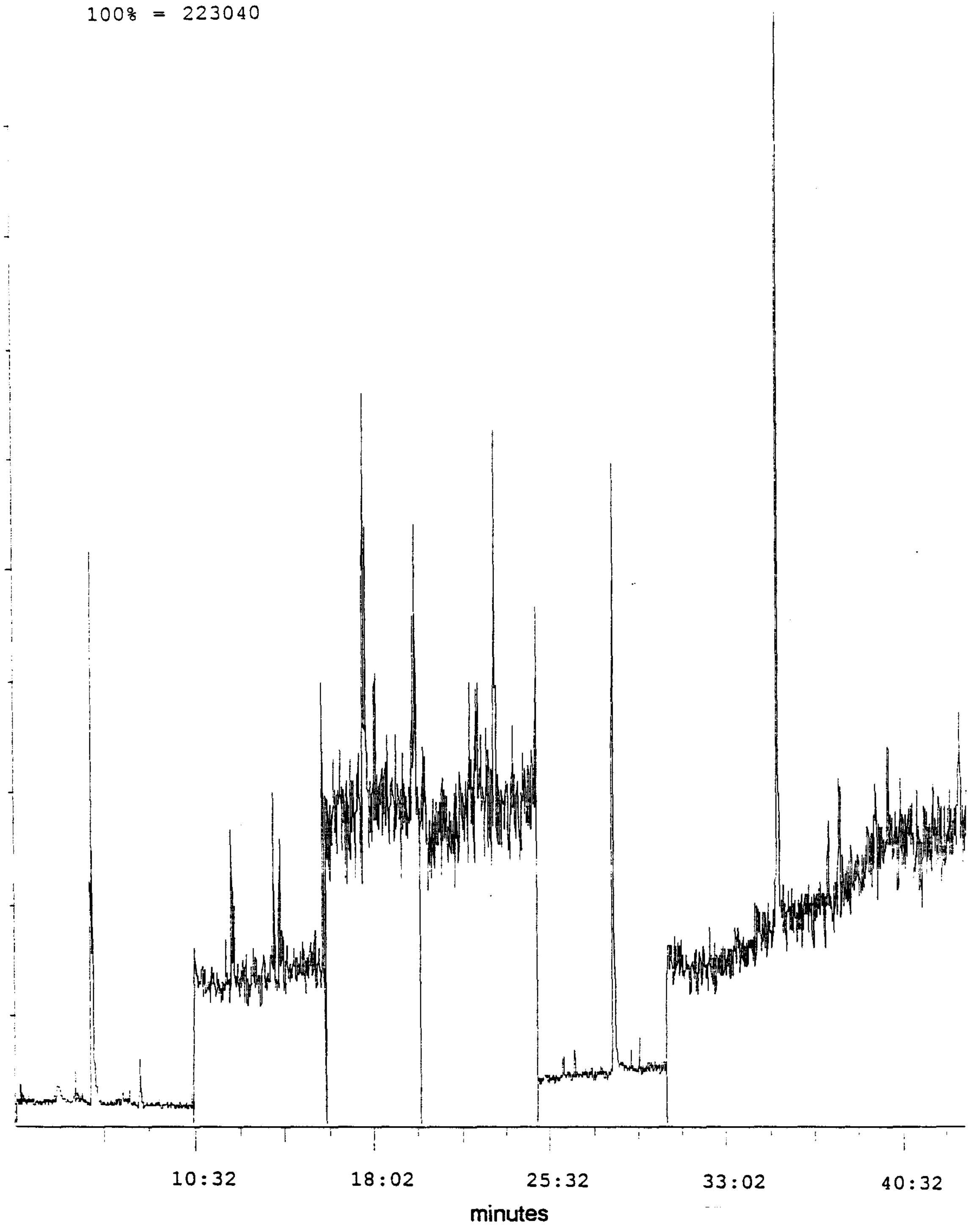


Figure 8. Example Chromatogram of water blank.

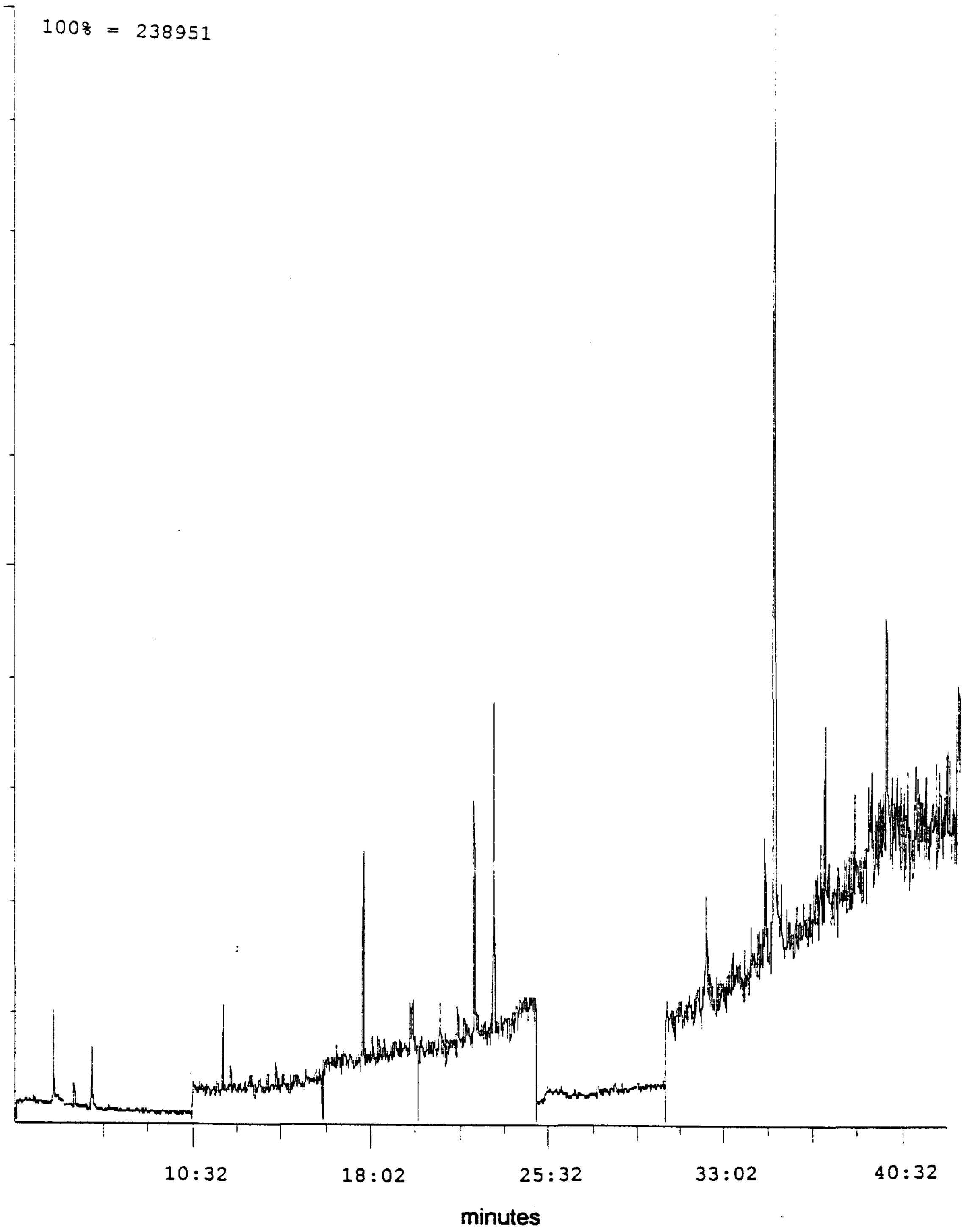


Figure 9. Example Chromatogram of water filter blank.

Spike Recoveries

Spike recoveries were done for most compounds in each media (Tables A-7 to A-9) to correct for losses during analytical work-up. PUF recoveries were better, in general, for the larger PUF where they approached 100% for the higher molecular weight compounds, (i.e. benzo(a)anthracene and greater). Better recoveries of higher molecular weight compounds were also observed for filters. Low recoveries of low molecular weight compounds (i.e. naphthalene to fluoranthene) in PUF and filters can be attributed to their high volatilities and thus increased losses during sample workup (i.e. sample concentrations steps). Although other researchers have reported similar recoveries for the high molecular weight compounds, most past studies have had recoveries higher than this study for the low molecular weight compounds (Table 9). For example, Yamasaki et al. (1982)[149] found 71.3% recovery of anthracene from PUF and 79.3% from air filters, while values from the present study were 58.9% and 78.1% from small and large PUF, respectively and 45.3% and 37.8% from small and large air filters. Grosjean (1983)[117] reported 52% recovery of anthracene from air filters, while Crosby et al. (1981)[150] found 67% recovery from the same media. Gardener et al. (1995)[124] reported recoveries for PUF (30 - 86%) and filters (13 - 84%) for acenaphthene through dibenzo(ah)anthracene which were closer to those found in this study.

Total recoveries for water (dissolved + particulate) were relatively low for all compounds with the majority in the dissolved phase (Table 10). These low recoveries may be due to incomplete extraction from water. This may have been caused by insufficient extraction time, insufficient extraction solvent volume, inadequate mixing of solvent and sample, or loss during storage. Variations in extraction time were noted (6-12 h), but did not affect recoveries. For example, phenanthrene had 80% recovery after 8 h, 75% after 9 h, 120 % after 15 h, 95% after 16 h, and 40% after 18 h. In similar studies, Nunez and Centrich (1990)[151] reported recoveries of 79% and greater for fluoranthene through benzo(ghi)perylene, while Crosby et al. (1981)[150] had recoveries similar to those found in this study. Although both also used liquid-liquid extraction (petroleum-diethyl ether and iso-octane, respectively), the former performed only the extraction (in a separatory funnel) while the latter used a laboratory shaker prior to extraction (similar to this study). Crosby et al. (1981)[150] also noted an increased recovery with the addition of solvent to the sample during storage.

All samples were corrected for spike recoveries as described later. Several compounds determined in samples were not analyzed during spike recovery experiments. For these compounds, quantitative experimental recoveries for similar compounds were used (i.e. phenanthrene % recovery for 2-methylphenanthrene and 1-methylphenanthrene; benzo(a)pyrene for benzo(e)pyrene; and indeno[1,2,3-cd]pyrene for perylene).

Duplicates

Duplicates were analyzed for two water samples at each site, with varying results. Some compounds were within experimental error, while others were extremely different. Unfortunately, there were no similarities among sample duplicates for individual compounds. Since the analytical workup for water samples was identical to that used for other media, and recoveries from those were different, the method employed for PAH extraction from water must be considered the problem. The very low recoveries from water for spikes supports this hypothesis. As was discussed earlier, addition of solvent to samples during storage and changes in extraction time, solvent volume and mixing procedures are possible solutions to the low recovery problem. Although the sample jug and stainless steel filtration container were cleaned with solvent before use, they were not rinsed after sample transfer and filtration, a step in which PAHs may have been lost due to adsorption to the glass/stainless steel container.[150]

Surrogate Recoveries

Surrogate compounds (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12}) were added directly to the front PUF prior to sampling and to water and air filters prior to extraction, to account for experimental losses. McVeety and Hites

(1988)[152] reported that isotopically labeled isomer standards generally experience losses similar to the analyte throughout the workup procedure. Samples were corrected for the mean surrogate blank values and adjusted for recovery, then divided by air or water volume to yield concentration (Table 11). For both size PUF, the surrogate compounds in samples yielded lower recovery values than the surrogates in spikes. This is likely due to losses during sampling, as the surrogates were spiked onto the PUF prior to sampling. Naphthalene-d_8 and acenaphthene-d_{10} were not found above LOD in any sample, possibly due to "blow-off effects" for the low molecular weight compounds at ambient conditions. Phenanthrene-d_{10} surrogate recoveries were less than 50% for each site while chrysene-d_{12} was greater than 65% for all sites. Due to extremely high blank values for acenaphthene-d_{10} in both size PUF, recovery determinations were not possible and thus sample concentrations were not adjusted for recovery for this surrogate. Samples and spike air filters followed the same trend with better experimental surrogate recoveries for the higher molecular weight compounds (i.e. phenanthrene-d_{10} and chrysene-d_{12}). Leister and Baker (1994),[147] recognized a similar trend finding recoveries of anthracene-d_{10}, pyrene-d_{10}, fluoranthene-d_{10}, and benzo(b)fluoranthene-d_{12} to be 63%, 73%, 65% and 87% for surrogates added prior to extraction of PUF and filters. Recoveries for spike experiments and Meander and Pennsylvania air filters are higher, reflecting losses due only to analytical error, not sampling. The lower recovery from Youngstown air filters (both weeks) may be attributed to decreased extraction efficiency from filters more heavily loaded with ambient particulate matter- a phenomena which has been documented elsewhere.[117,150] The surrogate recoveries for water samples were similar to that of surrogate recoveries from spikes.

SRM 1649

Figure 10 shows the chromatogram from SRM 1649 and Table 12 gives concentrations for triplicate analyses of SRM 1649 (Urban Dust/Organics) and values reported by other researchers. Values in this study were within 54-90% error of the

Table 11: Average Surrogate Recoveries (%)

		NAP-d8	ACE-d10	PHEN-d10	CHR-d12	
PUF	YAFP(1) *	0.17	0.00	47.36	110.43	(n = 9)
	YAFP(2) *	0.17	0.00	18.84	66.40	(n = 8)
	YA Spike P	19.97	bd	57.09	134.23	(n = 5)
	MAFP	0.13	0.00	6.74	73.15	(n = 4)
	PAFP	0.00	0.00	10.20	70.55	(n = 4)
	MA Spike P	27.28	bd	74.81	157.11	(n = 5)
Filters	YAFF(1) *	8.32	11.82	27.04	76.94	(n = 9)
	YAFF(2) *	8.89	8.86	25.01	77.15	(n = 9)
	YA Spike F	21.14	32.39	62.98	186.59	(n = 4)
	MAFF	9.88	15.28	39.14	124.99	(n = 4)
	PAFF	10.96	17.47	47.43	149.73	(n = 4)
	MA Spike F	8.11	16.66	45.27	143.43	(n = 5)
	MA Blank F	23.66	33.02	55.52	153.40	(n = 3)
Water	Y Water(1) *	13.75	21.72	35.29	60.06	(n = 7)
	Y Water(2) *	14.19	17.66	32.01	88.63	(n = 5)
	M Water	27.19	34.20	58.87	157.59	(n = 7)
	P Water	28.91	35.24	50.68	144.09	(n = 7)
	Spike W	31.55	31.95	49.87	177.17	(n = 5)
	Blank W	57.65	51.38	82.77	191.12	(n = 5)
Water filters	Y wf (1) *	6.73	16.54	36.41	178.03	(n = 5)
	Y wf (2) *	10.77	23.92	37.64	154.48	(n = 5)
	M wf	0.20	0.53	1.16	29.79	(n = 7)
	P wf	0.82	2.31	3.50	31.55	(n = 7)
	Spike wf	0.00	0.10	0.00	2.18	(n = 5)
	Blank wf	0.22	1.20	0.00	1.66	(n = 5)
Total Water	Y Water(1) *	20.48	38.26	71.70	238.09	(n = 5)
	Y Water(2) *	24.96	41.58	69.66	243.10	(n = 5)
	M Water	27.39	34.73	60.03	187.39	(n = 7)
	P Water	29.73	37.55	54.18	175.63	(n = 7)
	Spike W	31.55	32.05	49.87	179.34	(n = 5)
	Blank W	57.86	52.58	82.77	192.78	(n = 5)
		NAP-d8	**ACE-d10**	**PHEN-d10**	**CHR-d12**	

* (1) = Youngstown Week 1 and (2) = Youngstown Week 2.
bd = below LOD; n = Number of Samples

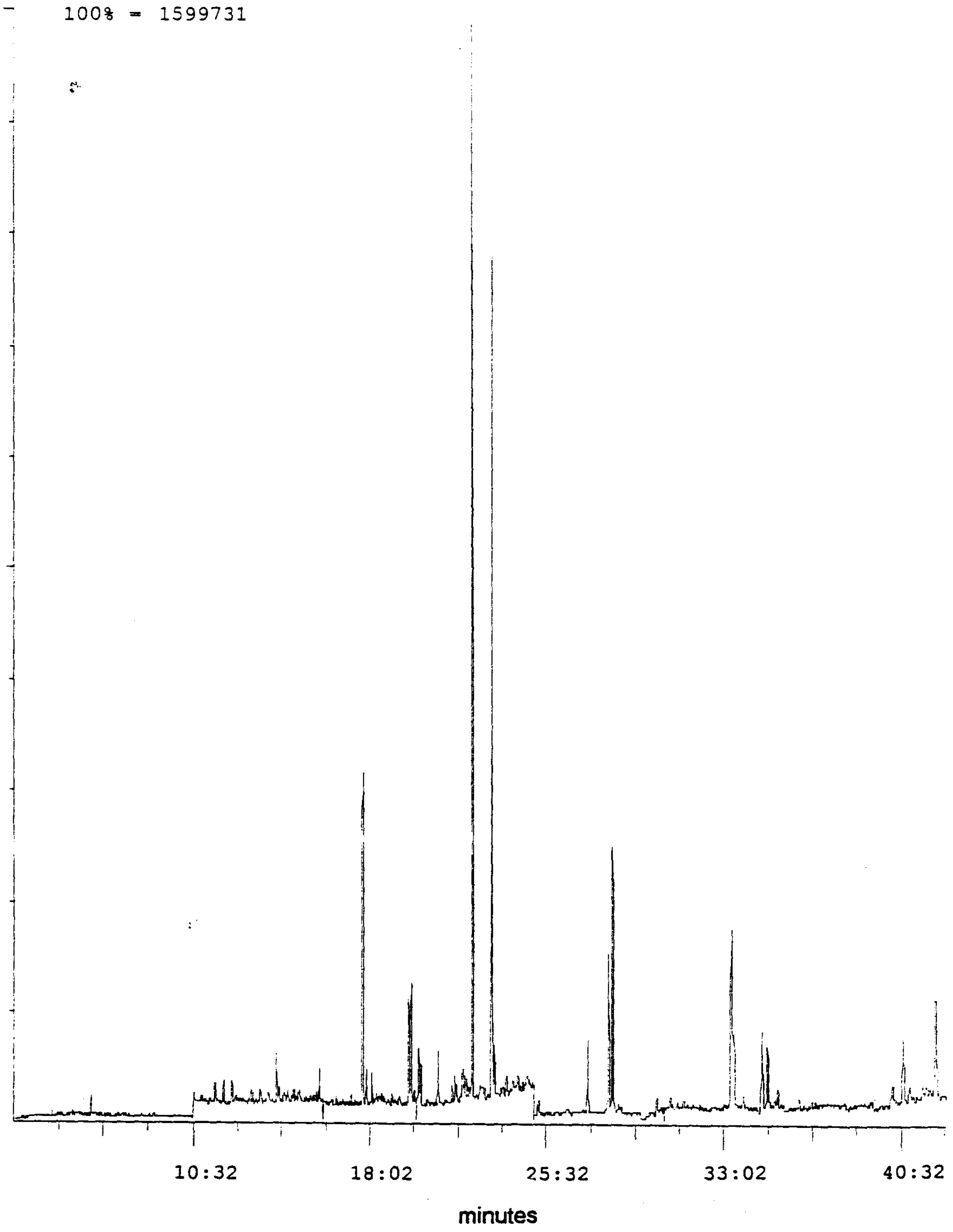


Figure 10. Chromatogram of SRM 1649.

Table 12: Results for Three Extractions of SRM 1649 (mg/kg)

	SRM1	SRM2	SRM3	AVG (+/-) S.D.		% Error		GC †	LC-I ‡	LC-II ƒ	Ngabe§
NAP	0.212	0.087	0.037	0.112	0.090	-		-	-	-	-
ACY	0.167	0.031	0.023	0.074	0.081	-		-	-	-	-
ACE	0.092	0.049	0.016	0.052	0.038	-		-	-	-	-
FLU	0.079	0.084	0.026	0.063	0.032	-		-	-	-	-
DBT	0.042	0.040	0.013	0.032	0.016	-		-	-	-	-
PHEN	1.619	1.339	0.536	1.165	0.562	74.118		-	-	4.500	5.000
ANT	0.199	0.164	0.082	0.148	0.060	-		-	-	-	-
2-MP	0.359	0.353	0.111	0.274	0.142	-		-	-	-	1.100
1-MP	0.178	0.192	0.062	0.144	0.071	-		-	-	-	-
FLT	0.983	0.893	0.391	0.756	0.319	89.646	*	7.300	7.000	6.800	5.700
PYR	1.729	1.682	0.801	1.404	0.523	80.502		7.200	6.300	6.200	4.800
BAA	0.812	0.728	0.387	0.642	0.225	73.240	*	2.400	2.800	2.400	2.600
CHR	1.902	1.430	0.745	1.359	0.581	61.177		-	3.500	3.700	4.200
BBF	3.183	2.643	1.190	2.339	1.031	62.281		-	6.200	-	7.700
BKF	0.793	0.836	0.053	0.561	0.440	71.965		-	2.000	2.100	-
BEP	0.728	0.547	0.350	0.542	0.189	83.578		3.300	-	-	3.000
BAP	0.826	0.534	0.481	0.614	0.186	79.544	*	3.000	2.600	2.600	2.200
PERY	0.336	0.282	0.192	0.270	0.073	67.872		0.840	0.800	0.650	-
IND	1.780	1.744	0.999	1.508	0.441	54.315	*	3.300	3.400	3.600	3.600
DBA	0.364	0.340	0.249	0.318	0.060	22.537		-	-	0.410	-
BGH	2.056	1.545	0.818	1.473	0.622	68.657	*	4.700	3.900	5.200	3.600

† GC = NIST values determined by gas chromatography. (153)

‡ LC-I = NIST values determined by liquid chromatography; using 7-methylfluoranthene as internal standard. (153)

ƒ LC-II = NIST values determined by liquid chromatography; using perylene-d$_{12}$ as internal standard. (153)

§ Values determined by GC/Mass Spectrometry; using anthracene-d$_{10}$, chrysene-d$_{12}$, benzo(a)anthracene-d$_{12}$, and benzo(ghi)perylene-d$_{12}$ as internal standards. (157)

* Compounds with NIST certified values. (153)

reported NIST value,[153] except for dibenzo(ah)anthracene (22.4%). These discrepancies may exist because of differences in extraction and workup procedure or because the Urban dust was not corrected for extraction recoveries. If recovery studies for Urban dust were similar to those for other media (i.e. as low as 24% for fluoranthene from large filters), the results may appear more reasonable.

Total Particulate Carbon (TPC)

Total particulate carbon (TPC) was determined for two air filters for each site (three for Youngstown, week 2) by Desert Analytics Laboratories in Tucson, AZ (Tables 5 and 6). Youngstown air filters showed the highest TPC values for all the samples analyzed (ranging from 20.0 to 56.3 μg carbon/filter) while the Meander and Pennsylvania filters yielded lower TPC results (ranging from 11.5 to 16.9 μg carbon/ filter). Previous studies have shown higher levels of TPC are associated with urban sites.[86,154,155] Back filters from each site ($n = 4$) and blank filters ($n = 3$) all yielded < 2.0 μg carbon/filter. Results of analysis of NIST SRM 1649 Urban dust/organics were 17.57% (by weight, acid treated) and 18.06% (by weight, non-acid treated). Acid treatment destroys inorganic carbon suggesting that inorganic carbon contributes only a minor amount to TPC for these samples. Klouda et al.[156] reported total carbon (17.7%) for NIST SRM 1649 Urban dust/organics. Many researchers report Total Suspended Particulate (TSP) which has been shown to be linearly related to TPC by $TPC/TSP = 0.14$.[157]

FIELD SAMPLES

Samples exceeding the LOD (mean blank + 3 x SD) for a given compound were corrected for the mean blank value and adjusted for recovery, then divided by air or water volume to yield concentration (Tables 13-16 and 23-26). Analysis of fraction 1 for several different media showed no PAHs, as expected.

Air and water samples were taken at three sites: Meander Reservoir, Ohio; Youngstown, Ohio; and New Wilmington, Pennsylvania. The Youngstown site is in the heart of an urban center on the Youngstown State University campus. Meander Reservoir is a suburban location 10 miles west of Youngstown and southeast of another major industrial area (Akron, OH). The Pennsylvania site is a rural location 18 miles directly east of Youngstown. These sites were chosen to run along a west to east path to determine if pollutants in the region are primarily locally derived or atmospherically transported from regions with higher pollution levels. Concurrent air samples were taken in Youngstown, Ohio (Y1 air) and at Meander Reservoir (M air) from July 22, 1996 to July 26, 1996; and in Youngstown, Ohio (Y2 air) and New Wilmington, Pennsylvania (P air) from July 29, 1996 to August 2, 1996.

Air

Tables 13-16 list the total air concentration (gaseous + particulate, ng/m^3) for each site; Tables 17-20 list the mean (+/- standard deviation), maximum and minimum values (ng/m^3) for air samples as gaseous or particulate at each site. Table 21 lists the sum of the 21 PAHs analyzed in this study on a daily basis for each site (ng/m^3). In all air samples, the PUF contained primarily the low to mid-range molecular weight compounds (naphthalene to chrysene) while the filters contained primarily the higher molecular weight compounds (benzo(b)fluoranthene to benzo(ghi)perylene) (Tables A-10, A-17). Figures 11 and 12 show typical chromatograms for Youngstown front PUF and filters, respectively. This distribution between the two phases was expected due to differences in vapor pressure and has been reported by a number of other researchers.[41,75,124,158] Phenanthrene had the highest concentration, in all air samples, followed by fluoranthene, fluorene, and pyrene. This same trend was observed in atmospheric samples taken over Chesapeake Bay[147], and in four urban sites in the United Kingdom (London, Stevenage, Manchester, Cardiff).[41] Table 22 compares atmospheric concentrations for a number of sites, including this study. The Youngstown sites were similar in concentration for the

Table 13: Youngstown Air Concentrations (Week 1)- Gaseous + Particulate, (ng/m^3)

	YA11	YA12	YA13	YA14	YA15	YA16	YA17	YA18	YA19	AVG
NAP	0.018	0.006	bd	bd	bd	bd	bd	bd	bd	0.003
ACY	0.543	1.394	0.127	0.126	0.055	0.194	0.102	0.455	0.194	0.354
ACE	0.672	8.764	bd	bd	0.787	2.450	bd	1.584	0.569	1.647
FLU	3.262	4.924	1.893	0.913	1.893	2.760	2.223	38.039	1.707	6.402
DBT	1.261	3.009	0.994	0.172	1.395	1.101	0.960	1.073	0.543	1.168
PHEN	21.082	34.011	17.928	2.694	65.953	45.559	36.492	110.954	48.446	42.569
ANT	1.587	3.270	0.806	0.089	1.792	0.358	0.654	1.046	0.636	1.137
2-MP	4.711	9.626	2.722	0.609	2.227	2.641	2.351	2.837	1.337	3.229
1-MP	2.043	3.619	1.585	0.266	1.925	1.308	1.173	1.920	1.172	1.668
FLT	9.154	11.565	6.511	0.796	33.345	3.823	4.922	20.068	2.289	10.275
PYR	3.600	2.569	3.654	0.297	11.264	1.955	2.751	7.938	4.013	4.227
BAA	0.483	0.517	0.536	0.160	0.468	0.445	0.479	0.419	0.427	0.437
CHR	0.364	0.866	0.262	0.119	0.342	0.105	0.155	0.188	0.196	0.289
BBF	bd	0.030	0.379	0.572	0.325	0.018	0.028	0.404	0.219	0.219
BKF	0.115	0.207	0.037	0.054	0.047	0.015	0.020	0.027	0.075	0.066
BEP	bd	0.049	bd	0.117	bd	bd	bd	bd	bd	0.019
BAP	bd	0.077	0.033	0.047	bd	bd	bd	bd	0.023	0.020
PERY	0.022	bd	0.020	0.018	bd	bd	bd	bd	bd	0.007
IND	0.052	0.180	0.088	0.219	0.064	0.023	0.054	0.051	0.067	0.089
DBA	0.005	0.006	0.017	0.038	0.014	bd	0.012	0.007	0.012	0.012
BGH	0.142	0.208	0.087	0.267	0.057	0.027	0.076	0.052	0.095	0.112

bd = below LOD (mean blank + 3S.D.

Table 14: Meander Air Concentrations- Gaseous + Particulate, (ng/m^3)

	MA11	MA12	MA13	MA14	AVG
NAP	0.003	bd	0.058	0.023	0.021
ACY	0.019	bd	bd	0.047	0.016
ACE	0.025	bd	bd	bd	0.006
FLU	0.250	bd	0.136	0.278	0.166
DBT	0.131	0.053	0.044	0.082	0.077
PHEN	15.468	13.690	12.896	11.746	13.450
ANT	0.200	0.099	0.073	0.067	0.110
2-MP	0.418	0.141	0.103	0.160	0.206
1-MP	0.138	0.068	0.050	0.052	0.077
FLT	1.413	0.508	0.449	0.701	0.768
PYR	1.116	0.386	0.464	0.460	0.606
BAA	0.013	0.007	0.087	0.015	0.030
CHR	0.222	0.019	0.031	0.021	0.073
BBF	0.052	0.031	0.086	0.236	0.101
BKF	0.214	0.019	0.049	0.023	0.076
BEP	0.113	0.035	0.049	0.088	0.071
BAP	0.140	0.027	0.063	0.081	0.078
PERY	bd	bd	0.010	0.016	0.007
IND	0.233	0.039	0.117	0.203	0.148
DBA	0.028	0.009	0.017	0.037	0.023
BGH	0.248	0.041	0.175	0.331	0.199

bd = below LOD (mean blank + 3S.D.

Table 15: Youngstown Air Concentrations (Week 2)- Gaseous + Particulate, (ng/m^3)

	YA21	YA22	YA23	YA24	YA25	YA26	YA27	YA28	YA29 *	AVG
NAP	0.094	0.175	0.127	bd	bd	bd	bd	bd	bd	0.050
ACY	0.110	0.460	0.036	bd	bd	0.102	0.041	0.932	bd	0.210
ACE	0.538	1.004	bd	bd	bd	bd	bd	3.646	bd	0.649
FLU	1.243	2.377	0.467	1.288	0.515	3.097	0.497	8.321	bd	2.225
DBT	0.804	0.995	0.301	0.147	0.350	0.369	0.182	0.806	bd	0.494
PHEN	81.124	11.970	6.931	50.124	60.082	76.409	5.206	121.346	0.033	46.025
ANT	1.257	0.151	0.249	0.019	0.292	5.722	0.107	1.203	bd	1.125
2-MP	2.653	1.430	1.050	0.295	1.239	0.735	0.691	2.376	bd	1.309
1-MP	1.848	0.719	0.423	0.112	0.551	0.277	0.371	0.944	bd	0.656
FLT	23.893	5.376	2.157	1.385	4.664	1.894	2.057	3.215	0.092	4.970
PYR	8.814	1.750	1.699	0.603	7.650	0.981	1.659	1.831	bd	2.776
BAA	0.652	0.401	0.341	0.237	0.362	0.099	0.163	0.189	0.195	0.305
CHR	0.313	0.160	0.079	0.049	0.103	0.060	0.051	0.237	0.086	0.132
BBF	1.955	0.028	0.803	0.553	0.855	0.019	0.014	0.202	0.086	0.554
BKF	0.092	0.031	0.025	0.004	0.009	0.007	0.006	0.200	0.092	0.047
BEP	bd	bd	bd	bd	0.023	bd	bd	bd	bd	0.003
BAP	0.070	bd	bd	0.147	bd	bd	bd	0.094	bd	0.039
PERY	0.029	bd	bd	bd	bd	bd	bd	0.062	0.026	0.011
IND	0.112	0.026	0.057	0.028	0.048	0.021	bd	0.319	0.086	0.076
DBA	bd	0.024	bd	bd	bd	0.013	bd	0.057	0.015	0.012
BGH	0.107	0.042	0.062	0.024	0.042	0.022	0.017	0.433	0.106	0.094

bd = below LOD (mean blank + 3S.D.

* Sample YA29 is particulate fraction concentration only due to loss of PUF sample.

Table 16: Pennsylvania Air Concentrations- Gaseous + Particulate, (ng/m^3)

	PA11	PA12	PA13	PA14	AVG
NAP	bd	bd	bd	bd	0.000
ACY	0.009	bd	0.012	bd	0.005
ACE	bd	bd	bd	bd	0.000
FLU	0.122	bd	0.114	bd	0.059
DBT	0.060	0.063	0.051	0.062	0.059
PHEN	9.511	9.802	7.009	7.834	8.539
ANT	0.064	0.051	0.042	0.060	0.054
2-MP	0.138	0.235	0.153	0.151	0.169
1-MP	0.064	0.146	0.049	0.043	0.075
FLT	0.532	0.837	0.716	0.561	0.661
PYR	0.339	1.238	1.046	0.248	0.718
BAA	0.016	0.102	0.015	0.009	0.035
CHR	0.123	0.046	0.016	0.024	0.052
BBF	0.010	0.170	0.122	0.525	0.207
BKF	0.054	0.070	0.027	0.049	0.050
BEP	0.011	0.072	0.058	0.068	0.052
BAP	0.080	0.077	0.084	0.057	0.075
PERY	bd	0.019	0.024	0.013	0.014
IND	0.088	0.161	0.105	0.114	0.117
DBA	0.014	0.025	0.020	0.026	0.021
BGH	0.064	0.229	0.196	0.131	0.155

bd = below LOD (mean blank + 3S.D.

Table 17: Summary of Youngstown Air Concentrations (Week 1): Gaseous, Particulate and Total, (ng/m³)

	Youngstown (1) Front PUF					Youngstown (1) Front Filter					Youngstown (1) AIR			
	mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000		0.003	0.006	0.000	0.018		0.003	0.006	0.000	0.016
ACY	0.343	0.424	0.055	1.394		0.012	0.021	0.000	0.060		0.354	0.423	0.055	1.394
ACE	1.647	2.790	0.000	8.764		0.000	0.000	0.000	0.000		1.647	2.790	0.000	8.764
FLU	6.393	11.922	0.913	38.039		0.009	0.027	0.000	0.080		6.402	11.919	0.923	38.039
DBT	1.167	0.782	0.172	3.001		0.001	0.003	0.000	0.009		1.168	0.784	0.175	3.009
PHEN	42.561	31.718	2.654	110.943		0.041	0.037	0.011	0.104		42.569	31.693	2.694	110.954
ANT	1.133	0.955	0.089	3.226		0.005	0.015	0.000	0.044		1.137	0.968	0.098	3.270
2-MP	3.222	2.637	0.609	9.598		0.007	0.015	0.000	0.037		3.229	2.648	0.612	9.626
1-MP	1.663	0.901	0.266	3.573		0.005	0.015	0.000	0.046		1.668	0.913	0.275	3.619
FLT	10.244	10.423	0.796	33.345		0.031	0.063	0.000	0.156		10.275	10.423	0.796	20.068
PYR	4.227	3.347	0.297	11.264		0.000	0.000	0.000	0.000		4.227	3.347	0.297	7.938
BAA	0.335	0.145	0.000	0.495		0.103	0.064	0.000	0.160		0.437	0.111	0.161	0.536
CHR	0.211	0.200	0.032	0.704		0.078	0.049	0.020	0.162		0.289	0.235	0.105	0.866
BBF	0.165	0.174	0.000	0.397		0.055	0.053	0.000	0.175		0.219	0.211	0.000	0.572
BKF	0.004	0.004	0.000	0.013		0.062	0.058	0.015	0.194		0.066	0.061	0.016	0.207
BEP	0.005	0.016	0.000	0.049		0.013	0.039	0.000	0.117		0.019	0.041	0.000	0.117
BAP	0.000	0.000	0.000	0.000		0.020	0.028	0.000	0.077		0.020	0.028	0.000	0.077
PERY	0.005	0.009	0.000	0.022		0.002	0.006	0.000	0.018		0.007	0.010	0.000	0.022
IND	0.000	0.000	0.000	0.000		0.089	0.066	0.023	0.219		0.089	0.066	0.029	0.219
DBA	0.000	0.000	0.000	0.000		0.012	0.011	0.000	0.038		0.012	0.011	0.000	0.038
BGH	0.000	0.001	0.000	0.003		0.112	0.079	0.027	0.267		0.112	0.079	0.027	0.267
Σ PAH	73.323	52.966	6.322	186.820		0.658	0.393	0.229	1.264		73.948	52.780	7.573	187.061
	n = 9					n = 9					n = 9			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 18: Summary of Meander Air Concentrations: Gaseous, Particulate and Total, (ng/m^3)

	Meander Front PUF					Meander Front Filter					Meander AIR			
	mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000		0.021	0.027	0.000	0.124		0.021	0.027	0.000	0.058
ACY	0.009	0.018	0.000	0.035		0.008	0.009	0.000	0.019		0.016	0.022	0.000	0.047
ACE	0.000	0.000	0.000	0.038		0.006	0.012	0.000	0.025		0.006	0.012	0.000	0.025
FLU	0.166	0.127	0.000	0.278		0.000	0.000	0.000	0.000		0.166	0.127	0.000	0.278
DBT	0.071	0.035	0.044	0.122		0.007	0.009	0.000	0.019		0.077	0.039	0.047	0.131
PHEN	0.895	1.799	10.908	15.232		0.268	0.395	0.000	0.838		13.450	1.564	11.746	15.468
ANT	0.110	0.062	0.067	0.200		0.000	0.000	0.000	0.000		0.110	0.062	0.079	0.200
2-MP	0.166	0.103	0.095	0.319		0.039	0.045	0.000	0.099		0.206	0.143	0.103	0.418
1-MP	0.077	0.042	0.050	0.138		0.000	0.000	0.000	0.000		0.077	0.042	0.053	0.138
FLT	0.645	0.298	0.449	1.089		0.123	0.156	0.000	0.325		0.768	0.444	0.472	1.413
PYR	13.182	0.211	0.386	0.852		0.066	0.132	0.000	0.263		0.606	0.341	0.427	1.116
BAA	0.011	0.004	0.007	0.015		0.020	0.040	0.000	0.079		0.030	0.038	0.036	0.087
CHR	0.028	0.009	0.019	0.039		0.046	0.091	0.000	0.182		0.073	0.099	0.021	0.222
BBF	0.000	0.000	0.000	0.000		0.101	0.092	0.031	0.236		0.101	0.092	0.034	0.236
BKF	0.001	0.002	0.000	0.003		0.075	0.093	0.016	0.214		0.076	0.093	0.019	0.214
BEP	0.003	0.001	0.002	0.005		0.068	0.036	0.032	0.111		0.071	0.036	0.035	0.113
BAP	0.002	0.002	0.000	0.005		0.075	0.049	0.022	0.138		0.078	0.047	0.027	0.140
PERY	0.000	0.000	0.000	0.000		0.007	0.008	0.000	0.016		0.007	0.008	0.000	0.016
IND	0.000	0.000	0.000	0.000		0.148	0.088	0.039	0.233		0.148	0.088	0.041	0.233
DBA	0.000	0.000	0.000	0.000		0.023	0.012	0.009	0.037		0.023	0.012	0.014	0.037
BGH	0.000	0.000	0.000	0.000		0.199	0.123	0.041	0.331		0.199	0.123	0.043	0.331
Σ PAH	15.011	2.392	12.548	18.257		1.299	1.007	0.190	2.184		16.310	2.762	14.667	20.441
	n = 4					n = 4					n = 4			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 19: Summary of Youngstown Air Concentrations (Week 2): Gaseous, Particulate and Total, (ng/m^3)

	Youngstown (2) Front PUF					Youngstown (2) Front Filter					Youngstown (2) AIR			
	mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000		0.044	0.069	0.000	0.175		0.050	0.069	0.000	0.175
ACY	0.203	0.326	0.000	0.932		0.006	0.013	0.000	0.034		0.210	0.315	0.000	0.932
ACE	0.649	1.267	0.000	3.646		0.000	0.000	0.000	0.000		0.649	1.204	0.000	3.646
FLU	2.211	2.642	0.467	8.321		0.013	0.028	0.000	0.077		2.225	2.579	0.480	8.321
DBT	0.492	0.320	0.147	0.984		0.002	0.005	0.000	0.011		0.494	0.345	0.148	0.995
PHEN	51.110	41.589	4.816	120.994		0.063	0.116	0.000	0.352		46.025	42.634	5.206	121.346
ANT	1.125	1.921	0.019	5.722		0.000	0.000	0.000	0.000		1.125	1.835	0.026	5.722
2-MP	1.290	0.808	0.295	2.597		0.017	0.026	0.000	0.057		1.309	0.887	0.312	2.653
1-MP	0.656	0.547	0.112	1.848		0.000	0.000	0.000	0.000		0.656	0.556	0.132	1.848
FLT	5.495	7.496	1.366	23.727		0.086	0.084	0.003	0.259		4.970	7.279	1.385	23.893
PYR	3.123	3.197	0.603	8.814		0.000	0.000	0.003	0.000		2.776	3.166	0.842	8.814
BAA	0.147	0.117	0.052	0.400		0.162	0.078	0.040	0.252		0.305	0.168	0.099	0.652
CHR	0.078	0.069	0.025	0.232		0.058	0.046	0.018	0.163		0.132	0.093	0.049	0.313
BBF	0.094	0.266	0.000	0.751		0.418	0.448	0.014	1.203		0.554	0.641	0.041	1.955
BKF	0.002	0.003	0.000	0.008		0.050	0.066	0.004	0.200		0.047	0.066	0.005	0.200
BEP	0.003	0.008	0.000	0.023		0.000	0.000	0.000	0.000		0.003	0.008	0.000	0.023
BAP	0.018	0.052	0.000	0.146		0.018	0.037	0.000	0.094		0.039	0.055	0.000	0.147
PERY	0.000	0.000	0.000	0.000		0.013	0.022	0.000	0.062		0.011	0.022	0.000	0.062
IND	0.000	0.000	0.000	0.000		0.077	0.097	0.000	0.319		0.076	0.097	0.000	0.319
DBA	0.000	0.000	0.000	0.000		0.012	0.019	0.000	0.057		0.012	0.019	0.000	0.057
BGH	0.001	0.004	0.000	0.012		0.094	0.132	0.017	0.433		0.094	0.131	0.017	0.433
Σ PAH	67.296	50.080	10.966	144.102		1.134	0.829	0.099	2.412		68.467	52.474	11.064	146.414
	n = 9					n = 8					n = 8			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 20: Summary of Pennsylvania Air (Week 1) Concentrations: Gaseous, Particulate and Total, (ng/m^3)

	Pennsylvania Front PUF					Pennsylvania Front Filter					Pennsylvania AIR			
	mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000
ACY	0.000	0.000	0.000	0.000		0.005	0.006	0.000	0.012		0.005	0.006	0.000	0.012
ACE	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000
FLU	0.059	0.068	0.000	0.122		0.000	0.000	0.000	0.000		0.059	0.068	0.000	0.122
DBT	0.053	0.008	0.043	0.060		0.007	0.005	0.000	0.012		0.059	0.006	0.051	0.063
PHEN	0.813	1.567	6.589	9.731		0.284	0.257	0.067	0.578		8.539	1.339	7.009	9.802
ANT	0.054	0.010	0.042	0.064		0.000	0.000	0.000	0.000		0.054	0.010	0.061	0.064
2-MP	0.134	0.056	0.096	0.217		0.036	0.021	0.018	0.055		0.169	0.044	0.138	0.235
1-MP	0.075	0.048	0.043	0.146		0.000	0.000	0.000	0.000		0.075	0.048	0.045	0.146
FLT	0.524	0.224	0.343	0.837		0.137	0.165	0.000	0.332		0.661	0.142	0.561	0.837
PYR	8.255	0.472	0.248	1.238		0.186	0.371	0.000	0.743		0.718	0.497	0.397	1.238
BAA	0.017	0.009	0.009	0.030		0.018	0.036	0.000	0.072		0.035	0.045	0.031	0.102
CHR	0.028	0.013	0.016	0.046		0.024	0.049	0.000	0.097		0.052	0.049	0.051	0.123
BBF	0.012	0.024	0.000	0.048		0.195	0.227	0.010	0.525		0.207	0.223	0.025	0.525
BKF	0.003	0.003	0.000	0.008		0.047	0.016	0.025	0.062		0.050	0.018	0.027	0.070
BEP	0.004	0.002	0.002	0.007		0.048	0.026	0.010	0.065		0.052	0.028	0.011	0.072
BAP	0.001	0.001	0.000	0.003		0.074	0.013	0.055	0.084		0.075	0.012	0.057	0.084
PERY	0.000	0.000	0.000	0.000		0.014	0.010	0.000	0.024		0.014	0.010	0.000	0.024
IND	0.000	0.000	0.000	0.000		0.117	0.031	0.088	0.161		0.117	0.031	0.091	0.161
DBA	0.000	0.000	0.000	0.000		0.021	0.006	0.142	0.264		0.021	0.006	0.020	0.026
BGH	0.000	0.000	0.000	0.000		0.155	0.073	0.064	0.229		0.155	0.073	0.067	0.229
Σ PAH	9.750	2.246	7.660	12.414		1.368	0.783	0.511	2.199		11.119	1.619	9.858	13.342
	n = 4					n = 4					n = 4			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 21: Sum of PAHs (21 compounds studied) in Air and Water for Each Sample

WEEK 1

Sample Name	Total PAH (ng/m^3)	Sample Name	Total PAH (ng/L)
YA11	49.113	YW11A	55.804
		YW11B	178.427
YA12	84.896		
YA13	37.678	YW12	243.666
YA14	7.573		
YA15	121.952	YW13	240.058
YA16	62.784		
YA17	52.454	YW14	172.158
YA18	187.061		
YA19	62.018	YW15A	347.786
		YW15B	189.838
MA11	20.441	MW11A	95.435
		MW11B	34.136
MA12	15.171	MW12	120.936
MA13	14.960	MW13	36.307
MA14	14.667	MW14	117.333
		MW15A	138.916
		MW15B	36.392

WEEK 2

Sample Name	Total PAH (ng/m^3)	Sample Name	Total PAH (ng/L)
YA21	125.706	YW21	233.054
YA22	27.120		
YA23	14.807	YW22	201.048
YA24	55.016		
YA25	77.785	YW23	2859.309
YA26	89.827		
YA27	11.064	YW24	1629.332
YA28	146.414		
YA29	* 0.81675	YW25	129.977
PA11	11.298	PW11A	25.720
		PW11B	65.402
PA12	13.342	PW12	156.194
PA13	9.858	PW13	59.216
PA14	9.977	PW14	18.075
		PW15A	4.492
		PW15B	60.855

* Sample YA29 is particulate fraction concentration only due to loss of PUF sample.

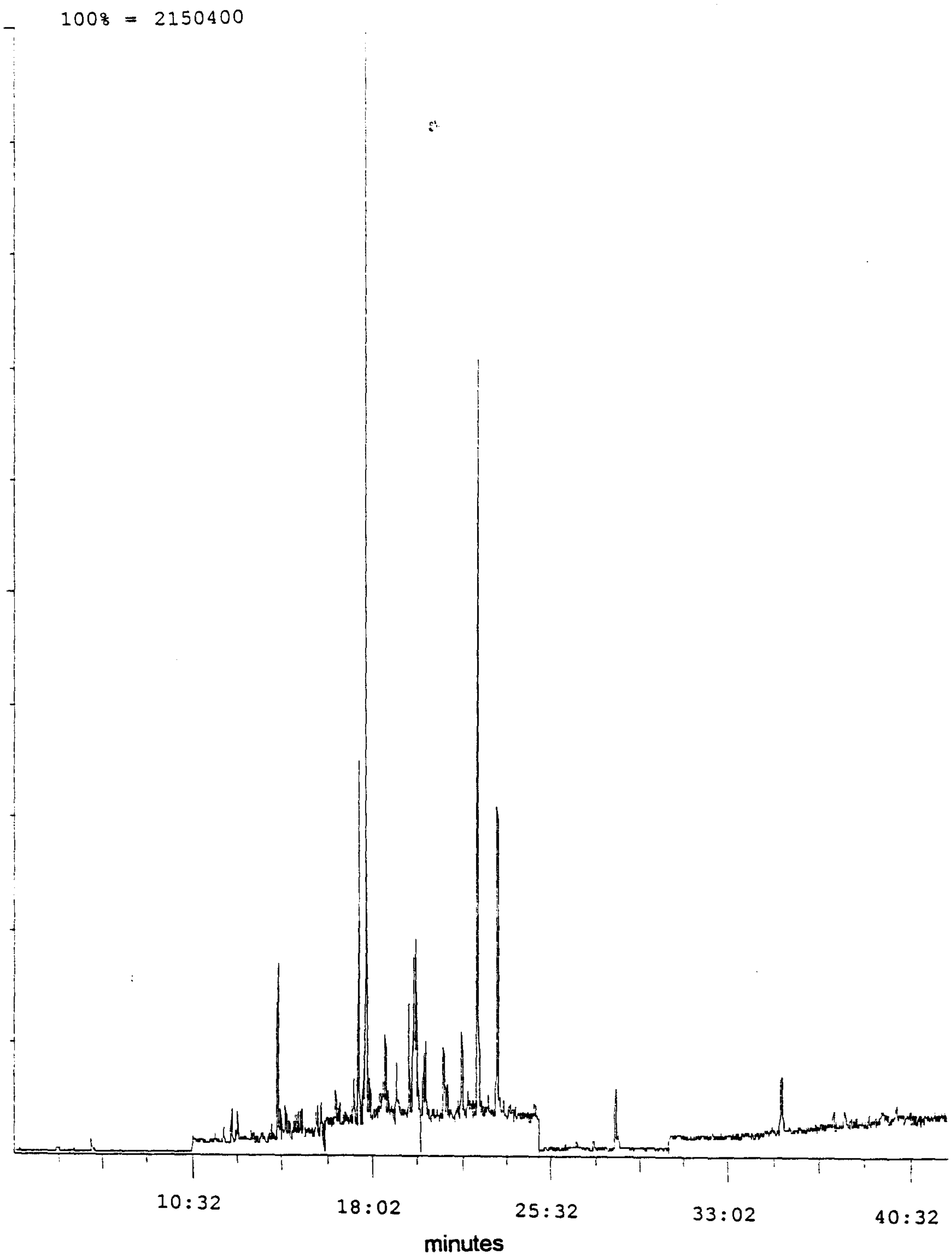


Figure 11. Chromatogram of YA11 front PUF.

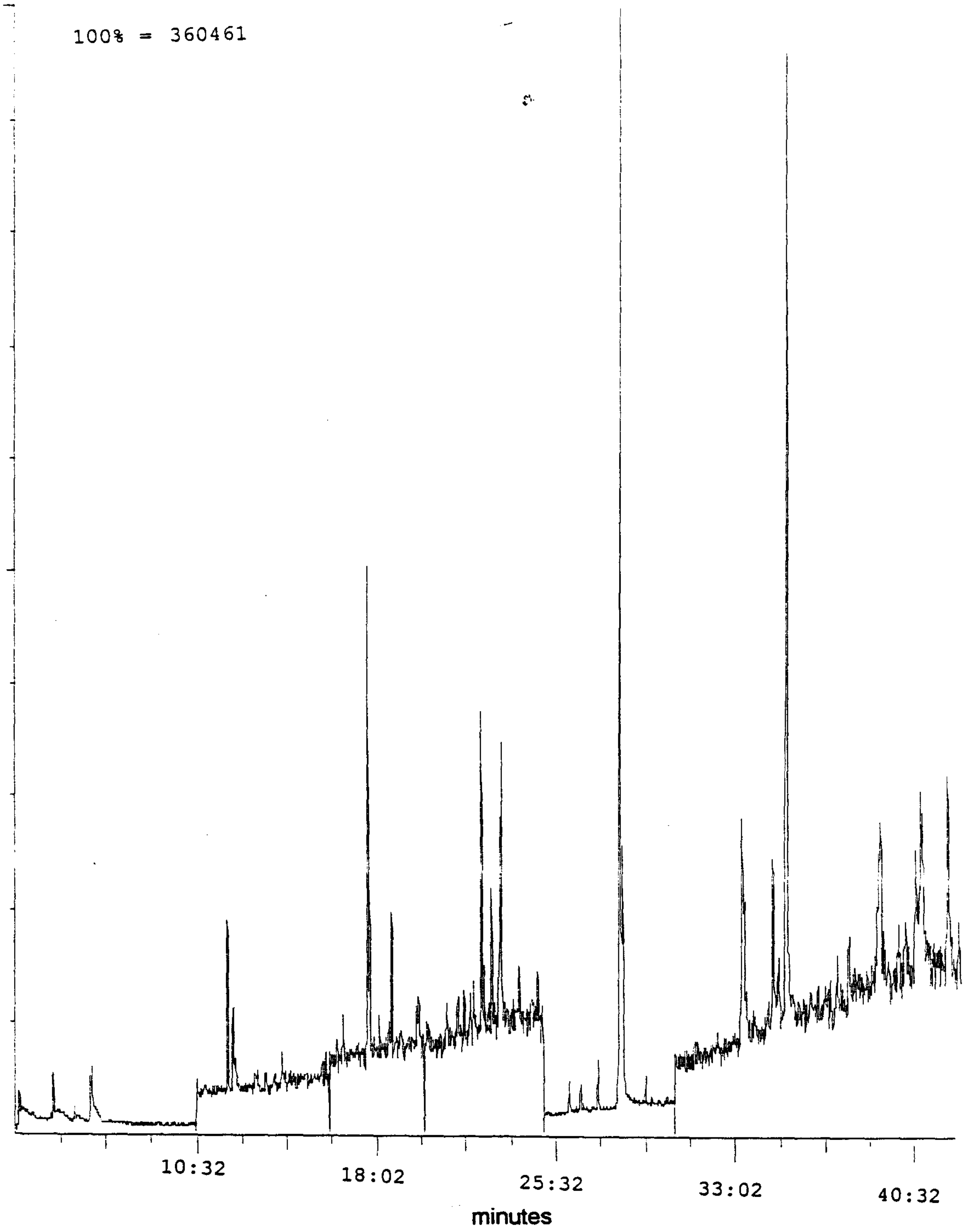


Figure 12. Chromatogram of YA25 front air filter.

Table 22: Comparison of Atmospheric PAH Concentrations, (pg/m^3)‡

	Y Air (1)†	Y (Air (2)†	M Air †	P Air †	Chicago (urban)[154]	Chicago (rural)[154]	Denver[159]	Portland[160,161]	Baltimore[162]
FLU	6402	2225	166	59	92000	4100		6100	
PHEN	42569	46025	13450	8539	159000	9600	38000	27000	1800
ANT	1137	1125	110	54	15000	50	3200	2800	2900
FLT	10275	4970	768	661	56000	1700	12600	8300	20000
PYR	4227	2776	606	718	36000	760	21200	7500	27000
BAA	437	305	30	35	21000	160		1500	7600
CHR	289	132	73	52				1800	
CHR/tri					19000	430			12000
BBF	219	554	101	207					
BKF	66	47	76	50					
B(B+K)F					39000	570	830	3500	21200
BEP	19	3	71	52	12000	190		1200	5000
BAP	20	39	78	75	14000	120	1700	1200	5800
pery	7	11	7	14					
IND	89	76	148	117	13000	130	3600		4600
DBA	12	12	23	21			4200		
BGH	112	94	199	155	11000	190	4200	2000	8000

‡Concentrations are Gaseous + Particulate

† Samples from this study.

Table 22: Comparison of Atmospheric PAH Concentrations, (pg/m^3)‡ (cont.)

	Y Air (1)†	Y (Air (2)†	M Air †	P Air†	Niagara R.[163]	L. Superior[147]	Ches. Bay[75]	Baltic Sea[164]	L. Superior[152]
FLU	6402	2225	166	59		449.9	323		110
PHEN	42569	46025	13450	8539	13800	2662.7	1440	740	92
ANT	1137	1125	110	54			24	20	5.6
FLT	10275	4970	768	661	5100	180.6	308	340	
PYR	4227	2776	606	718	4200	344.8	344	180	8
BAA	437	305	30	35	2800	124.7	20	30	22
CHR	289	132	73	52	3900		69		
CHR/tri						65.8		110	67
BBF	219	554	101	207					
BKF	66	47	76	50					
B(B+K)F					1100	43.5	66	110	
BEP	19	3	71	52	420	6.3	24	70	44
BAP	20	39	78	75	230	5	13	140	22
pery	7	11	7	14					
IND	89	76	148	117		18.1	17	110	50
DBA	12	12	23	21			3		
BGH	112	94	199	155	530	21.4	24	70	41

‡Concentrations are Gaseous + Particulate

† Samples from this study.

lower molecular weight PAHs to those found in Denver, CO and Portland, OR, but had much lower concentrations for the higher molecular weight PAHs than these studies. This may be due, in part, to the increased efficiency of PAH collection on filters at colder temperatures (i.e. - 4 to 12°C for Denver,[159] < 6°C for Portland,[160,161] and 21 to 26°C for this study) which has been documented elsewhere.[41] Most compounds in Meander air were similar in concentration to values found in rural sites near Chicago, IL,[154] while those in Pennsylvania air were closer to levels in a more remote region such as Baltic Sea air. It should be noted how repeated samplings of a location can often lead to varying results (i.e. Lake Superior[75,152]), thus exemplifying the dynamic state of the atmosphere.

On average, Youngstown air samples (both weeks) yielded higher concentrations than Meander and Pennsylvania air samples. This finding is not surprising since urban centers typically have increased levels of pollutants due to enhanced traffic and industrial releases. For all air samples, both PUF and filters showed the presence of 1- and 2-methylphenanthrene, two compounds which are often associated with low temperature pyrolytic processes such as combustion of diesel oil, gasoline or coal in residential stoves and possibly traffic.[104] The presence of dibenzothiophene at all sites implies the combustion of sulfur-containing fuels (e.g. coal and diesel fuel)[165] and perylene at less than 10 % of the total PAH concentration further indicates low temperature combustion.[77]

Water

Tables 23-26 list the total water concentration (dissolved + particulate, ng/L) for each site; Tables 27-30 list the mean (+/- standard deviation), maximum and minimum values (ng/L) for water samples as dissolved or particulate at each site. Table 21 lists the sum of the 21 PAHs studied on a daily basis for each site (ng/L). The Youngstown water samples (dissolved and particulate) from both weeks contained almost the entire range of PAHs, with highest concentrations for the mid-range compounds (phenanthrene to pyrene) in the dissolved phase (Tables A-18, A-20) and greater concentrations of the high molecular weight compounds (benzo(a)anthracene to benzo(ghi)perylene) on the filters

Table 23: Total Youngstown Water Concentration (Week 1)- Dissolved + Particulate, (ng/L)

	YW11A	YW11B	YW12	YW13	YW14	YW15A	YW15B	AVG
NAP	bd	bd	bd	1.581	0.928	0.681	bd	0.456
ACY	bd	bd	bd	0.445	0.232	0.804	bd	0.212
ACE	0.921	bd	bd	9.842	2.186	3.696	4.802	3.064
FLU	bd	0.328	2.554	12.283	7.109	7.894	10.322	5.784
DBT	bd	bd	0.560	2.517	0.357	1.537	1.296	0.895
PHEN	bd	6.900	7.720	58.401	15.353	34.098	16.898	19.910
ANT	0.540	1.348	3.195	4.847	1.961	4.698	4.046	2.948
2-MP	bd	bd	2.777	10.246	3.764	5.834	bd	3.232
1-MP	bd	0.582	1.560	5.041	4.076	4.422	0.894	2.368
FLT	18.039	45.777	31.878	32.893	28.456	43.166	40.011	34.317
PYR	4.741	18.733	59.951	24.039	20.661	64.153	49.425	34.529
BAA	bd	31.407	25.595	15.583	17.427	21.869	8.670	17.221
CHR	bd	bd	12.680	0.985	8.418	16.015	4.205	6.043
BBF	5.645	11.406	43.670	18.558	19.137	45.036	11.455	22.129
BKF	5.322	2.797	3.483	5.843	5.624	13.833	7.662	6.366
BEP	2.247	7.977	6.284	5.472	5.455	11.719	4.514	6.238
BAP	3.505	6.278	10.793	3.583	8.555	16.995	6.274	7.997
PERY	1.998	2.647	3.113	6.612	2.165	6.565	2.686	3.684
IND	6.099	21.258	14.799	9.282	8.336	18.869	7.935	12.368
DBA	0.586	6.862	2.355	1.344	1.245	4.211	0.258	2.409
BGH	6.162	14.126	10.700	10.660	10.716	21.690	8.487	11.792

bd = below LOD (mean blank + 3S.D.)

Table 24: Total Meander Water Concentration- Dissolved + Particulate, (ng/L)

	MW11A	MW11B	MW12	MW13	MW14	MW15A	MW15B	AVG
NAP	0.897	bd	bd	0.837	0.099	bd	bd	0.262
ACY	bd	bd	bd	bd	bd	bd	bd	bd
ACE	bd	bd	1.332	bd	4.997	bd	bd	0.904
FLU	0.249	bd	1.605	0.665	7.566	bd	bd	1.441
DBT	0.199	bd	0.484	0.057	0.880	1.235	bd	0.408
PHEN	17.185	bd	bd	6.757	43.285	29.234	bd	13.780
ANT	1.737	1.160	0.780	2.904	2.206	3.132	1.741	1.952
2-MP	2.215	bd	bd	1.099	1.892	12.142	bd	2.478
1-MP	1.018	4.567	1.161	2.548	2.033	3.825	0.234	2.198
FLT	13.228	1.193	8.340	2.781	5.672	45.635	3.741	11.513
PYR	41.414	15.812	75.393	6.919	27.149	24.630	24.790	30.872
BAA	2.353	0.839	0.771	2.402	0.218	0.459	0.853	1.128
CHR	0.828	0.013	0.016	0.133	0.095	0.032	0.027	0.164
BBF	4.466	0.617	2.191	3.461	6.736	6.002	1.226	3.528
BKF	1.316	0.554	0.317	1.518	2.022	1.388	1.122	1.177
BEP	0.095	0.549	0.158	0.476	1.778	1.181	0.407	0.663
BAP	3.648	0.163	15.643	1.438	2.774	2.627	0.355	3.807
PERY	2.834	7.558	12.745	2.150	5.886	3.419	1.319	5.130
IND	0.349	0.412	bd	0.161	0.622	1.066	0.169	0.397
DBA	0.131	0.699	bd	bd	bd	bd	bd	0.119
BGH	1.272	bd	bd	bd	1.424	2.908	0.408	0.859

bd = below LOD (mean blank + 3S.D.)

Table 25: Total Youngstown Water Concentration (Week 2)- Dissolved + Particulate, (ng/L)

	YW21	YW22	YW23	YW24	YW25	AVG
NAP	4.156	2.903	4.717	2.674	0.541	2.998
ACY	0.928	0.373	0.194	bd	0.175	0.334
ACE	3.164	2.058	7.673	0.949	bd	2.769
FLU	13.998	1.215	14.853	0.992	0.113	6.234
DBT	1.119	1.327	2.340	0.416	0.772	1.195
PHEN	19.153	46.209	60.460	21.669	8.055	31.109
ANT	5.334	2.882	93.684	15.408	1.703	23.802
2-MP	7.677	2.580	38.740	4.496	bd	10.699
1-MP	14.166	3.003	8.507	1.351	0.238	5.453
FLT	30.573	24.513	179.694	46.037	38.112	63.786
PYR	17.511	23.941	2306.705	1411.031	13.157	228.648
BAA	20.665	17.467	18.402	18.051	8.386	16.594
CHR	10.845	8.289	11.625	12.759	4.512	9.606
BBF	24.322	21.057	31.358	26.741	7.405	22.177
BKF	6.588	6.149	7.363	6.612	3.347	6.012
BEP	8.198	3.812	11.385	7.831	4.804	7.206
BAP	10.914	7.419	17.132	12.922	6.765	11.030
PERY	3.622	4.402	10.104	5.198	3.737	5.412
IND	12.154	9.655	13.072	13.729	12.189	12.160
DBA	2.752	0.706	3.722	2.573	5.232	2.997
BGH	15.215	11.090	17.573	17.893	10.735	14.501

bd = below LOD (mean blank + 3S.D.)

Table 26: Total Pennsylvania Water Concentration- Dissolved + Particulate, (ng/L)

	PW11A	PW11B	PW12	PW13	PW14	PW15A	PW15B	AVG
NAP	bd	bd	bd	bd	bd	bd	bd	0.000
ACY	bd	bd	bd	bd	bd	bd	0.622	0.089
ACE	bd	bd	2.458	2.775	2.186	bd	2.770	1.456
FLU	bd	0.053	4.441	9.587	bd	bd	2.022	2.300
DBT	0.057	0.101	1.416	0.077	bd	bd	0.010	0.237
PHEN	11.876	16.581	36.815	16.656	0.940	bd	bd	11.838
ANT	0.071	1.145	5.080	2.009	0.697	bd	1.105	1.444
2-MP	bd	bd	14.241	bd	bd	bd	bd	2.034
1-MP	0.281	1.902	11.251	0.211	0.772	bd	3.717	2.591
FLT	1.992	2.155	36.233	9.512	5.150	bd	5.878	8.703
PYR	6.833	29.909	26.477	7.693	bd	bd	27.522	14.062
BAA	0.187	8.197	1.127	0.802	0.810	0.629	2.092	1.978
CHR	bd	0.297	0.900	0.113	0.133	bd	0.633	0.297
BBF	0.290	2.156	3.037	3.465	1.599	0.299	4.548	2.199
BKF	0.558	0.652	1.751	1.019	0.112	bd	1.792	0.840
BEP	0.396	0.937	1.408	1.178	1.065	0.114	0.776	0.839
BAP	bd	0.809	2.594	0.220	3.851	0.160	2.985	1.517
PERY	1.287	bd	3.021	2.813	0.761	bd	3.282	1.595
IND	1.223	0.509	2.377	0.331	bd	0.822	bd	0.752
DBA	bd	bd	bd	0.416	bd	2.468	0.345	0.461
BGH	0.667	bd	1.567	0.338	bd	bd	0.756	0.475

bd = below LOD (mean blank + 3S.D.)

Table 27: Summary of Youngstown Water Concentration (Week 1): Dissolved, Particulate and Total (ng/L)

	Youngstown (1) Water				Youngstown (1) Water Filter				Total Youngstown (1) Water			
	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000	0.638	0.669	0.000	2.295	0.456	0.629	0.000	1.581
ACY	0.000	0.000	0.000	0.000	0.296	0.339	0.000	0.804	0.212	0.312	0.000	0.804
ACE	3.064	3.500	0.000	9.842	0.000	0.000	0.000	0.652	3.064	3.500	0.000	9.842
FLU	5.140	4.978	0.000	11.282	0.902	1.013	0.000	2.554	5.784	4.877	0.000	12.283
DBT	0.581	0.766	0.000	1.813	0.440	0.276	0.000	0.704	0.895	0.932	0.000	2.517
PHEN	8.025	9.353	0.000	23.880	16.639	13.767	0.000	34.521	19.910	20.112	0.000	58.401
ANT	1.971	1.149	0.540	3.959	1.367	0.969	0.087	2.340	2.948	1.697	0.540	4.847
2-MP	0.000	0.000	0.000	0.000	4.524	3.826	0.000	10.246	3.232	3.825	0.000	10.246
1-MP	0.806	0.988	0.000	2.899	2.187	1.868	0.000	4.569	2.368	2.078	0.000	5.041
FLT	27.216	11.198	15.892	45.777	9.941	5.262	2.253	15.985	34.317	9.569	18.039	45.777
PYR	17.336	16.901	0.000	45.309	24.071	16.485	4.116	48.081	34.529	23.040	4.741	64.153
BAA	4.487	11.871	0.000	31.407	17.829	6.437	8.670	25.595	17.221	10.531	0.000	31.407
CHR	0.000	0.000	0.000	0.000	8.461	6.101	0.985	16.015	6.043	6.470	0.000	16.015
BBF	4.151	3.824	0.775	11.406	25.170	17.021	5.527	43.230	22.129	15.870	5.645	45.036
BKF	2.249	1.737	0.087	5.322	5.764	3.757	3.396	12.437	6.366	3.661	2.797	13.833
BEP	2.482	2.529	0.557	7.977	5.259	3.327	1.838	10.762	6.238	2.977	2.247	11.719
BAP	2.672	1.842	0.480	6.278	7.455	5.560	2.037	16.515	7.997	4.738	3.505	16.995
PERY	1.644	1.285	0.000	3.477	2.856	1.383	1.060	4.806	3.684	2.018	1.998	6.612
IND	4.806	7.533	0.376	21.258	10.587	5.377	4.694	18.138	12.368	5.943	6.099	21.258
DBA	1.138	2.537	0.000	6.862	1.779	1.302	0.258	3.692	2.409	2.364	0.576	6.862
BGH	3.695	5.030	0.000	14.126	11.335	5.565	5.936	20.734	11.792	4.995	6.162	21.690
Σ PAH	91.463	53.008	34.746	178.427	157.499	77.846	47.274	249.626	203.963	88.862	55.804	347.786
	n = 7				n = 5				n = 7			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 28: Summary of Meander Water Concentration: Dissolved, Particulate and Total (ng/L)

	Meander Water				Meander Water Filter				Total Meander Water			
	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000	0.262	0.415	0.000	1.662	0.262	0.415	0.000	0.897
ACY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.115	0.000	0.000	0.000	0.000
ACE	0.904	1.872	0.000	4.997	0.000	0.000	0.000	0.387	0.904	1.872	0.000	4.997
FLU	1.296	2.821	0.000	7.566	0.145	0.248	0.000	0.665	1.441	2.762	0.000	7.566
DBT	0.332	0.475	0.000	1.235	0.076	0.113	0.000	0.272	0.408	0.485	0.000	1.235
PHEN	7.419	12.810	0.000	29.234	6.361	8.958	0.000	20.586	13.780	17.029	0.000	43.285
ANT	1.737	0.813	0.702	3.038	0.214	0.221	0.000	0.549	1.952	0.862	0.780	3.132
2-MP	1.735	4.589	0.000	12.122	0.744	0.985	0.000	2.215	2.478	4.361	0.000	12.142
1-MP	1.814	1.600	0.188	4.236	0.384	0.342	0.025	1.036	2.198	1.567	0.234	4.567
FLT	9.538	16.053	0.552	45.635	1.975	2.976	0.000	8.383	11.513	15.570	2.781	45.635
PYR	25.576	21.843	0.000	71.033	5.296	7.954	0.000	22.288	30.872	22.300	10.003	75.393
BAA	0.000	0.000	0.000	0.000	1.128	0.884	0.218	2.402	1.128	0.884	1.046	2.402
CHR	0.000	0.000	0.000	0.000	0.164	0.296	0.013	0.828	0.164	0.296	3.212	0.828
BBF	3.180	2.250	0.235	6.325	0.348	0.351	0.000	1.045	3.528	2.340	0.617	6.736
BKF	0.954	0.455	0.199	1.533	0.223	0.165	0.000	0.488	1.177	0.581	0.317	2.022
BEP	0.562	0.605	0.000	1.636	0.101	0.083	0.000	0.229	0.663	0.606	0.110	1.778
BAP	3.483	5.462	0.163	15.643	0.324	0.579	0.000	1.430	3.807	5.375	0.382	15.643
PERY	5.130	4.001	1.319	12.745	0.000	0.000	0.000	0.252	5.130	4.001	1.529	12.745
IND	0.397	0.357	0.000	1.066	0.000	0.000	0.000	0.108	0.397	0.357	0.000	1.066
DBA	0.100	0.264	0.000	0.699	0.019	0.050	0.000	0.131	0.119	0.261	0.000	0.699
BGH	0.783	1.073	0.000	2.908	0.076	0.200	0.000	0.530	0.859	1.088	0.000	2.908
Σ PAH	64.940	46.659	14.213	135.783	17.839	21.108	1.012	58.336	82.779	45.896	34.136	138.916
	n = 7				n = 7				n = 7			

s.d. = standard deviation
Σ PAH = Sum of 21 PAHs included in this study
n = Number of Samples

Table 29: Summary of Youngstown Water Concentration (Week 2): Dissolved, Particulate and Total (ng/L)

	Youngstown (2) Water				Youngstown (2) Water Filter				Total Youngstown (2) Water			
	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max	mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000	2.998	1.616	0.541	4.717	2.998	1.616	0.541	4.717
ACY	0.000	0.000	0.000	0.000	0.334	0.358	0.000	0.928	0.334	0.358	0.000	0.928
ACE	2.288	3.171	0.000	7.673	0.480	0.453	0.000	0.949	2.769	2.987	0.000	7.673
FLU	4.237	6.018	0.000	12.853	1.997	2.158	0.113	5.666	6.234	7.495	2.631	14.853
DBT	0.738	0.620	0.000	1.714	0.457	0.263	0.016	0.660	1.195	0.728	0.772	2.340
PHEN	10.697	8.695	0.000	23.919	20.412	15.689	0.841	36.542	31.109	21.524	8.055	60.460
ANT	22.411	39.502	1.149	92.389	1.391	0.731	0.456	2.407	23.802	39.437	1.703	93.684
2-MP	6.880	15.385	0.000	34.402	3.818	2.817	0.000	7.677	10.699	15.924	0.000	38.740
1-MP	3.803	5.351	0.000	11.250	1.650	1.259	0.238	0.744	5.453	5.815	0.344	14.166
FLT	53.115	61.843	13.897	162.888	10.671	5.751	3.775	16.806	63.786	65.296	24.513	179.694
PYR	731.184	1045.539	0.000	2267.475	23.285	13.190	4.655	39.230	754.469	1056.744	13.157	2306.705
BAA	0.000	0.000	0.000	0.000	16.594	4.746	8.386	20.665	16.594	4.746	17.332	20.665
CHR	0.000	0.000	0.000	0.000	9.606	3.288	4.512	12.759	9.606	3.288	13.804	12.759
BBF	2.199	1.925	0.674	5.381	19.978	8.227	5.941	25.978	22.177	9.072	7.405	31.358
BKF	0.603	0.505	0.241	1.494	5.409	1.540	2.922	6.950	6.012	1.552	3.347	7.363
BEP	1.384	1.050	0.141	2.512	5.822	2.772	2.292	9.073	7.206	3.005	3.812	11.385
BAP	1.330	1.254	0.000	2.815	9.700	3.865	4.953	14.318	11.030	4.244	6.765	17.132
PERY	1.662	1.524	0.000	3.892	3.751	1.970	1.281	6.212	5.412	2.697	3.622	10.104
IND	2.316	2.715	0.348	7.015	9.843	2.956	5.174	13.141	12.160	1.547	9.655	13.729
DBA	1.151	1.867	0.000	4.293	1.511	0.781	0.706	2.573	2.997	1.659	0.840	5.232
BGH	2.109	1.711	0.393	4.410	12.392	4.230	6.325	17.500	14.501	3.438	10.735	17.893
Σ PAH	848.108	1159.061	31.723	2630.694	162.100	66.424	53.535	226.938	1010.544	1207.891	129.977	2859.308
	n = 5				n = 5				n = 5			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

Table 30: Summary of Pennsylvania Water Concentration: Dissolved, Particulate and Total (ng/L)

	Pennsylvania Water					Pennsylvania Water Filter					Total Pennsylvania Water			
	mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max		mean	(+/-) s.d.	min	max
NAP	0.000	0.000	0.000	0.000		0.000	0.000	0.000	1.699		0.000	0.000	140.871	604.553
ACY	0.000	0.000	0.000	0.000		0.089	0.235	0.000	0.622		0.089	0.235	0.262	1.638
ACE	1.343	1.279	0.000	5.387		0.113	0.299	0.000	0.790		1.456	1.376	2.460	5.667
FLU	2.175	3.473	0.000	9.179		0.125	0.156	0.000	0.443		2.300	3.621	2.022	9.587
DBT	0.182	0.481	0.000	1.274		0.055	0.055	0.000	0.142		0.237	0.521	0.139	1.416
PHEN	4.483	9.537	0.000	25.541		7.356	6.859	0.000	16.581		11.838	13.345	2.477	36.815
ANT	1.248	1.698	0.000	4.951		0.196	0.345	0.000	0.957		1.444	1.745	0.362	5.080
2-MP	1.446	3.826	0.000	10.123		0.588	1.557	0.000	4.118		2.034	5.383	1.791	14.241
1-MP	2.198	3.634	0.000	9.975		0.393	0.446	0.000	1.276		2.591	4.037	0.772	11.251
FLT	7.410	11.705	0.000	33.394		1.292	1.340	0.000	3.417		8.703	12.536	1.992	36.233
PYR	12.418	13.741	0.000	29.909		1.644	3.023	0.000	7.693		14.062	13.384	4.138	32.823
BAA	0.000	0.000	0.000	6.891		1.978	2.804	0.187	8.197		1.978	2.804	3.413	9.425
CHR	0.000	0.000	0.000	10.776		0.297	0.345	0.000	0.900		0.297	0.345	7.508	10.822
BBF	1.672	1.187	0.000	3.192		0.528	0.614	0.000	1.356		2.199	1.604	0.374	4.548
BKF	0.675	0.628	0.000	1.499		0.166	0.113	0.000	0.343		0.840	0.721	0.129	1.792
BEP	0.575	0.396	0.000	1.074		0.265	0.323	0.000	0.964		0.839	0.452	0.118	1.408
BAP	1.207	1.449	0.000	3.851		0.310	0.392	0.000	0.950		1.517	1.586	0.299	4.020
PERY	1.368	1.262	0.000	2.794		0.227	0.226	0.000	0.488		1.595	1.428	0.640	3.282
IND	0.413	0.452	0.000	1.223		0.339	0.765	0.000	2.053		0.752	0.840	0.146	2.377
DBA	0.412	0.920	0.000	2.468		0.049	0.131	0.000	0.345		0.461	0.903	0.192	2.511
BGH	0.095	0.252	0.000	0.667		0.380	0.596	0.000	1.567		0.475	0.578	0.080	1.696
Σ PAH	39.319	40.516	3.290	122.894		16.389	12.755	1.202	33.300		55.708	50.281	4.492	156.194
	n = 7					n = 7					n = 7			

s.d. = standard deviation

Σ PAH = Sum of 21 PAHs included in this study

n = Number of Samples

(Tables A-22, A-24). Typical chromatograms for Youngstown dissolved water phase and water filters, respectively are shown in Figures 13 and 14. The Meander and Pennsylvania samples also contained almost the entire range of PAHs, but the majority of the compounds were found in the dissolved phase (Tables A-19, A-21, A-23, A-25). This difference in distribution of PAHs between dissolved and particulate for the different sites is most likely due to the greater amount of particulate matter in the Youngstown water samples.

In all water samples, pyrene was the most abundant PAH, followed by fluoranthene and phenanthrene. The same compounds also dominated in urban and rural freshwater in the United Kingdom,[65] in recreational (Esthwaite Waters) and industrialized (Castle Shaw Reservoir) waters in the United Kingdom,[124] and in Chesapeake Bay.[158] The concentrations found in rural United Kingdom and the Chesapeake Bay were much lower than this study, with the closest, pyrene and fluoranthene, being 10-20 fold more concentrated in this study. Excessive levels of fluoranthene and pyrene can be an indication of high temperature pyrolysis.[104]

On average, the second week of Youngstown water samples yielded higher total PAH concentrations than the first week primarily due to elevated levels of pyrene. Both Youngstown sample sets had higher PAH concentrations than the Meander and Pennsylvania water samples. The presence of 1- and 2-methylphenanthrene in all water samples (as for air), implies low temperature combustion[104] and the presence of dibenzothiophene at all sites implies combustion of coal and diesel fuel.[165] Perylene was less than 10% of the total PAHs in Youngstown and Pennsylvania water, indicating a combustion source.[77] However, it was near 10% in Meander water, indicating a possible source of natural production.[77] During the second week at the Youngstown site, pyrene concentrations soared 100-200 fold higher than the levels during the first week and anthracene rose, for the first time dominating its isomer (phenanthrene). This occurred on the third day of sampling, the effects decreasing by the next day and finally leveling

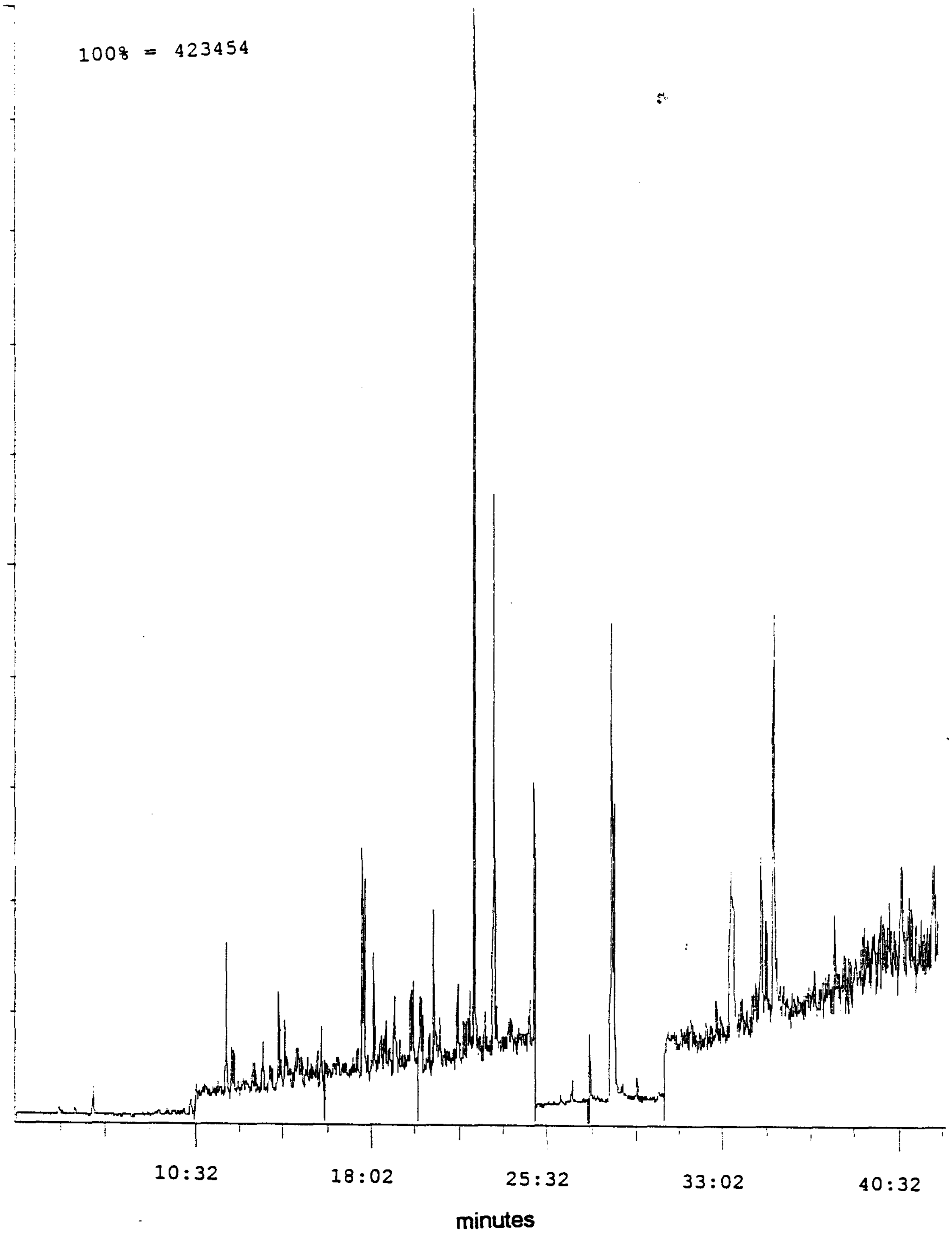


Figure 13. Chromatogram of YW11B water.

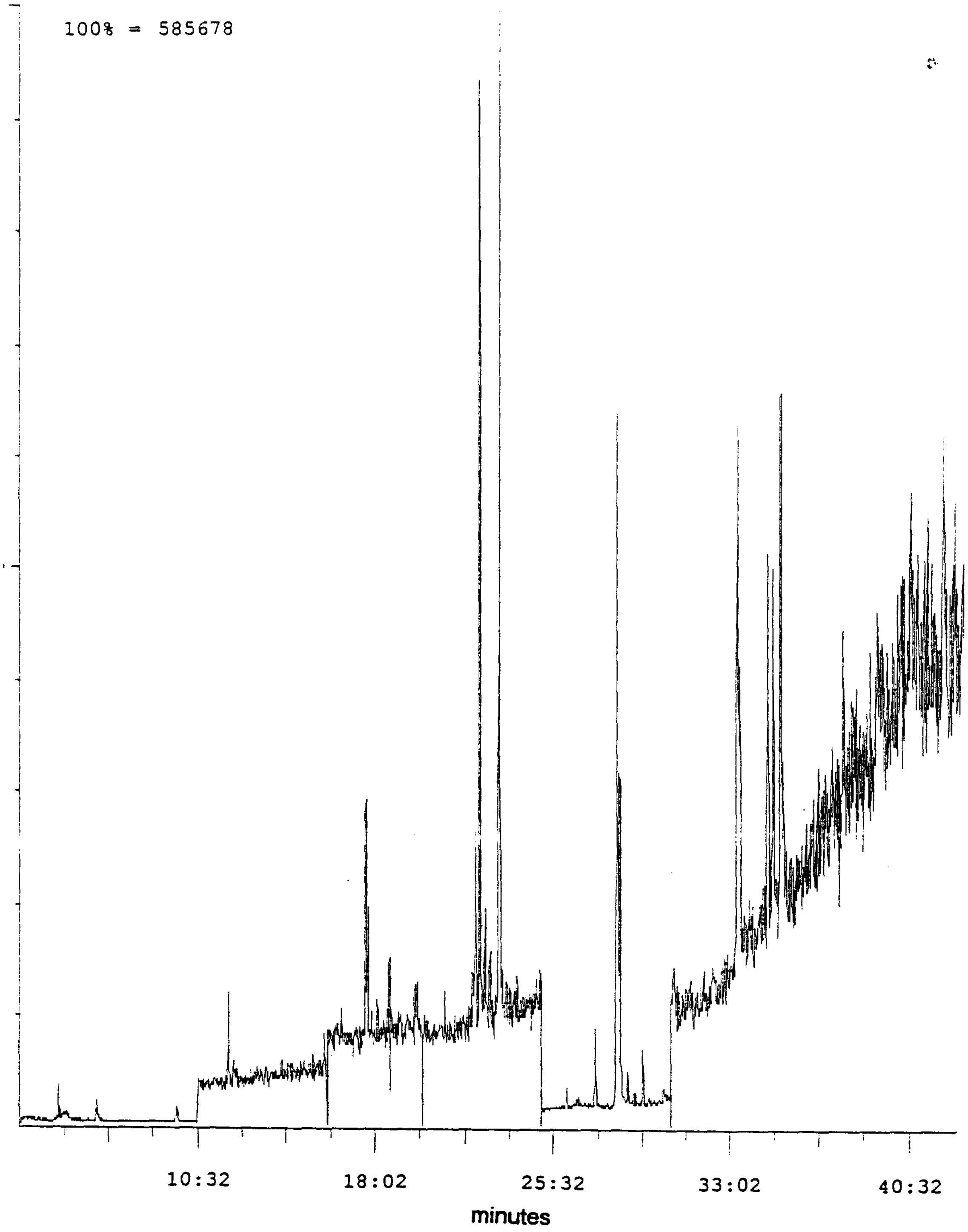


Figure 14. Chromatogram of YW15B water filter.

off by the end of the week. Such a sudden increase and deviation from the "norm" could be due to a fresh input to the system. Similar elevations in phenanthrene and anthracene were not observed in the Youngstown air samples from the third day of sampling (YA25 and YA26), but the previous day had the highest Youngstown rainfall for the two week sampling period. The sudden increase may have been caused by run-off from nearby roadways or increased atmospheric washout of particles following the rain.

CHAPTER SEVEN

DISCUSSION

SOURCE DETERMINATION

Isomeric Ratios

Table 31 compares ratios of specific isomers for this study and from previous studies (See Table 22). The actual value of the ratios in Table 31 is not significant, in itself, except that similarities (in the proportion of one isomer to another) from site to site become more apparent. This comparison is not meant to expose a specific source but to determine a parallel among sample sites. In addition to this, many implications can be made by comparing the less stable, kinetic isomer (numerator) with the more stable, thermodynamic isomer (denominator). Low temperature processes (formation of petroleum fuels) produce more of the stable isomers (yielding lower ratios) while combustion (e.g. low temperature-automobiles, residential burning of wood, oil or coal; high temperature-industrial processes) processes tend to produce more of the less stable, kinetic compounds. For example, the more stable parent compound can be compared to its alkylated derivatives. A derivative-to-parent ratio for unused petroleum would be low because the product was formed in the earth at low temperatures, using primarily thermodynamic processes. Once this fuel is combusted, the ratio would increase (the extent of which is dependent on temperature) as kinetic processes become dominant.[27,85,88] Comparison of isomer ratios can be used as a simple way to compare different sites.

The first and second week at the Youngstown site yielded similar ratios for ANT/PHEN, IND/BGH, and 2MP/PHEN, however, the BAP/BEP ratio was about 13 times higher the second week. All three sites yielded similar ratios for IND/BGH and 2MP/PHEN, with the presence of the alkylated compound indicating combustion sources.[27,85,88] Differences in the three sites were apparent, however, for the BAA/CHR

Table 31: Comparison of Isomeric Ratios from Several Studies (Kinetic/Thermodynamic)

	ANT/PHEN	FLT/PYR	BAA/CHR	BAP/BEP	IND/BGH	2-MP/PHEN
YAIR (1) †	0.03	2.43	1.50	1.10	0.79	0.11
YAIR (2) †	0.02	1.79	2.30	13.00	0.81	0.14
MAIR †	0.01	1.30	0.41	1.08	0.74	0.17
PAIR †	0.01	0.90	0.67	1.44	0.75	0.15
YWater (1)	0.15	0.99	2.85	1.28	1.05	0.16
YWater (2)	0.77	0.08	1.70	1.53	0.83	0.34
MWater	0.14	0.37	6.90	5.75	0.45	0.18
PWater	0.12	0.62	6.60	1.81	1.60	0.17
Chicago						
urban (154)	0.09	1.56	-	1.17	1.18	-
rural (154)	0.01	2.23	-	0.63	0.68	-
Denver (159)	0.08	0.59	-	-	0.86	-
Portland (160,161)	0.10	1.11	0.83	1.00	-	-
Baltimore (162)	1.60	0.74	-	1.16	0.58	-
Niagara R. (163)	-	1.21	0.72	0.55	-	-
L. Superior (147)	-	0.52	-	0.79	0.85	-
Ches. Bay (75)	0.02	0.90	0.29	0.54	0.71	-
Baltic Sea (165)	0.03	1.89	-	2.00	1.57	-
L. Superior (152)	0.06	-	-	0.50	1.22	-

† Samples from this study.
Other Ref in ( ).

and FLT/PYR ratios where Youngstown had higher BAA/CHR ratios than Meander and Pennsylvania, signifying a distinct local source- maybe indicating a particular industrial emission that at this time cannot be identified. Similarities between Youngstown and Meander for ANT/PHEN may indicate a source impacting urban/suburban sites such as a specific industrial process.

In comparing these isomer ratios with other studies (Table 31), Youngstown air showed similar results to urban Chicago (for ANT/PHEN, FLT/PYR and BAP/BEP) while Meander air was similar to Portland for all the ratios available, possibly showing the similarities of sources to urban areas. Pennsylvania air exhibited similarities to Chesapeake Bay for all ratios except BAP/BEP, possibly indicative of the more rural locations.

Characteristic Source Ratios

Table 32 lists atmospheric ratios indicative of certain sources (e.g. general combustion and anthropogenic sources, traffic emissions, coal and coke burning, industrial emissions, residential oil burning, and wood burning). Since exact ratios can be lost by using weekly averages, specific ratios were determined for each site on a sample by sample basis. In Tables 33-36, the characteristic ratios are listed under the appropriate sources for each site.

Youngstown Air (Week 1)

Youngstown air exhibited general "anthropogenic" sources with ANT/(ANT + PHEN) ratios from 0.026 to 0.088 and IND/(IND + BGH) ratios from 0.27 to 0.53, as well as combustion sources with PHEN/ANT from 10.4 to 127 and a BEP/BAP of 2.49. Characteristic traffic ratios (relative to BEP) were apparent for a number of samples, with high ratios of FLT/BEP, PYR/BEP, BAA/BEP, CHR/BEP, BKF/IND indicating diesel fuel combustion. Industrial ratios suggested coal and coke combustion, and municipal incineration. It has been estimated that ~ 90% of PAH emissions can be attributed to coal combustion processes (e.g. coal fire furnaces, coal

Table 32: Characteristic Ratios for Specific Sources

	TRAFFIC ‡				INDUSTRY ƒ		RESIDENTIAL †	
PAH/BEP	traffic	gasoline	diesel	coal/coke	refinery	municipal incineration	Oil burning	PAH/BAP • Wood burning
PHEN	5.7	0.59	7.4, 1966	-	-	-	-	15 - 80
ANT	2.2 - 3.7	0.21	3.3, 88	0.3 - 0.4	-	-	0.6	-
FLT	1.0 - 4.5	0.34	1.1, 159	-	-	-	-	6.1 - 21
PYR	0.6 - 1.7, 6.3	0.85, 10	0.81, 42 - 87	-	-	-	-	5.9 - 7.4, 20
BAA	0.6 - 2.5	0.1, 2.5	2.6 - 3.6	1.2 - 1.4	-	-	1	1.0 - 3.2
CHR	1.7 - 5.5	0.12, 2.7	1.4 - 5.4, 19	1.8 - 2.5	-	-	2.6	2.3 - 5.0
BBF	0.77 - 1.2	0.14	0.91 - 2.0	1.3 - 1.4	-	-	1.7	0.3, 1.6 - 6.6
BKF	0.79	0.11	0.76	-	-	-	-	0.2
BEP	1	1	1	1	1	-	-	0.64 - 3.0
BAP	0.2 - 2.0	1	1.9	0.6 - 1.0	3.85	-	0.9	1
PERY	0.2	-	-	0.08 - 0.30	-	-	0.25	-
IND	0.23 - 1.5	-	1.3	0.6	-	-	1	0.6 - 1.8
DBA	0.24	0.24	0.51	-	-	-	-	-
BGH	0.37 - 3.0	0.047	0.6 - 1.3	0.6 - 0.7	2.46	-	1	0.2 - 0.8
BGH/IND	-	3.5 - 3.8	1.1 - 1.2	-	-	-	-	0.8 - 0.9
BKF/IND	-	0.2 - 0.4	0.3 - 0.5	-	-	-	-	0.6
BAP/BGH	1.25 - 1.3	-	-	-	0.65 - 1.7	0.14 - 0.6	-	-
CHR/BEP	-	1.2 - 3.5	1.6	-	-	-	-	2.2 - 2.4
BEP/BAP	13	-	-	-	-	-	-	-
FLT/PYR	0.6	-	-	-	-	0.15	-	-
PHEN/(PHEN+ANT)	0.77	-	-	0.67	-	-	-	-
BAA/(BAA+CHR+TRI)	-	-	-	0.43	-	-	-	-
BEP/(BEP+BAP)	0.53	-	-	0.23	-	-	-	-
IND/(IND+BGH)	0.18	-	-	-	-	-	-	-
	ANTHROPOGENIC SOURCES £				COMBUSTION SOURCES ¥			
ANT/(ANT+PHEN), FLT/(FLT+PYR), IND/(IND+BGH) ~0.03 - 0.4 (low)					PHEN/ANT ~10; BEP/BAP ~3; FLT/PYR ~1			

• PAH/BAP for Wood Burning ratio. All others PAH/BEP.

‡ References: 17, 78, 87, 101, 110, 128; ƒ References: 42, 99, 101, 128; † References: 17, 101, 110; £ References: 85; ¥ References: 29

Table 33: Calculated Characteristic Ratios for Individual Youngstown Air (Week 1) Samples [#]

			RESIDENTIAL	
	TRAFFIC	INDUSTRY	OIL	WOOD
PAH/BEP	PAH/BEP	PAH/BEP	PAH/BEP	PAH/BAP *
PHEN	23, 688	-	-	24, 57, 439, 540
ANT	66	-	0.75	-
FLT	6.8, 234	2.3	-	16.9
PYR	2.5, 52	-	-	6.3
BAA	1.4, 10.5	1.4	-	3.4
CHR	1.0, 17.5	-	-	2.5
BBF	-	-	-	0.38
BKF	-	-	-	-
BEP	-	-	-	0.64, 2.5
BAP	1.6, 0.40	-	-	-
PERY	0.2	0.16	-	-
IND	-	-	-	2.3, 2.7
DBA	0.32	-	-	-
BGH	2.27	-	-	-
BGH/IND	1.01, 1.16, 1.17,	-	-	0.99, 0.89, 1.01
	1.22, 1.41, 1.42	-	-	-
BKF/IND	0.25, 0.37, 0.42	-	-	0.63, 0.52
BAP/BGH	-	0.18, 0.24,	-	-
		0.37, 0.38		
CHR/BEP	-	-	-	-
BEP/BAP	-	-	-	-
FLT/PYR	-	-	-	-
PHEN/(PHEN+ANT)	-	-	-	-
BAA/(BAA+CHR+TRI)	-	0.37	-	-
BEP/(BEP+BAP)	-	-	-	-
IND/(IND+BGH)	0.27	-	-	-

ANTHROPOGENIC	
ANT/(ANT+PHEN)	0.007, 0.009, 0.013, 0.018, 0.026, 0.032 0.043, 0.070, 0.088
IND/(IND+BGH)	0.27, 0.41, 0.42, 0.45, 0.46, 0.46, 0.50, 0.50, 0.53
COMBUSTION	
PHEN/ANT	10.4, 13.3, 22.3, 30.4, 36.8, 55.8, 76.2, 106, 127
BEP/BAP	2.49

* PAH/BAP for Wood Burning ratio. All others PAH/BEP.

Sample ratios only listed when similar to characteristic ratios from other studies (See Table 32).

Table 34: Calculated Characteristic Ratios for Individual Meander Air Samples [#]

			RESIDENTIAL			
	TRAFFIC	INDUSTRY	OIL	WOOD		
PAH/BEP	PAH/BEP	PAH/BEP	PAH/BEP	PAH/BAP *	ANTHROPOGENIC	
PHEN	133, 137, 262, 389	-	-	111, 144, 206, 516	ANT/(ANT+PHEN)	0.006, 0.006
ANT	1.8, 2.8, 1.5	-	-	-		0.007, 0.013
FLT	9.1, 8.0, 12.5, 14.4	-	-	7.2, 8.6, 10.1, 19.1		
PYR	5.2, 9.4, 9.9, 11.0	-	-	5.7, 7.4,8.0 , 14.5	FLT/(FLT+PYR)	0.49
BAA	0.11, 0.19, 0.17, 1.8	-	-	1.39		
CHR	1.95	-	-	-	IND/(IND+BGH)	0.38, 0.40
BBF	0.88, 1.75	-	1.75	0.374, 2.89		0.48, 0.49
BKF	-	-	-	0.281		
BEP	-	-	-	0.79, 0.81, 1.08, 1.33		
BAP	1.2, 0.75, 1.3, 0.92	0.75, 0.92	0.92	-	COMBUSTION	
PERY	0.21	0.18, 0.21	0.18, 0.21	-	PHEN/ANT	77.5, 138,
IND	1.1	-	1.1	1.1		176, 177
DBA	0.24, 0.25	-	-	-		
BGH	1.2, 2.2	2.19	-	-		
BGH/IND	1.06, 1.07, 1.5	-	-	1.06, 1.07		
BKF/IND	0.42. 0.49	-	-	-		
BAP/BGH	-	0.25, 0.36,	-	-		
		0.56, (0.65)				
CHR/BEP	-	1.96	-	1.96		
BEP/BAP	-	-	-	-		
FLT/PYR	-	-	-	-		
PHEN/(PHEN+ANT)	-	-	-	-		
BAA/(BAA+CHR+TRI)	-	0.412	-	-		
BEP/(BEP+BAP)	0.45, 0.44, 0.52, 0.57	-	-	-		
IND/(IND+BGH)	-	-	-	-		

* PAH/BAP for Wood Burning ratio. All others PAH/BEP.

\# Sample ratios only listed when similar to characteristic ratios from other studies (See Table 32).

Table 35: Calculated Characteristic Ratios for Individual Youngstown Air (Week 2) Samples #

			RESIDENTIAL			
	TRAFFIC	INDUSTRY	OIL	WOOD		
PAH/BEP	PAH/BEP	PAH/BEP	PAH/BEP	PAH/BAP *	ANTHROPOGENIC	
PHEN	2609	-	-	341, 1158, 1295	ANT/(ANT+PHEN)	0.0004, 0.005,
ANT	12.5	-	-	-		0.01, 0.012,
FLT	199	-	-	9.43, 34.3, 341		0.015, 0.02,
PYR	327	-	-	19.5, 126		0.07, 0.35
BAA	15.4	-	-	1.6, 2.0		
CHR	4.41	-	-	2.5, 4.5	FLT/(FLT+PYR)	0.38
BBF	-	-	-	2.2, 3.8		
BKF	-	-	-	-	IND/(IND+BGH)	0.38, 0.42, 0.44
BEP	-	-	-	-		
BAP	-	-	-	-		
PERY	-	-	-	-		
IND	-	-	-	1.59	COMBUSTION	
DBA	-	-	-	-	PHEN/ANT	13.4, 27.8, 48.5,
BGH	1.81	1.81	-	0.17		64.5, 79.3,101,
						209, 2702
BGH/IND	1.09, 1.05, 1.24, 1.36	-	-	0.87, 0.88, 0.95		
				1.05, 1.09		
BKF/IND	0.15, 0.19, 0.32, 0.45	-	-	0.63		
BAP/BGH	-	0.22, 0.66	-	-		
CHR/BEP	-	-	-	-		
BEP/BAP	-	-	-	-		
FLT/PYR	0.61	-	-	-		
PHEN/(PHEN+ANT)	-	-	-	-		
BAA/(BAA+CHR+TRI)	-	0.44	-	-		
BEP/(BEP+BAP)	-	-	-	-		
IND/(IND+BGH)	-	-	-	-		

* PAH/BAP for Wood Burning ratio. All others PAH/BEP.

Sample ratios only listed when similar to characteristic ratios from other studies (See Table 32).

Table 36: Calculated Characteristic Ratios for Individual Pennsylvania Air Samples #

			RESIDENTIAL			
	TRAFFIC	INDUSTRY	OIL	WOOD		
PAH/BEP	PAH/BEP	PAH/BEP	PAH/BEP	PAH/BAP *	ANTHROPOGENIC	
PHEN	8.50, 115, 122, 137	-	-	83, 119, 127, 138	ANT/(ANT+PHEN)	0.005, 0.006
ANT	5.73	-	0.71, 0.73	-		0.007, 0.008
FLT	8.2, 11.7, 12.4, 47.5	-	-	6.6, 8.5, 9.9, 10.9		
PYR	3.6, 17.2, 18.2, 30.3	-	-	4.2, 4.4, 12.4, 16.1	FLT/(FLT+PYR)	0.403, 0.406
BAA	1.41, 1.42	1.41, 1.42	-	1.33		
CHR	10.98	-	-	-	IND/(IND+BGH)	0.35, 0.41, 0.46
BBF	0.85	-	-	1.45, 2.20		
BKF	0.72, 0.97	-	-	0.32		
BEP	-	-	-	0.68, 0.93, 1.2		
BAP	0.84, 1.07, 1.46	0.84, 1.1	0.84, 1.07	-	COMBUSTION	
PERY	0.19, 0.27	0.19, 0.27	0.27	-	PHEN/ANT	130, 148,
IND	1.7, 1.8	-	-	-		168, 193
DBA	0.34, 0.35, 0.39	-	-	-		
BGH	1.9, 3.2, 3.4	1.9	-	0.8		
BGH/IND	1.2, 1.4	-	-	0.72		
BKF/IND	0.25, 0.43, 0.43	-	-	0.61		
BAP/BGH	1.3	0.70, 0.87,	-	-		
		1.4, (0.54)				
CHR/BEP	-	-	-	-		
BEP/BAP	-	-	-	-		
FLT/PYR	0.676, 0.684	-	-	-		
PHEN/(PHEN+ANT)	-	-	-	-		
BAA/(BAA+CHR+TRI)	-	0.48	-	-		
BEP/(BEP+BAP)	0.406, 0.482, 0.545	-	-	-		
IND/(IND+BGH)	-	-	-	-		

* PAH/BAP for Wood Burning ratio. All others PAH/BEP.

Sample ratios only listed when similar to characteristic ratios from other studies (See Table 32).

refuse burning, and coke production), and the highest PAH concentrations are often found in the Midwestern states such as Ohio and Pennsylvania.[31] Although steel production has been greatly reduced in the Youngstown area over the past 20 years, there are a number of large industrial sites which are still active. Residential oil burning was indicated in only one sample, while wood burning was apparent in a number of samples. This finding was surprising considering the urban location and high ambient temperature.

Meander Air

Meander air exhibited general anthropogenic source signatures with ANT/(ANT + PHEN) ratios from 0.006 to 0.013, a FLT/(FLT+PYR) ratio of 0.492 and IND/(IND + BGH) ratios from 0.38 to 0.49. Combustion sources were also apparent with PHEN/ANT from 77.5 to 176 as well as the characteristic traffic ratios (high ratios of PHEN/BEP, BBF/BEP, FLT/BEP, PYR/BEP, BKF/IND, BGH/IND) once again, indicating diesel combustion. Industrial ratios implied coal and coke combustion, municipal incineration and petrol refinery emissions. Wood burning was apparent in a number of samples and residential oil burning was more elevated than in Youngstown air.

Although Meander is less urban than Youngstown, traffic is still a significant source, although whether this is from local traffic or atmospheric transport of PAHs from nearby urban sites is not known. Atmospheric transport may be more important when considering the sources of industrial emissions to Meander air, as there are no known sources of industrial emissions in the area. Oil burning emissions may be indicative of the more suburban location as compared to Youngstown air.

Youngstown Air (Week 2)

Week 2 Youngstown air also exhibited general "anthropogenic" sources with ANT/(ANT + PHEN) ratios from 0.02 to 0.035, a FLT/(FLT+PYR) ratio of 0.38 and IND/(IND + BGH) ratios from 0.38 to 0.44. Combustion sources were also apparent with PHEN/ANT from 13.4 to 2702. Characteristic traffic ratios (relative to BEP) were apparent for a number of samples, with a few high ratios (BAA/BEP, BGH/IND) once again, indicating diesel combustion. Industrial ratios suggested coal and coke combustion, and petrol refinery emissions. Residential oil burning was not revealed in any sample although wood burning (relative to BAP) was again apparent in a number of samples.

Pennsylvania Air

Pennsylvania air exhibited general anthropogenic source signatures with ANT/(ANT + PHEN) ratios from 0.005 to 0.008, FLT/(FLT+PYR) ratio of 0.403 to 0.406 and IND/(IND + BGH) ratios from 0.35 to 0.46. Combustion sources were also apparent with PHEN/ANT from 130 to 193. Characteristic traffic ratios (high ratios of CHR/BEP, FLT/BEP, PYR/BEP, BKF/IND, BGH/IND) indicated diesel combustion. Industrial ratios implied coal and coke combustion, municipal incineration and petrol refinery emissions. Wood and oil burning was evident in a number of samples.

Although the Pennsylvania site is rural, traffic is still an important source, either from local traffic or atmospheric transport of PAHs from Youngstown. Diesel combustion is not surprising in a rural location because of the use of diesel-driven farm equipment. In particular, the caretakers at the Pennsylvania site attempted to mow the field every few days (weather permitting). Industrial emissions are likely the result of atmospheric transport from Youngstown as there are no local industries in this area. Wood and oil burning emissions may be indicative of the more rural location.

It is clear that the use of ratios is a useful qualitative tool, but many ratios are very similar and rely on small differences to distinguish sources. This lack of specificity along with no analysis of individual sources in this region makes it difficult to draw any definitive conclusions about specific sources of PAHs.

Principal Components Analysis

Unsupervised principal components analysis (PCA) was performed using the nonlinear iterative partial least squares (NIPALS) algorithm by a program (Einsight; Infometrix, Inc.) that allowed a detailed examination of both sample and variable projections (respectively, scores and loadings). Because different units were used for air and water samples and source determining data, each sample (data set) was "autoscaled" (resulting variables all have a mean of zero and a constant variance) before PCA was performed.[13,85]

In a previous study,[23] it was determined that if only the particle-associated PAH data were to be introduced to PCA, the resulting principal component (PC) pattern for these semivolatile compounds would merely reflect the volatility of the various PAH species. Thus the use of total PAH species was recommended. PCA was used for a multivariate comparison of the PAH composition in air (gaseous + particulate) from Youngstown, Meander, and Pennsylvania to known source compositions, Mahoning River sediment data and to each other. The known sources included diesel particulate,[35] diesel soot, gasoline soot, wood soot,[111] stratified and unstratified Lake Superior porewater,[166] a stove burning brown coal,[167] Baltimore Harbour roadway tunnel particulate,[162] Birmingham, UK total atmospheric samples (summer),[23] used oil, unused diesel fuel, unused gasoline (this study), and Mahoning River sediments[145] (Campbell and Lowellville sites) (See Table A-26). PCA was applied only to PAHs that were reported in the referenced data and naphthalene was omitted from all analyses due to high blank values and low recoveries in this study.

The loadings (variable projections) plot (See Figure A-24 for an example) shows quantitatively how each original variable contributes to each PC. The variables contributing most to differences between samples have the highest loadings.[115,116] The scores (sample projections) plot distributes samples with high data (variable) correlation adjacent to one another and is more reliable when it encounters greater variance between the variables. Samples exhibiting some degree of correlation are grouped together and are circled for clarity. In each case, the first and second principal components were utilized for analysis and, when combined, these accounted for 70 to 101% of the total variance.

Air versus Air

An intercomparison of Youngstown air (week 2) and Pennsylvania air showed a correlation for several sample days (Figure 15). No air-to-air correlation, however, was seen between any Youngstown air (week 1) and Meander air samples (Figure 16). This suggests some of the PAHs in Pennsylvania atmosphere may be attributable to atmospheric transport from Youngstown. Loadings revealed a strong dependence on compounds from benzo(e)pyrene to benzo(ghi)perylene for Meander air, benzo(e)pyrene and benzo(a)pyrene for Pennsylvania air and the low to moderate molecular weight PAHs (fluorene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene and benzo(ghi)perylene) for Youngstown air. Figure A-24 depicts a typical loading plot (variables) generated by PCA.

Air versus Water

Analysis of air and water samples for corresponding sites showed distinctly different patterns for each media, signifying no air-to-water correlation, except for a few Pennsylvania water samples which were slightly correlated with the Pennsylvania air samples. Figures 17 (and Figures A-25 and A-26) are PCA plots of corresponding air and water that exhibit no correlation while Figure 18 is a similar PCA plot showing some correlation. This eliminates air as the primary source of PAHs for water samples at these sites, particularly for Youngstown and Meander. This is not surprising since high levels of PAHs have been found in Mahoning River sediments[91,145] and resuspension of these sediments could provide a source of PAHs to the water column. The concentrations and compound by compound content of PAHs in sediments is expected to be very different from air due to different degradation and transport processes. The high concentrations of PAHs found in the water compared to the air (Table 21) also suggests the atmosphere is not a significant source, which may explain the lack of correlation between air and water. Analysis of the loadings revealed a high contribution of phenanthrene to Youngstown air,

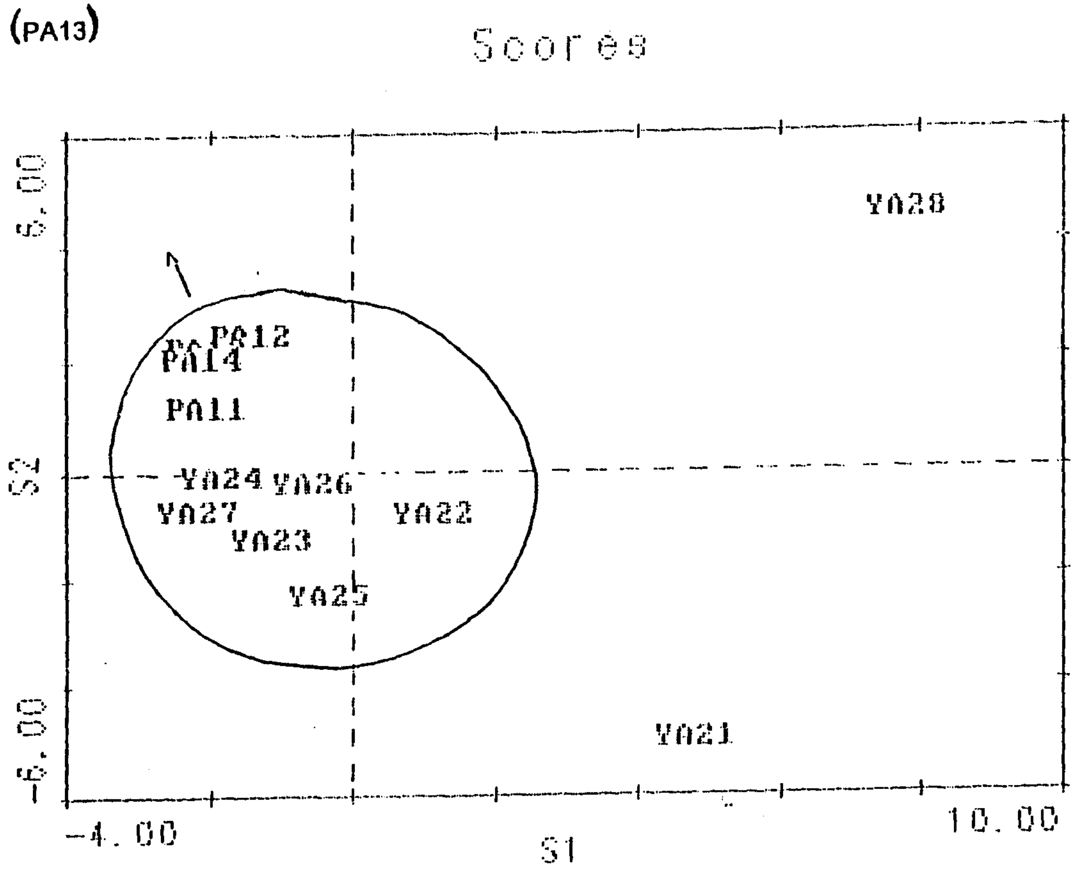


Figure 15. PCA plot of Youngstown Air (Week 2) vs. Pennsylvania Air Scores showing some correlation.

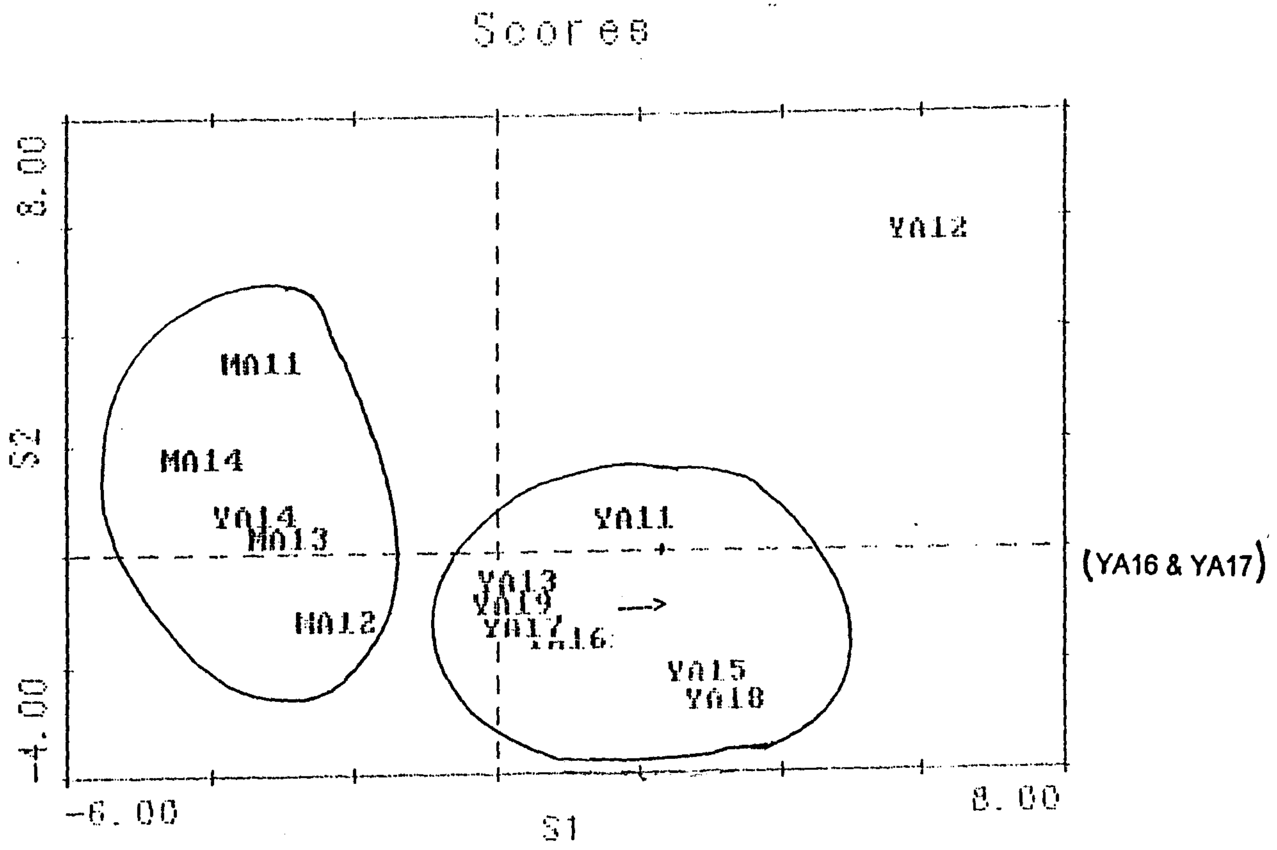


Figure 16. PCA plot of Youngstown Air (Week 1) vs. Meander Air Scores showing the lack of correlation for most samples.

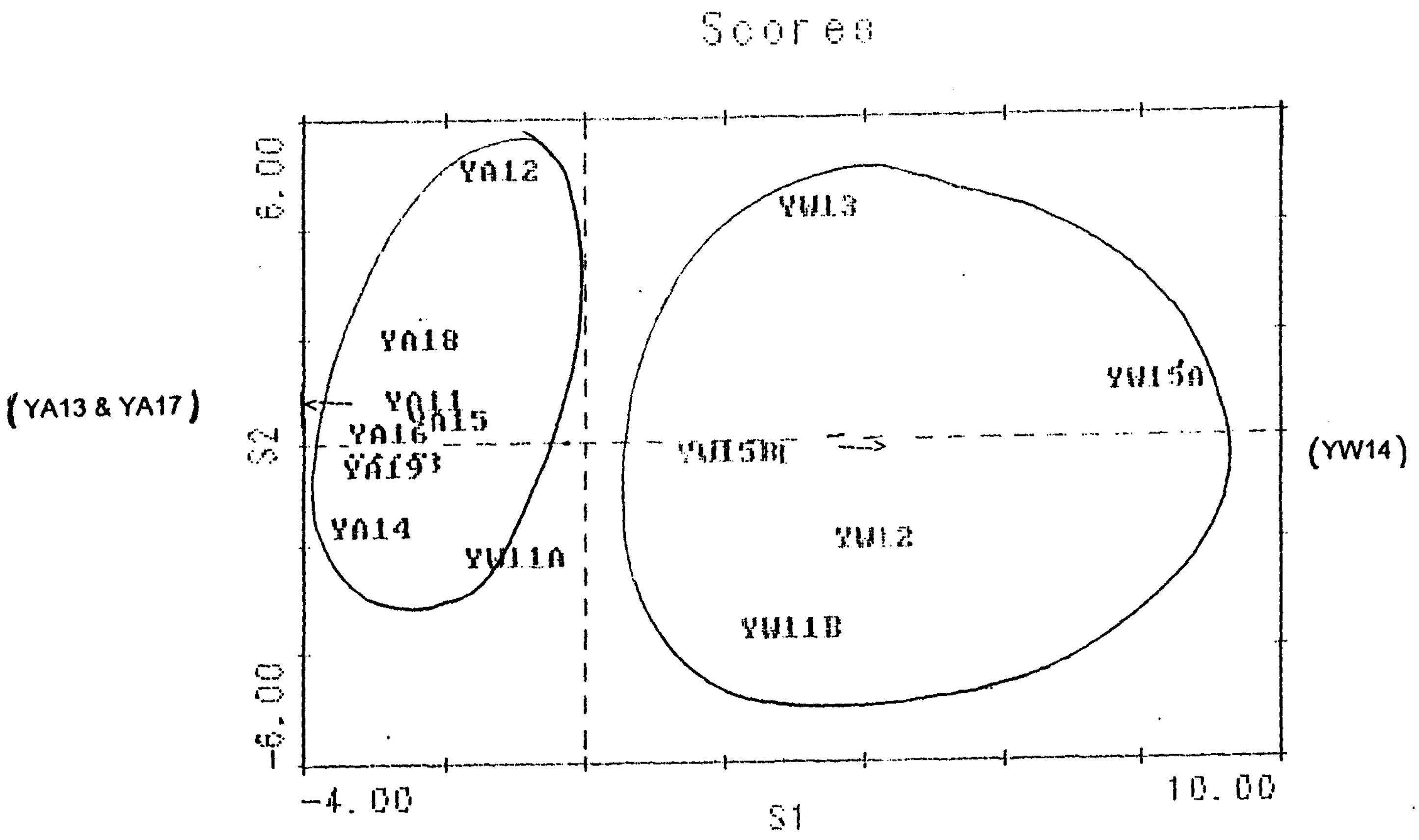


Figure 17. PCA plot of Youngstown Air vs. Youngstown Water (Both Week 1) Scores showing the lack of correlation for most samples.

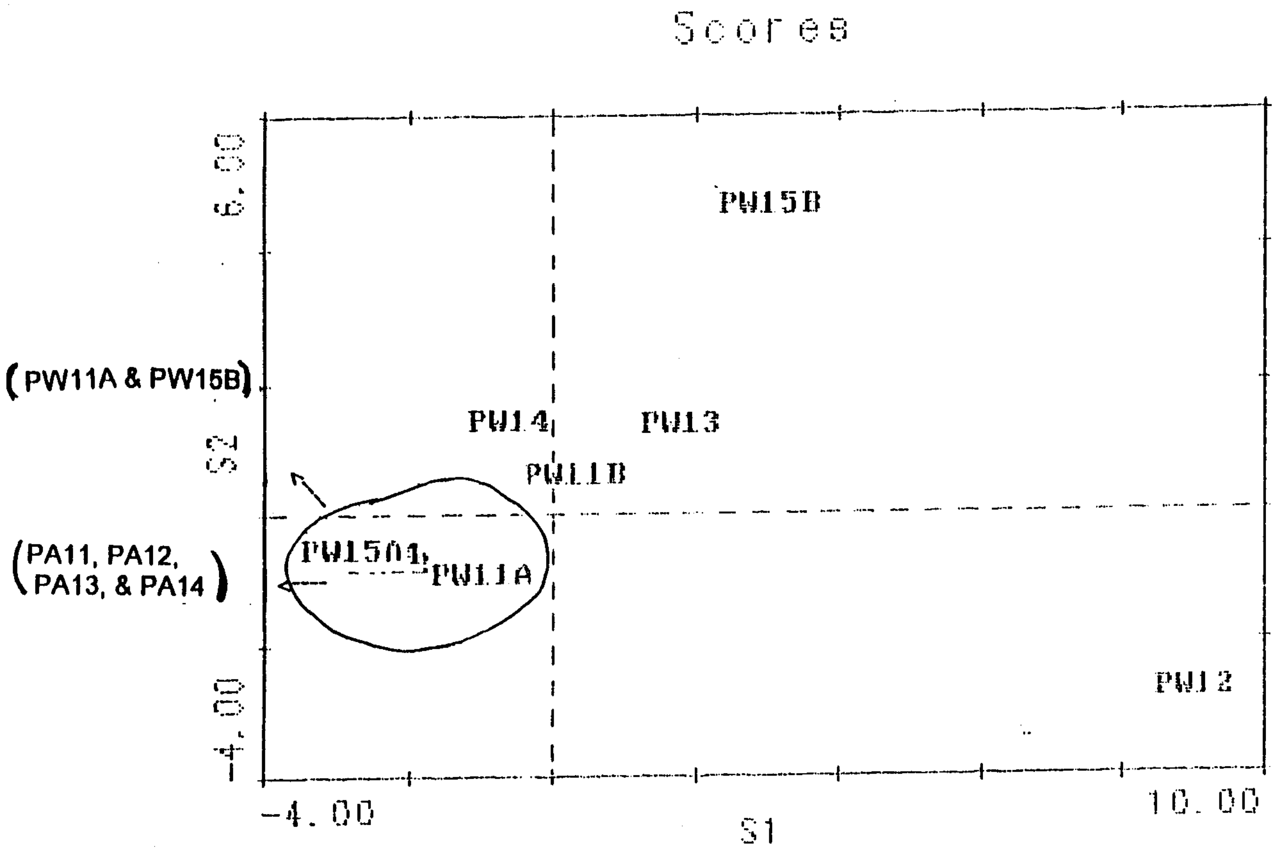


Figure 18. PCA plot of Pennsylvania Air vs. Pennsylvania Water Scores showing some correlation for several samples.

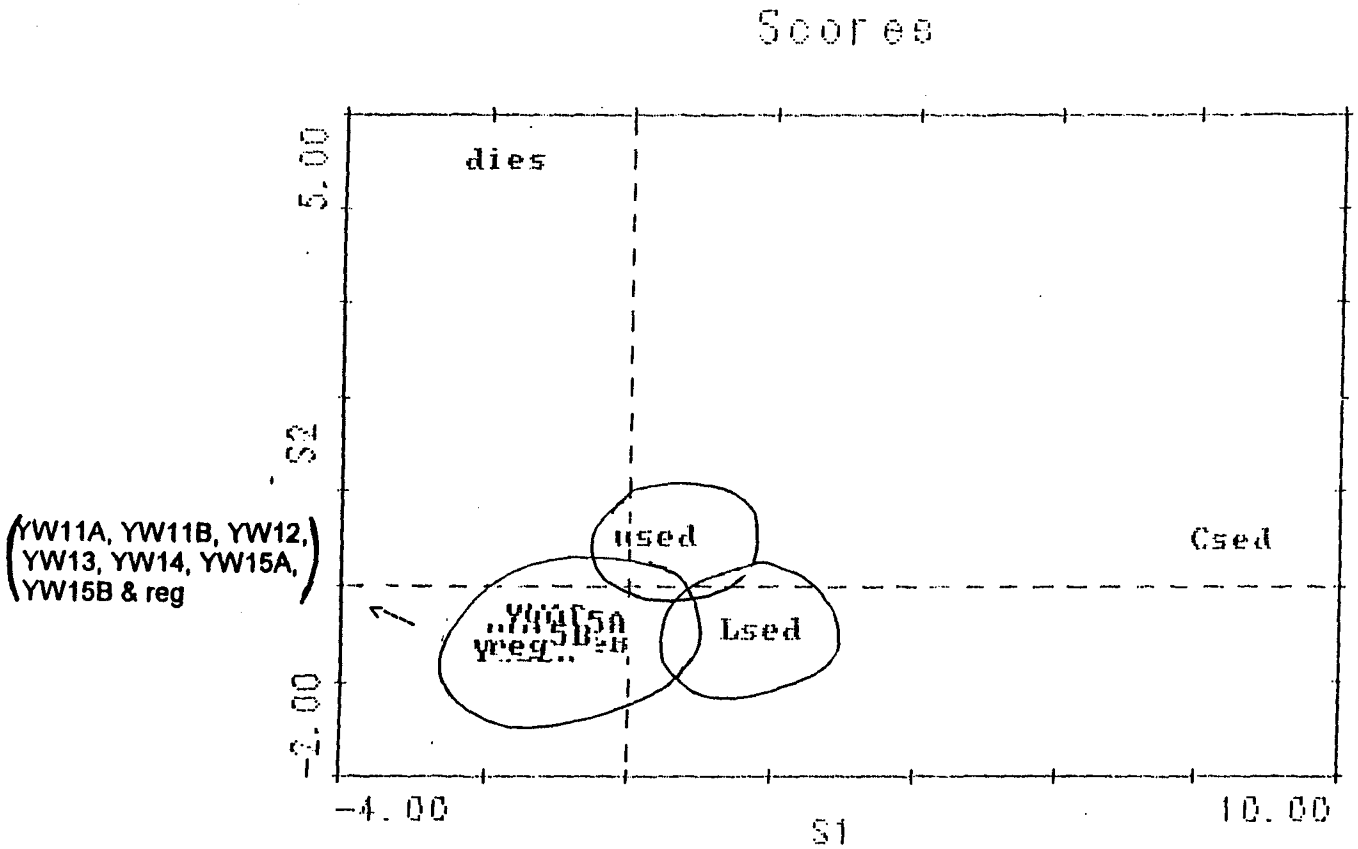
acenaphthylene to Meander air and a significant contribution of dibenzo(ah)anthracene to Pennsylvania air.

Water/Air versus Mahoning Sediments

When air and water samples from each site were analyzed (separately) against Mahoning River sediment (Campbell = Csed, Lowellville = Lsed),[145] as expected, no correlation was observed between air and sediment. However, a slight correlation can be inferred between Lowellville sediment and the water samples (Figure 19). Youngstown water (Lake Newport) is actually derived from a tributary of the Mahoning River, as is Meander Reservoir (Figure 1) and resuspension of pollutants from the sediment may be a more significant source than atmospheric deposition. Pennsylvania water (Brittain Lake) is a man-made lake, separate from the Mahoning River and its tributaries, yet there seems to be a similar correlation to the sediments as Youngstown and Meander water. This may reflect past atmospheric transport and deposition of PAHs from Youngstown which have since been incorporated into sediments. It may also reflect similarities in concentration and compound content between water and sediments due to deposition and resuspension of pollutants.

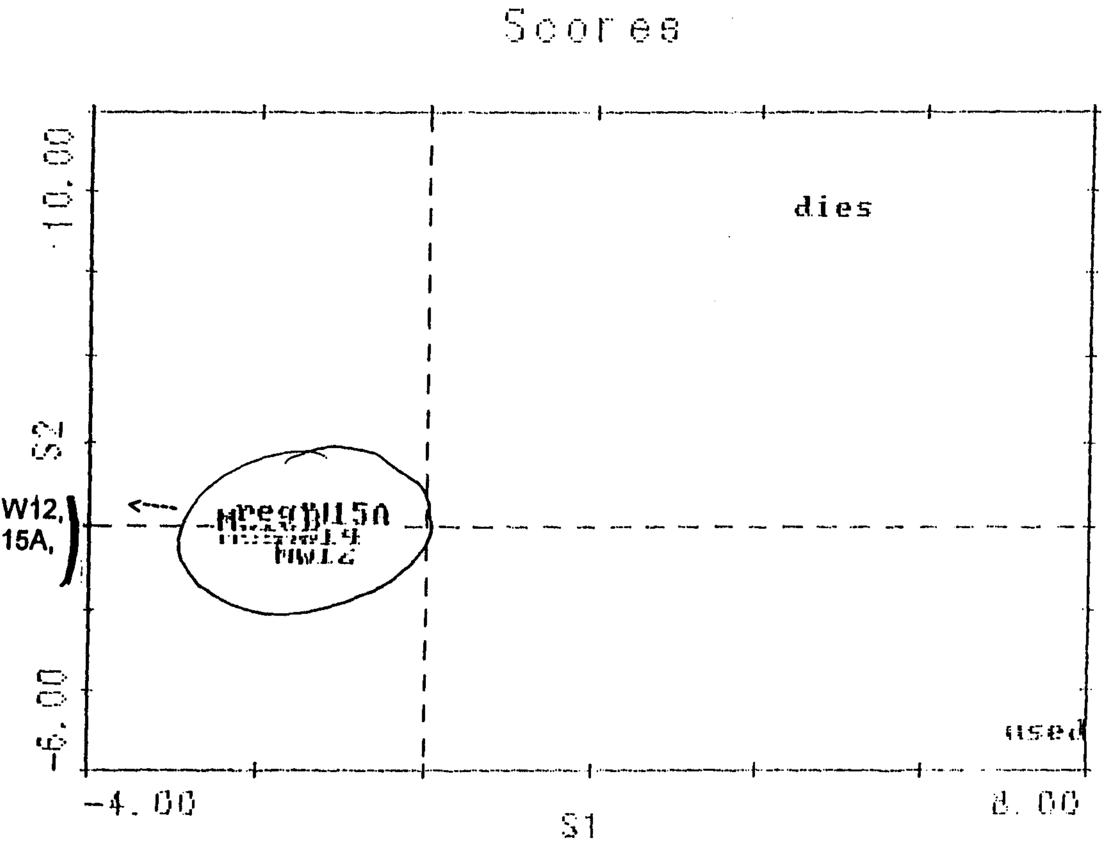
Air/Water versus Sources

When air and water samples from each site were analyzed separately against used motor oil (used), unused diesel fuel (dies) and unused gasoline (reg), every site/media was associated with the gasoline and had little correlation with diesel or used oil (Figure 20). Corresponding air and water samples were analyzed against the following: diesel particulate (DP1, DP2, DP3),[35] diesel soot (DS), gasoline soot (GS), wood soot (WS),[111] stratified and unstratified Lake Superior porewater (LSS and LSU),[166] a stove burning brown coal (BC),[167] Baltimore Harbour roadway tunnel particulate (BT),[162] and summer Birmingham, UK total atmospheric samples (BKS).[23] Both air and water samples from all three sites correlated well with Lake Superior porewater (LSS and LSU), a stove burning brown coal (BC), Baltimore Harbour roadway tunnel particulate (BT) and



(YW11A, YW11B, YW12, YW13, YW14, YW15A, YW15B & reg)

Figure 19. PCA plot of Youngstown Water (Week 1) vs. Mahoning Sediments Scores showing some correlation to "Lsed".
(Csed = Campbell)[145]; Lsed = (Lowellville)[145]



(MW11A, MW11B, MW12, MW13, MW14, MW15A, MW15B & reg)

Figure 20. PCA plot of Meander Water vs. Fuels Scores showing correlation to "reg".
(used = used oil), (dies = unused diesel fuel) and (reg = unused gasoline) from this study.

summer Birmingham, UK total atmospheric samples (BKS). The correlation to burning brown coal and Baltimore Tunnel particulate implies a significant pyrolytic source derived from coal use and traffic pollution. The correlation to the Birmingham air sample may simply be due to similarities between two sets of summer air sample data. Correlations between water samples and Lake Superior porewater is probably due to the sediments being a major source of PAHs to water (Figure 21). The relationship of air samples to porewater is surprising and cannot be explained. Perylene seems to be a significant loading in all these samples (Figure A-27).

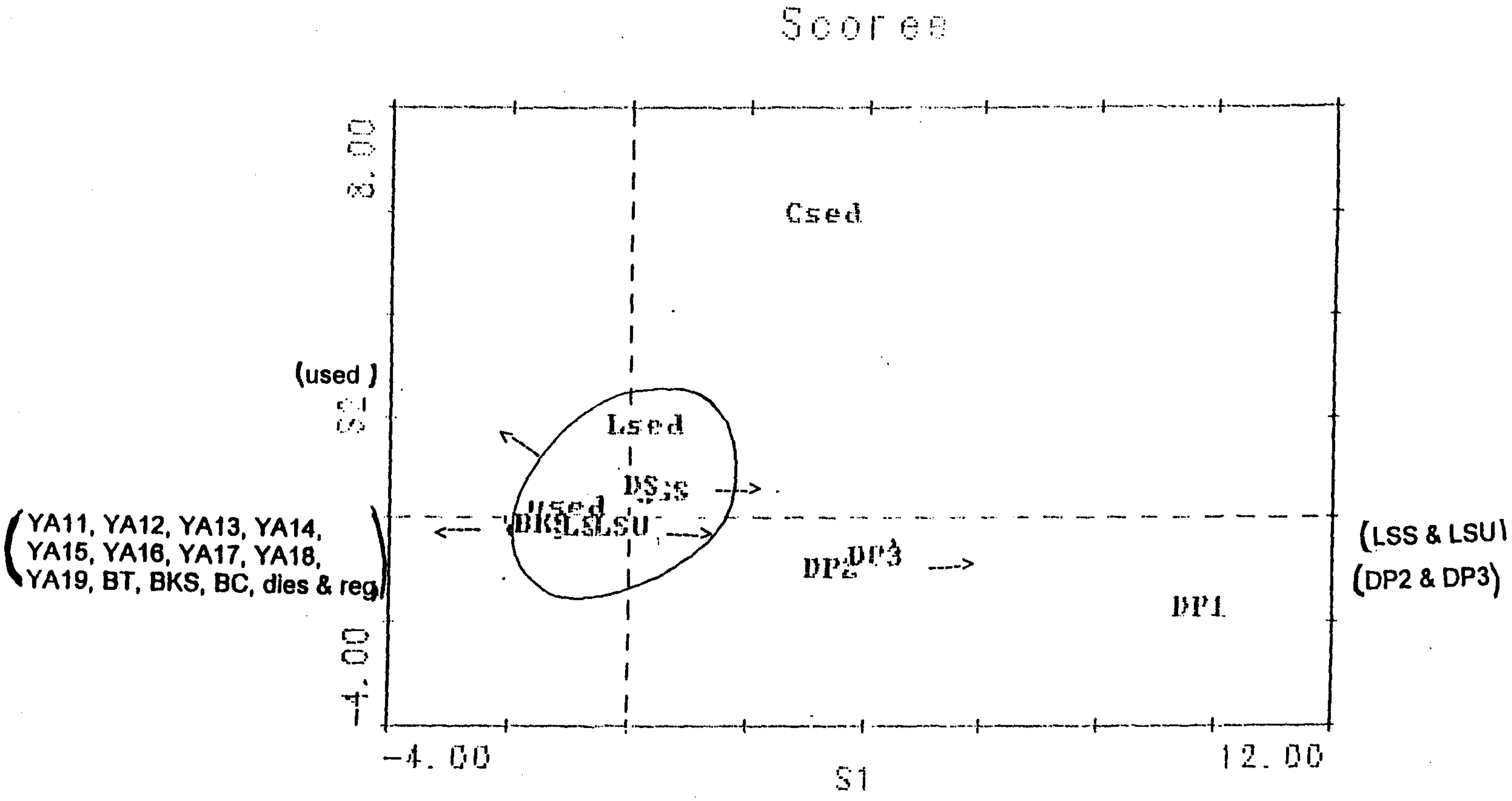


Figure 21. PCA plot of Youngstown Air (Week 1) vs. Sources Scores showing correlation to "BKS", "BC", "BT". "LSS" and "LSU".
(DP1, DP2, DP3 = diesel particulate)[35]; (DS = diesel soot)[111]; (GS = gasoline soot)[111]; (WS = wood soot)[111]; (LSS and LSU = stratified and unstratified Lake Superior porewater),[166] (BC = brown coal)[167]; (BT = Baltimore Harbour roadway tunnel particulate)[162]; and (BKS = Birmingham, UK total atmospheric samples from summer)[23].

CHAPTER EIGHT

CONCLUSIONS

Atmospheric and water concentrations at three sites associated along a west to east path (Meander Reservoir, Youngstown/Lake Newport, and New Wilmington, Pennsylvania/Lake Brittain) reveal Youngstown, as an urban center, with the highest levels of PAHs in air (average total PAHs 73.9 ng/m^{3}for week 1 and 68.5 ng/m^3 for week 2) and water (204.0 ng/L and 1010.5 ng/L). A conspicuous increase in several PAHs in the water during the second week in Youngstown are most likely due to a fresh source. The suburban site, Meander, was 4-5 times less concentrated (16.3 ng/m^3) in PAHs in air while the water was 3-10 times lower (82.8 ng/L). The rural site in Pennsylvania had air concentrations similar to Meander (11.1 ng/m^3), but the water was slightly less concentrated in PAHs (55.7 ng/L).

Characteristic ratios of PAHs for particular sources were compared to PAH ratios at each site. Analysis of these ratios reveals anthropogenic, or man-made, inputs to each site including definite indications of combustion. Emission ratios are indicative of traffic sources, industrial sources and wood burning at each site and residential oil burning at the Meander and Pennsylvania sites. Although compelling, characteristic ratios used alone are not conclusive and do not definitively distinguish sources. Principal components analysis (PCA) is a method of multivariate analysis which can help in recognition of similarities and differences between data sets. PCA corroborated the relation of each site to traffic and coal burning (industrial source), and found a connection between these samples and others taken under similar conditions.

In conjunction with the information derived from the characteristic ratios, PCA suggested a correlation between Youngstown and Pennsylvania air, but not between Youngstown and Meander air. This implies Youngstown as a source to Pennsylvania air through atmospheric transport. Meander and Youngstown have similar source inputs, one through direct urban inputs and the other through atmospheric transport from nearby urban locations. This can be seen by the higher concentration of PAHs in Youngstown versus Meander but similar characteristic ratios for the two sites.

PCA found no correlation between air and water for Youngstown and Meander, but exposed a correlation between water and Mahoning River sediments. This is likely due to both Lake Newport and Meander Reservoir being connected to the Mahoning River as tributaries. This finding suggests the sediments as a primary source of PAHs to the water column while contributions from air deposition are probably of lesser importance. Considering the extremely high levels of PAHs in the Mahoning sediments[91,145] and the increases in air pollution controls, this is not surprising. Pennsylvania water also showed some correlation to Pennsylvania air and Mahoning River sediments. Brittain Lake is a man-made lake separated from the Mahoning River with limited direct sources. As such, it is likely to have less of a sediment base than the other sites as well as lower sediment PAH concentrations. Because of this, air-water transfer of PAHs may be an important source of PAHs to the lake. If air-water transfer has been occurring in Brittain Lake for years, but with no direct inputs (industrial dumping)- it is likely that there would be similarities in air, water and sediments.

This work was a preliminary study of PAHs in the Mahoning Valley which proved PAHs do exist in detectable quantities in air and water. Future studies should include an examination into improvements in the extraction method for water and, because characteristic ratios alone can be misleading, direct measurement of specific local sources would be helpful in pinpointing the major contributors to each of the three sites. Some important sources to consider include smoke stack emissions from various local industries, air samples taken adjacent to major roadways, and repeated analyses of sediment samples immediately beneath water samples. Likewise, the scope of the study could be widened to include additional biomarker compounds, such as metals and trace elements to further define the sampling sites and local sources. In addition, a longer sampling period and samples taken throughout the year (different seasons) would allow recognition of seasonal patterns (both for concentration and source analysis) and analysis of gas-particle distributions. Because previous studies have reported high PAH levels in the sediment and biota of the Mahoning River,[91,144,145] it is essential to monitor the levels in air and water in this region and determine possible sources. These studies can increase public awareness and assist in designing regulations to control and minimize pollutant releases and effects.

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APPENDIX

Table A-1: Blank Values for Small PUF, (ng)

	Blank11	Blank12	Blank13	Blank14	Blank15	Blank16	Blank17	Blank18	Blank19	AVG	S.D.	3xSD
NAP-d8	0.000	0.076	0.000	0.021	2.065	0.000	0.000	0.000	0.000	0.240	0.685	2.054
NAP	109.350	86.288	12.851	35.295	208.957	10.228	6.547	54.800	86.860	67.908	64.873	194.619
ACY	1.138	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.126	0.379	1.138
ACE-d10	33.454	174.798	20.226	53.709	0.000	34.407	5.105	46.625	27.399	43.969	52.084	156.253
ACE	23.831	23.352	1.221	3.678	36.771	1.777	0.000	19.960	25.566	15.128	13.582	40.745
FLU	23.911	17.899	1.224	3.796	39.633	4.518	0.000	28.242	29.922	16.572	14.665	43.996
DBT	0.000	2.275	0.000	0.000	8.995	0.000	0.000	0.000	0.000	1.252	2.999	8.998
PHEN-d10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PHEN	40.615	30.374	1.657	5.122	115.990	5.022	1.138	69.160	47.296	35.153	38.697	116.092
ANT	2.505	1.999	0.360	0.718	6.780	0.532	0.000	4.626	4.157	2.409	2.336	7.007
2-MP	7.702	5.188	0.400	2.376	27.241	1.386	0.000	10.848	8.964	7.123	8.496	25.488
1-MP	7.003	3.091	0.741	0.000	15.751	0.985	0.404	8.285	0.000	4.029	5.373	16.118
FLT	0.740	0.685	0.525	0.577	{20.175}	0.335	0.230	1.368	1.276	0.717	0.410	1.230
PYR	14.623	9.855	7.009	10.335	{482.751}	5.467	4.780	4.950	9.420	8.305	3.404	10.211
BAA	0.000	0.000	0.129	0.348	1.556	0.000	0.000	0.000	0.000	0.226	0.512	1.537
CHR-d12	0.000	0.000	0.249	0.000	0.000	1.130	0.000	0.000	0.000	0.153	0.375	1.126
CHR	0.000	0.000	0.100	0.309	2.900	0.000	0.000	0.000	0.000	0.368	0.955	2.866
BBF	0.000	6.170	0.000	0.000	0.000	0.000	0.229	0.000	8.615	1.668	3.303	9.910
BKF	0.000	0.412	0.000	0.000	0.000	0.000	0.063	0.000	0.448	0.103	0.187	0.561
BEP	0.115	0.000	0.035	0.215	2.175	0.044	0.000	0.361	0.000	0.327	0.704	2.111
BAP	0.000	1.443	8.517	5.988	0.000	0.288	1.765	4.020	1.023	2.560	2.997	8.992
PERY	2.878	0.495	0.271	0.044	0.818	0.810	0.374	0.770	0.874	0.815	0.825	2.476
IND	0.000	0.000	0.668	0.000	0.000	0.000	1.812	0.000	1.078	0.395	0.660	1.980
DBA	0.000	0.000	1.977	0.000	0.000	0.000	5.562	5.893	1.780	1.690	2.425	7.274
BGH	0.000	0.000	0.000	0.000	0.000	0.000	0.115	0.000	0.000	0.013	0.038	0.115

{ } These values were omitted from mean blank following the Q-test (96 % confidence interval)- Ref 168.

Table A-2: Blank Values for Large PUF, (ng)

	Blank11	Blank13	Blank14	Blank15	Blank16	Blank17	Blank18	Blank19	Blank20	AVG	S.D.	3xSD
NAP-d8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.677	0.075	0.226	0.677
NAP	14.557	13.537	0.000	3.165	166.608	940.519	185.959	69.920	86.269	164.504	299.186	897.558
ACY	2.408	0.000	0.000	0.000	0.000	7.774	0.000	0.000	0.000	1.131	2.615	7.846
ACE-d10	0.000	10.270	3.064	4.847	162.477	0.000	145.563	114.014	36.746	52.998	67.820	203.459
ACE	2.918	4.931	0.000	1.099	66.353	81.443	45.350	25.206	22.128	27.714	30.287	90.862
FLU	1.123	6.024	3.715	3.611	79.087	87.938	17.896	29.276	19.608	27.586	33.100	99.300
DBT	0.442	0.000	0.000	0.000	7.853	6.856	7.026	3.143	2.997	3.146	3.317	9.950
PHEN-d10	0.938	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.104	0.313	0.938
PHEN	5.152	55.513	0.000	92.608	122.776	96.765	115.577	42.834	43.088	63.813	45.446	136.339
ANT	1.562	3.325	0.000	5.040	4.215	5.362	3.931	4.273	2.476	3.354	1.733	5.199
2-MP	4.347	19.484	33.064	12.020	14.234	29.265	23.741	7.957	14.887	17.667	9.584	28.753
1-MP	4.194	9.509	0.000	8.041	11.907	0.000	12.598	4.876	6.940	6.452	4.616	13.849
FLT	1.190	19.229	0.464	2.285	1.550	13.154	14.603	6.059	11.632	7.796	6.985	20.954
PYR	6.205	25.405	3.092	9.321	3.061	12.521	18.102	{112.180}	40.804	14.814	13.003	39.009
BAA	1.364	1.925	0.000	0.000	0.000	0.471	0.000	0.476	3.528	0.863	1.213	3.638
CHR-d12	0.000	0.000	0.000	0.000	0.000	3.155	0.000	0.700	15.068	2.103	4.971	14.914
CHR	0.777	1.616	0.000	0.000	0.000	1.451	0.000	0.063	1.152	0.562	0.690	2.070
BBF	3.279	11.552	0.000	0.000	0.000	1.694	0.000	1.065	8.448	2.893	4.246	12.739
BKF	0.711	0.181	0.000	0.000	0.000	1.555	0.000	0.039	0.226	0.301	0.523	1.570
BEP	0.733	0.208	0.316	0.137	0.409	0.201	0.163	0.124	0.054	0.261	0.206	0.619
BAP	1.221	0.201	1.809	2.203	0.708	1.788	0.462	1.963	0.984	1.260	0.716	2.149
PERY	3.635	2.011	2.091	2.797	1.805	3.546	3.026	0.561	1.723	2.355	0.988	2.964
IND	5.356	0.000	0.000	0.000	0.000	6.156	0.000	0.000	0.000	1.279	2.546	7.638
DBA	2.327	0.000	0.000	0.000	0.000	10.510	0.000	0.000	10.667	2.612	4.586	13.759
BGH	9.049	0.000	0.000	0.000	0.000	1.012	0.000	0.000	0.000	1.118	2.993	8.979

{ } These values were omitted from mean blank following the Q-test (96 % confidence interval)- Ref 168

Table A-3: Blank Values for Small Air Filters, (ng)

	Blank11	Blank12	Blank13	Blank14	Blank15	AVG	S.D.	3xSD
NAP-d8	0.000	0.302	0.037	0.000	0.000	0.068	0.132	0.396
NAP	2.268	2.735	10.831	5.575	6.817	5.645	3.469	10.408
ACY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ACE-d10	0.000	0.000	6.279	2.473	3.268	2.404	2.614	7.841
ACE	0.433	0.320	5.380	1.631	1.453	1.843	2.062	6.187
FLU	0.560	0.360	0.000	0.000	2.013	0.587	0.833	2.499
DBT	0.000	0.137	0.000	0.509	0.000	0.129	0.220	0.661
PHEN-d10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PHEN	1.091	1.207	5.280	3.156	3.504	2.848	1.748	5.244
ANT	0.187	0.792	{22.252}	1.673	1.193	0.961	0.629	1.888
2-MP	0.232	1.217	4.512	1.614	2.620	2.039	1.626	4.878
1-MP	0.000	0.806	6.051	2.165	0.000	1.804	2.533	7.600
FLT	0.099	1.999	{22.254}	3.215	0.803	1.529	1.371	4.112
PYR	0.691	62.738	{335.311}	26.173	5.226	23.707	28.289	84.867
BAA	0.165	0.386	0.950	0.000	2.446	0.789	0.993	2.980
CHR-d12	0.000	0.000	0.000	0.000	4.910	0.982	2.196	6.587
CHR	0.035	0.303	0.649	0.000	1.686	0.535	0.694	2.083
BBF	0.287	0.097	{54.486}	0.000	0.000	0.096	0.135	0.406
BKF	0.000	0.019	0.404	0.000	0.000	0.085	0.179	0.536
BEP	17.277	0.000	0.823	0.330	0.196	3.725	7.582	22.745
BAP	0.218	8.437	1.356	0.971	0.940	2.384	3.408	10.225
PERY	0.000	0.317	1.527	0.465	3.921	1.246	1.602	4.805
IND	0.000	0.000	0.000	0.844	0.000	0.169	0.377	1.132
DBA	0.000	0.315	0.000	0.000	0.000	0.063	0.141	0.423
BGH	0.000	0.804	0.000	0.000	0.000	0.161	0.360	1.079

{ } These values were omitted from mean blank following the Q-test (96 % confidence interval)- Ref 168.

Table A-4: Blank Values for Large Air Filters, (ng)

	Blank11	Blank12	Blank13	AVG	S.D.	3xSD
NAP-d8	24.666	17.280	29.031	23.659	5.940	17.820
NAP	8.768	12.307	13.738	11.604	2.558	7.675
ACY	0.000	0.492	1.250	0.581	0.630	1.889
ACE-d10	36.568	14.846	51.812	34.409	18.577	55.732
ACE	0.000	2.518	2.775	1.764	1.533	4.600
FLU	0.000	0.000	7.809	2.603	4.509	13.526
DBT	0.000	0.000	0.904	0.301	0.522	1.566
PHEN-d10	67.121	39.548	60.666	55.778	14.422	43.265
PHEN	21.773	8.111	4.842	11.575	8.981	26.944
ANT	0.000	14.156	0.000	4.719	8.173	24.519
2-MP	5.521	6.872	4.021	5.471	1.426	4.278
1-MP	11.915	2.002	2.123	5.347	5.689	17.066
FLT	0.000	18.051	0.000	6.017	10.422	31.265
PYR	51.266	(211.848)	2.884	27.075	34.211	102.634
BAA	0.000	36.552	25.417	20.656	18.735	56.206
CHR-d12	188.100	109.588	155.715	151.134	39.456	118.368
CHR	0.000	2.359	25.690	9.350	14.200	42.601
BBF	0.628	0.000	0.000	0.209	0.363	1.088
BKF	4.356	0.000	0.277	1.544	2.439	7.317
BEP	0.000	0.000	0.000	0.000	0.000	0.000
BAP	0.446	0.000	2.064	0.837	1.086	3.258
PERY	0.701	1.462	3.227	1.797	1.296	3.887
IND	0.000	0.000	0.000	0.000	0.000	0.000
DBA	0.000	0.000	0.000	0.000	0.000	0.000
BGH	0.000	0.000	0.000	0.000	0.000	0.000

( ) These values were omitted from mean blank following the Q-test (96 % confidence interval)- Ref 168.

Table A-5: Blank Values for Distilled Water (Dissolved Fraction Blanks), (ng)

	Blank11	Blank12	Blank13	Blank14	Blank15	AVG	S.D.	3xSD
NAP-d8	40.075	28.417	55.770	108.650	55.317	57.646	30.714	92.142
NAP	49.461	38.092	58.521	100.986	102.378	69.888	29.917	89.751
ACY	2.885	0.000	0.000	3.055	0.000	1.188	1.628	4.884
ACE-d10	34.756	16.784	53.465	109.268	55.007	53.856	34.681	104.043
ACE	5.976	6.647	4.744	10.909	7.539	7.163	2.329	6.988
FLU	5.273	6.872	10.512	13.406	14.616	10.136	4.038	12.113
DBT	1.368	0.000	1.365	2.358	2.155	1.449	0.927	2.781
PHEN-d10	49.046	46.623	80.362	143.129	68.185	77.469	39.259	117.778
PHEN	8.192	10.074	18.535	33.855	34.148	20.961	12.526	37.578
ANT	0.642	0.689	0.980	2.501	2.338	1.430	0.914	2.743
2-MP	3.729	2.495	2.746	8.729	17.989	7.138	6.572	19.715
1-MP	4.351	4.942	5.143	7.508	6.408	5.670	1.272	3.816
FLT	2.264	2.492	3.282	2.582	4.828	3.090	1.043	3.130
PYR	7.386	44.348	17.347	23.250	22.912	23.049	13.524	40.571
BAA	26.510	35.691	16.872	0.000	20.959	20.006	13.222	39.666
CHR-d12	128.283	117.428	187.154	281.215	143.179	171.452	66.851	200.552
CHR	2.372	1.065	33.674	44.235	22.949	20.859	19.030	57.091
BBF	0.269	0.000	0.616	0.566	0.587	0.408	0.267	0.802
BKF	0.216	0.000	0.451	0.312	0.218	0.239	0.165	0.494
BEP	0.154	0.206	0.264	0.363	0.000	0.197	0.135	0.405
BAP	0.656	1.150	1.044	1.016	0.459	0.865	0.294	0.881
PERY	0.782	1.640	0.471	2.348	0.201	1.088	0.888	2.664
IND	0.568	0.000	0.147	0.369	0.246	0.266	0.216	0.649
DBA	0.719	0.000	0.000	0.291	0.000	0.202	0.315	0.946
BGH	1.260	0.000	0.000	0.417	0.451	0.426	0.515	1.544

Table A-6: Blank Values for Water Filters, (ng)

	Blank11	Blank12	Blank13	Blank14	Blank15	AVG	S.D.	3xSD
NAP-d8	0.000	1.083	0.000	0.000	0.000	0.217	0.484	1.453
NAP	8.641	13.035	13.543	7.612	7.772	10.121	2.924	8.773
ACY	0.400	1.096	0.000	0.000	0.519	0.403	0.452	1.357
ACE-d10	0.000	2.247	4.018	0.000	0.000	1.253	1.826	5.479
ACE	1.203	5.024	2.397	1.701	1.252	2.315	1.588	4.764
FLU	1.674	3.632	3.341	2.406	1.704	2.551	0.908	2.725
DBT	0.859	0.935	1.204	1.052	0.691	0.948	0.194	0.582
PHEN-d10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PHEN	17.449	14.385	25.945	11.482	11.687	16.190	5.968	17.903
ANT	0.314	1.626	1.583	1.658	1.406	1.317	0.569	1.708
2-MP	4.553	6.323	3.992	5.995	0.000	4.173	2.527	7.580
1-MP	1.588	3.324	0.990	2.777	2.305	2.197	0.928	2.784
FLT	6.803	9.076	12.008	7.828	6.263	8.396	2.287	6.861
PYR	14.005	21.138	32.786	46.366	15.646	25.988	13.560	40.681
BAA	0.482	0.623	0.796	0.841	1.816	0.912	0.525	1.576
CHR-d12	0.959	1.769	0.490	2.953	1.258	1.486	0.943	2.828
CHR	0.433	0.891	0.963	0.519	1.047	0.771	0.276	0.829
BBF	0.000	0.740	0.000	0.000	0.000	0.148	0.331	0.993
BKF	0.000	0.223	0.000	0.000	0.000	0.045	0.100	0.299
BEP	0.151	0.134	0.000	0.000	0.459	0.149	0.188	0.563
BAP	1.218	2.220	0.573	1.196	0.663	1.174	0.656	1.967
PERY	1.289	0.633	0.000	2.169	1.817	1.182	0.879	2.636
IND	0.000	0.759	0.000	1.687	1.349	0.759	0.768	2.305
DBA	0.000	0.495	0.000	0.909	0.000	0.281	0.411	1.234
BGH	0.000	1.473	0.000	0.700	0.000	0.435	0.655	1.965

Table A-7: % Spike Recoveries for PUF

	Small PUF							Large PUF				
	Spike11	**Spike12**	**Spike13**	**Spike14**	**Spike15**	**AVG**		**Spike11**	**Spike12**	**Spike13**	**Spike14**	**Spike15**
NAP-d8	29.544	0.514	9.363	28.844	32.766	20.206		30.409	8.716	39.146	36.596	21.896
NAP	106.781	3.443	50.981	107.056	116.408	76.934		137.428	134.295	188.056	587.820	96.396
ACY	57.238	0.000	15.359	52.565	58.701	36.773		67.961	19.200	78.208	68.182	42.335
ACE-d10	49.434	2.399	16.934	59.210	61.955	37.986		54.459	18.600	70.767	61.888	43.151
ACE	80.860	0.400	23.583	70.989	78.990	50.964		117.982	71.062	120.206	293.656	54.741
FLU	69.189	1.348	36.063	92.035	117.244	63.176		102.780	125.213	154.699	316.509	62.802
DBT	2.098	0.000	0.797	2.017	3.755	1.733		4.592	6.068	5.032	29.558	2.412
PHEN-d10	78.869	6.832	20.433	89.382	91.239	57.351		90.578	21.867	116.932	76.323	70.599
PHEN	92.823	11.019	30.424	121.242	153.400	81.782		150.384	115.516	186.586	465.570	87.782
ANT	85.629	7.898	20.430	84.600	108.006	61.313		92.350	23.265	119.197	111.516	60.959
2-MP	11.508	0.690	1.848	8.467	12.769	7.056		14.296	9.269	13.258	49.921	7.518
1-MP	6.944	0.695	1.067	6.459	8.097	4.652		0.000	4.635	12.487	3.688	3.950
FLT	47.139	7.632	13.535	43.164	54.343	33.163		69.329	9.938	51.144	36.316	33.709
PYR	106.024	27.996	50.235	109.964	164.612	91.766		26.465	31.261	122.049	93.350	82.953
BAA	119.590	22.711	26.172	114.768	113.082	79.265		138.752	24.655	136.292	100.555	84.435
CHR-d12	168.351	71.390	94.532	164.060	163.698	132.406		216.526	85.867	194.753	150.295	137.010
CHR	102.909	14.438	18.926	127.417	104.616	73.661		118.520	17.541	116.368	106.367	98.062
BBF	93.385	16.863	15.860	33.583	85.298	48.998		3.810	17.624	90.119	45.937	27.861
BKF	89.772	15.243	17.650	126.962	84.181	66.762		97.729	17.612	111.195	69.980	85.525
BEP	0.246	0.514	0.475	0.699	0.000	0.387		0.612	0.000	0.000	0.130	0.269
BAP	91.127	15.142	19.054	83.648	79.777	57.750		136.974	20.048	105.694	80.558	58.101
PERY	7.061	0.319	0.169	1.995	0.115	1.932		0.000	0.000	1.212	1.199	1.074
IND	72.885	20.744	26.599	102.966	108.079	66.255		100.007	25.332	142.925	104.735	80.615
DBA	118.310	21.254	26.997	102.421	112.530	76.302		125.427	22.841	145.010	98.436	91.479
BGH	101.118	19.393	23.687	88.209	100.636	66.609		109.087	22.344	125.151	96.677	60.193

Table A-8: % Spike Recoveries for Air Filters

	Small Air Filter						Large Air Filter					
	Spike11	**Spike12**	**Spike14**	**Spike15**	**AVG**		**Spike11**	**Spike12**	**Spike13**	**Spike14**	**Spike15**	**AVG**
NAP-d8	21.296	15.055	0.000	48.498	21.212		25.388	9.724	0.544	0.838	4.413	8.181
NAP	28.479	26.352	3.146	93.401	37.845		38.119	15.454	7.548	7.367	46.583	23.014
ACY	32.745	22.250	0.305	85.408	35.177		38.442	32.166	7.984	1.187	18.203	19.596
ACE-d10	26.448	20.858	0.000	97.315	36.155		44.526	42.543	0.000	0.000	11.733	19.760
ACE	33.523	26.042	2.913	86.936	37.354		37.645	34.346	6.231	1.994	21.310	20.305
FLU	40.602	26.982	9.471	111.067	47.031		54.114	45.560	13.094	5.553	29.381	29.540
DBT	0.971	1.017	0.496	3.334	1.455		1.063	0.694	0.955	0.798	0.000	0.702
PHEN-d10	54.137	46.202	14.506	138.215	63.265		62.458	97.598	33.387	20.483	13.471	45.479
PHEN	60.256	49.940	19.555	177.908	76.915		67.341	71.152	40.892	22.619	19.649	44.331
ANT	8.920	39.094	16.546	120.495	46.264		70.610	61.847	37.907	26.553	15.604	42.504
2-MP	0.000	7.218	2.201	19.004	7.106		4.731	0.000	0.000	7.548	0.000	2.456
1-MP	0.000	6.727	2.910	15.110	6.187		4.367	4.630	0.000	6.424	0.000	3.084
FLT	34.579	38.962	17.657	85.482	44.170		38.475	45.174	26.856	34.988	8.702	30.839
PYR	72.554	82.035	47.748	166.250	92.147		89.255	110.733	70.285	88.571	33.247	78.418
BAA	106.580	138.895	88.719	125.828	115.006		133.235	117.468	92.521	93.693	21.196	91.623
CHR-d12	159.617	234.381	134.637	210.620	184.814		179.434	167.570	135.122	153.757	75.598	142.296
CHR	88.929	112.362	69.527	125.716	99.134		111.156	116.726	88.848	129.304	18.098	92.826
BBF	85.309	127.437	192.628	8.253	103.407		111.262	73.660	71.561	52.870	14.946	64.860
BKF	83.485	102.460	98.047	79.417	90.852		104.511	73.649	68.271	84.978	20.214	70.325
BEP	0.803	1.542	2.087	0.406	1.210		2.447	4.196	0.000	0.000	3.611	2.051
BAP	99.201	130.303	67.516	71.709	92.182		94.777	76.410	64.513	73.607	18.940	65.649
PERY	9.537	3.984	1.598	2.043	4.291		13.204	0.000	2.554	1.592	0.087	3.487
IND	78.213	102.149	119.030	119.100	104.623		122.754	108.247	104.249	107.376	20.703	92.666
DBA	93.604	126.182	103.776	124.674	112.059		128.138	119.268	87.365	114.202	23.818	94.558
BGH	93.095	110.644	221.548	99.969	131.314		111.807	103.387	77.701	98.837	23.819	83.110

Table A-9: % Spike Recoveries for Water and Water Filters

	SPIKE Water							SPIKE Water Filter					
	Spike11	**Spike12**	**Spike13**	**Spike14**	**Spike15**	**AVG**		**Spike11**	**Spike12**	**Spike13**	**Spike14**	**Spike15**	**AVG**
NAP-d8	9.082	17.956	62.791	26.000	41.904	31.547		0.000	0.000	0.000	0.000	0.000	0.000
NAP	24.977	43.427	124.245	62.624	82.523	67.559		27.498	13.866	10.834	12.872	8.151	14.644
ACY	10.594	19.897	60.246	35.441	39.381	33.112		0.000	1.126	0.887	0.000	0.955	0.594
ACE-d10	10.705	24.462	54.871	37.822	40.082	33.588		0.000	0.000	0.000	0.000	0.507	0.101
ACE	9.583	21.462	62.834	36.780	49.606	36.053		4.633	2.000	1.849	2.643	0.905	2.406
FLU	17.504	30.282	54.034	44.898	47.648	38.873		4.169	3.506	2.686	0.000	1.926	2.457
DBT	0.000	1.391	2.529	1.540	2.668	1.626		1.550	0.897	0.000	1.032	0.549	0.806
PHEN-d10	13.445	44.051	66.650	51.062	58.182	46.678		0.000	0.000	0.000	0.000	0.000	0.000
PHEN	19.147	67.791	114.924	75.291	95.632	74.557		19.799	13.418	10.637	10.226	6.857	12.187
ANT	13.393	46.535	56.080	55.217	51.930	44.631		1.562	0.999	0.991	1.139	1.228	1.184
2-MP	4.322	1.724	14.373	9.673	16.624	9.343		3.335	7.535	3.944	6.350	2.820	4.797
1-MP	1.770	6.665	9.853	6.088	6.198	6.115		0.000	2.730	1.633	0.000	2.417	1.356
FLT	9.110	38.967	40.905	34.215	40.767	32.793		6.352	6.202	6.043	6.921	6.755	6.455
PYR	40.922	117.360	100.050	101.958	100.369	92.132		23.038	18.604	18.578	17.016	22.409	19.929
BAA	19.774	99.351	88.357	95.646	101.386	80.903		4.190	4.554	10.182	3.133	4.829	5.378
CHR-d12	73.843	166.060	190.790	150.920	213.060	158.935		0.000	2.735	2.804	2.406	1.814	1.952
CHR	12.685	91.610	86.427	80.658	97.780	73.832		4.273	1.526	4.723	2.655	2.468	3.129
BBF	10.921	70.950	48.448	71.609	54.983	51.382		20.712	0.000	9.660	4.037	5.570	7.996
BKF	11.473	61.755	47.651	54.665	48.951	44.899		8.764	0.000	6.952	4.373	3.524	4.723
BEP	0.016	0.033	0.000	0.614	0.000	0.133		0.575	0.749	0.379	0.626	0.000	0.466
BAP	11.560	53.171	40.358	60.192	42.047	41.466		6.948	1.289	5.099	2.047	2.985	3.674
PERY	0.386	0.606	0.580	0.000	0.573	0.429		1.373	5.642	1.819	2.540	3.553	2.985
IND	9.478	51.968	49.604	62.987	40.742	42.956		20.971	19.990	32.651	25.202	22.255	24.214
DBA	8.498	52.842	43.684	63.899	37.226	41.230		22.875	16.661	12.872	14.576	16.916	16.780
BGH	10.202	52.457	55.251	65.142	48.725	46.355		17.084	9.908	24.766	12.539	18.165	16.492

Table A-10: Concentration on PUF, Youngstown Week 1, (ng/m^3)

	YA11	YA12	YA13	YA14	YA15	YA16	YA17	YA18	YA19
NAP	bd	bd	bd	bd	bd	bd	bd	bd	bd
ACY	0.483	1.394	0.115	0.092	0.055	0.194	0.102	0.455	0.194
ACE	0.672	8.764	bd	bd	0.787	2.450	bd	1.584	0.569
FLU	3.182	4.924	1.893	0.913	1.893	2.760	2.223	38.039	1.707
DBT	1.261	3.001	0.994	0.172	1.395	1.101	0.960	1.073	0.543
PHEN	20.978	33.910	17.885	2.654	65.931	45.544	36.479	110.943	48.729
ANT	1.587	3.226	0.806	0.089	1.792	0.358	0.654	1.046	0.636
2-MP	4.673	9.598	2.722	0.609	2.227	2.641	2.351	2.837	1.337
1-MP	2.043	3.573	1.585	0.266	1.925	1.308	1.173	1.920	1.172
FLT	9.028	11.409	6.511	0.796	33.345	3.823	4.922	20.068	2.289
PYR	3.600	2.569	3.654	0.297	11.264	1.955	2.751	7.938	4.013
BAA	0.483	0.495	0.403	bd	0.314	0.334	0.319	0.377	0.286
CHR	0.219	0.704	0.192	0.032	0.282	0.085	0.103	0.161	0.118
BBF	bd	bd	0.311	0.397	0.276	bd	bd	0.374	0.125
BKF	bd	0.013	0.005	0.005	0.007	bd	bd	0.004	0.004
BEP	bd	0.049	bd	bd	bd	bd	bd	bd	bd
BAP	bd	bd	bd	bd	bd	bd	bd	bd	bd
PERY	0.022	bd	0.020	bd	bd	bd	bd	bd	bd
IND	bd	bd	bd	bd	bd	bd	bd	bd	bd
DBA	bd	bd	bd	bd	bd	bd	bd	bd	bd
BGH	bd	0.003	bd	bd	bd	bd	bd	bd	bd

bd = below LOD (mean blank + 3S.D.)

Table A-11: Concentration on PUF, Meander, (ng/m^3)

	MA11	MA12	MA13	MA14
NAP	bd	bd	bd	bd
ACY	bd	bd	bd	0.035
ACE	bd	bd	bd	bd
FLU	0.250	bd	0.136	0.278
DBT	0.122	0.053	0.044	0.063
PHEN	15.232	13.690	12.896	10.908
ANT	0.200	0.099	0.073	0.067
2-MP	0.319	0.141	0.095	0.111
1-MP	0.138	0.068	0.050	0.052
FLT	1.089	0.508	0.449	0.534
PYR	0.852	0.386	0.464	0.460
BAA	0.013	0.007	0.008	0.015
CHR	0.039	0.019	0.031	0.021
BBF	bd	bd	bd	bd
BKF	bd	0.003	0.003	bd
BEP	0.002	0.003	0.005	0.003
BAP	0.002	0.005	0.002	bd
PERY	bd	bd	bd	bd
IND	bd	bd	bd	bd
DBA	bd	bd	bd	bd
BGH	bd	bd	bd	bd

bd = below LOD (mean blank + 3S.D.)

Table A-12: Concentration on PUF, Youngstown Week 2, (ng/m^3)

	YA21	YA22	YA23	YA24	YA25	YA26	YA27	YA28
NAP	bd	bd	bd	bd	bd	bd	bd	bd
ACY	0.086	0.426	0.036	bd	bd	0.102	0.041	0.932
ACE	0.538	1.004	bd	bd	bd	bd	bd	3.646
FLU	1.243	2.299	0.467	1.247	0.515	3.097	0.497	8.321
DBT	0.804	0.984	0.301	0.147	0.350	0.369	0.182	0.796
PHEN	80.992	11.939	6.931	50.124	61.080	76.409	5.206	120.994
ANT	1.257	0.151	0.249	0.019	0.292	5.722	0.107	1.203
2-MP	2.597	1.430	0.994	0.295	1.239	0.735	0.691	2.338
1-MP	1.848	0.719	0.423	0.112	0.551	0.277	0.371	0.944
FLT	23.727	5.287	2.061	1.366	4.621	1.891	2.054	2.956
PYR	8.814	1.750	1.699	0.603	7.650	0.981	1.659	1.831
BAA	0.400	0.228	0.127	0.052	0.125	0.057	0.123	0.066
CHR	0.232	0.115	0.040	0.025	0.060	0.042	0.033	0.075
BBF	0.751	bd	bd	bd	bd	bd	bd	bd
BKF	0.005	0.008	bd	bd	bd	bd	bd	bd
BEP	bd	bd	bd	bd	0.023	bd	bd	bd
BAP	bd	bd	bd	0.147	bd	bd	bd	bd
PERY	bd	bd	bd	bd	bd	bd	bd	bd
IND	bd	bd	bd	bd	bd	bd	bd	bd
DBA	bd	bd	bd	bd	bd	bd	bd	bd
BGH	bd	0.012	bd	bd	bd	bd	bd	bd
IND	0.005	0.007	0.004	0.005	0.006	0.005	0.006	0.005
DBA	0.018	0.012	0.021	0.019	0.021	0.018	0.022	0.018
BGH	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000

bd = below LOD (mean blank + 3S.D.)

Table A-13: Concentration on PUF, Pennsylvania, (ng/m^3)

	PA11	PA12	PA13	PA14
NAP	bd	bd	bd	bd
ACY	bd	bd	bd	bd
ACE	bd	bd	bd	bd
FLU	0.122	bd	0.114	bd
DBT	0.060	0.057	0.043	0.050
PHEN	9.444	9.731	6.589	7.256
ANT	0.064	0.051	0.042	0.060
2-MP	0.120	0.217	0.101	0.096
1-MP	0.064	0.146	0.049	0.043
FLT	0.532	0.837	0.384	0.343
PYR	0.339	1.238	0.303	0.248
BAA	0.016	0.030	0.015	0.009
CHR	0.025	0.046	0.016	0.024
BBF	bd	0.048	bd	bd
BKF	bd	0.008	0.001	0.003
BEP	0.002	0.007	0.002	0.006
BAP	bd	bd	bd	0.002
PERY	bd	bd	bd	bd
IND	bd	bd	bd	bd
DBA	bd	bd	bd	bd
BGH	bd	bd	bd	bd

bd = below LOD (mean blank + 3S.D.)

Table A-14: Concentration on Air Filters, Youngstown Week 1, (ng/m^3)

	YA11	YA12	YA13	YA14	YA15	YA16	YA17	YA18	YA19
NAP	0.018	0.006	bd	bd	bd	bd	bd	bd	bd
ACY	0.060	bd	0.012	0.035	bd	bd	bd	bd	bd
ACE	bd	bd	bd	bd	bd	bd	bd	bd	bd
FLU	0.080	bd	bd	bd	bd	bd	bd	bd	bd
DBT	bd	0.009	bd	bd	bd	bd	bd	bd	bd
PHEN	0.104	0.100	0.043	0.040	0.021	0.015	0.013	0.011	0.017
ANT	bd	0.044	bd	bd	bd	bd	bd	bd	bd
2-MP	0.037	0.028	bd	bd	bd	bd	bd	bd	bd
1-MP	bd	0.046	bd	bd	bd	bd	bd	bd	bd
FLT	0.125	0.156	bd	bd	bd	bd	bd	bd	bd
PYR	bd	bd	bd	bd	bd	bd	bd	bd	bd
BAA	bd	0.022	0.133	0.160	0.154	0.111	0.160	0.041	0.141
CHR	0.146	0.162	0.070	0.087	0.060	0.020	0.053	0.027	0.078
BBF	bd	0.030	0.068	0.175	0.049	0.018	0.028	0.030	0.095
BKF	0.115	0.194	0.031	0.049	0.040	0.015	0.020	0.023	0.070
BEP	bd	bd	bd	0.117	bd	bd	bd	bd	bd
BAP	bd	0.077	0.033	0.047	bd	bd	bd	bd	0.023
PERY	bd	bd	bd	0.018	bd	bd	bd	bd	bd
IND	0.052	0.180	0.088	0.219	0.064	0.023	0.054	0.051	0.067
DBA	0.005	0.006	0.017	0.038	0.014	bd	0.012	0.007	0.012
BGH	0.142	0.205	0.087	0.267	0.057	0.027	0.076	0.052	0.095

bd = below LOD (mean blank + 3S.D.)

Table A-15: Concentration on Air Filters, Meander, (ng/m^3)

	MA11	MA12	MA13	MA14
NAP	0.003	bd	0.058	0.023
ACY	0.019	bd	bd	0.011
ACE	0.025	bd	bd	bd
FLU	bd	bd	bd	bd
DBT	0.008	bd	bd	0.019
PHEN	0.236	bd	bd	0.838
ANT	bd	bd	bd	bd
2-MP	0.099	bd	0.008	0.049
1-MP	bd	bd	bd	bd
FLT	0.325	bd	bd	0.167
PYR	0.263	bd	bd	bd
BAA	bd	bd	0.079	bd
CHR	0.182	bd	bd	bd
BBF	0.052	0.031	0.086	0.236
BKF	0.214	0.016	0.047	0.023
BEP	0.111	0.032	0.044	0.085
BAP	0.138	0.022	0.060	0.081
PERY	bd	bd	0.010	0.016
IND	0.233	0.039	0.117	0.203
DBA	0.028	0.009	0.017	0.037
BGH	0.248	0.041	0.175	0.331

bd = below LOD (mean blank + 3S.D.)

Table A-16: Concentration on Air Filters, Youngstown Week 2, (ng/m^3)

	YA21	YA22	YA23	YA24	YA25	YA26	YA27	YA28	YA29
NAP	0.094	0.175	0.127	bd	bd	bd	bd	bd	bd
ACY	0.024	0.034	bd	bd	bd	bd	bd	bd	bd
ACE	bd	bd	bd	bd	bd	bd	bd	bd	bd
FLU	bd	0.077	bd	0.040	bd	bd	bd	bd	bd
DBT	bd	0.011	bd	bd	bd	bd	bd	0.011	bd
PHEN	0.132	0.031	bd	0.017	bd	bd	bd	0.352	0.033
ANT	bd	bd	bd	bd	bd	bd	bd	bd	bd
2-MP	0.056	bd	0.057	bd	bd	bd	bd	0.038	bd
1-MP	bd	bd	bd	bd	bd	bd	bd	bd	bd
FLT	0.166	0.089	0.096	0.020	0.042	0.003	0.004	0.259	0.092
PYR	bd	bd	bd	bd	bd	bd	bd	bd	bd
BAA	0.252	0.172	0.214	0.185	0.236	0.042	0.040	0.123	0.195
CHR	0.081	0.046	0.039	0.025	0.044	0.019	0.018	0.163	0.086
BBF	1.203	0.028	0.803	0.553	0.855	0.019	0.014	0.202	0.086
BKF	0.087	0.023	0.025	0.004	0.009	0.007	0.006	0.200	0.092
BEP	bd	bd	bd	bd	bd	bd	bd	bd	bd
BAP	0.070	bd	bd	bd	bd	bd	bd	0.094	bd
PERY	0.029	bd	bd	bd	bd	bd	bd	0.062	0.026
IND	0.112	0.026	0.057	0.028	0.048	0.021	bd	0.319	0.086
DBA	bd	0.024	bd	bd	bd	0.013	bd	0.057	0.015
BGH	0.107	0.031	0.062	0.024	0.042	0.022	0.017	0.433	0.106

bd = below LOD (mean + 3S.D.)

Table A-17: Concentration on Air Filters, Pennsylvania Air, (ng/m^3)

	PA11	PA12	PA13	PA14
NAP	bd	bd	bd	bd
ACY	0.009	bd	0.012	bd
ACE	bd	bd	bd	bd
FLU	bd	bd	bd	bd
DBT	bd	0.007	0.008	0.012
PHEN	0.067	0.071	0.420	0.578
ANT	bd	bd	bd	bd
2-MP	0.018	0.018	0.052	0.055
1-MP	bd	bd	bd	bd
FLT	bd	bd	0.332	0.218
PYR	bd	bd	0.743	bd
BAA	bd	0.072	bd	bd
CHR	0.097	bd	bd	bd
BBF	0.010	0.122	0.122	0.525
BKF	0.054	0.062	0.025	0.046
BEP	0.010	0.065	0.055	0.063
BAP	0.080	0.077	0.084	0.055
PERY	bd	0.019	0.024	0.013
IND	0.088	0.161	0.105	0.114
DBA	0.014	0.025	0.020	0.026
BGH	0.064	0.229	0.196	0.131

bd = below LOD (mean blank + 3S.D.)

Table A-18: Concentration in Dissolved Phase of Water, Youngstown Week 1, (ng/L)

	YW11A* #	YW11B* #	YW12	YW13	YW14	YW15A*	YW15B*
NAP	bd	bd	bd	bd	bd	bd	bd
ACY	bd	bd	bd	bd	bd	bd	bd
ACE	0.921	bd	bd	9.842	2.186	3.696	4.802
FLU	bd	0.328	bd	11.282	6.320	7.728	10.322
DBT	bd	bd	bd	1.813	bd	0.956	1.296
PHEN	bd	6.900	bd	23.880	bd	8.498	16.898
ANT	0.540	1.348	1.434	2.810	1.349	2.359	3.959
2-MP	bd	bd	bd	bd	bd	bd	bd
1-MP	bd	0.582	bd	0.472	2.899	0.791	0.894
FLT	18.039	45.777	15.892	21.412	20.987	30.650	37.757
PYR	4.741	18.733	11.870	bd	5.819	34.878	45.309
BAA	bd	31.407	bd	bd	bd	bd	bd
CHR	bd	bd	bd	bd	bd	bd	bd
BBF	5.645	11.406	0.775	2.546	0.951	1.805	5.928
BKF	5.322	2.797	0.087	1.783	1.011	1.396	3.346
BEP	2.247	7.977	1.305	1.657	0.557	0.957	2.676
BAP	3.505	6.278	2.529	1.546	2.411	0.480	1.959
PERY	1.998	2.647	bd	3.477	bd	1.759	1.626
IND	6.099	21.258	0.853	1.086	0.376	0.732	3.241
DBA	0.586	6.862	bd	bd	bd	0.519	bd
BGH	6.162	14.126	bd	1.410	0.660	0.956	2.551

bd = below LOD (mean blank + 3S.D.)

* A,B signify duplicate samples.

Total water concentrations (dissolved + particulate).

Table A-19: Concentration in Dissolved Phase of Water, Meander, (ng/L)

	MW11A*	MW11B*	MW12	MW13	MW14	MW15A*	MW15B*
NAP	bd	bd	bd	bd	bd	bd	bd
ACY	bd	bd	bd	bd	bd	bd	bd
ACE	bd	bd	1.332	bd	4.997	bd	bd
FLU	bd	bd	1.508	bd	7.566	bd	bd
DBT	bd	bd	0.484	bd	0.607	1.235	bd
PHEN	bd	bd	bd	bd	22.700	29.234	bd
ANT	1.188	1.121	0.702	2.427	1.945	3.038	1.741
2-MP	bd	bd	bd	bd	bd	12.142	bd
1-MP	0.638	4.236	0.613	2.523	0.997	3.502	0.188
FLT	4.845	1.193	6.608	0.552	4.191	45.635	3.741
PYR	19.126	15.812	71.033	bd	23.640	24.630	24.790
BAA	bd	bd	bd	bd	bd	bd	bd
CHR	bd	bd	bd	bd	bd	bd	bd
BBF	3.421	0.235	1.912	3.461	6.325	5.681	1.226
BKF	1.147	0.507	0.199	1.254	1.533	1.003	1.036
BEP	bd	0.549	bd	0.248	1.636	1.096	0.407
BAP	2.808	0.163	15.643	1.438	2.774	1.197	0.355
PERY	2.834	7.558	12.745	2.150	5.886	3.419	1.319
IND	0.349	0.412	bd	0.161	0.622	1.066	0.169
DBA	bd	0.699	bd	bd	bd	bd	bd
BGH	0.743	bd	bd	bd	1.424	2.908	0.408

bd = below LOD (mean blank + 3S.D.)
* A,B signify duplicate samples.

Table A-20: Concentration in Dissolved Phase of Water, Youngstown Week 2, (ng/L)

	YW21	YW22	YW23	YW24	YW25
NAP	bd	bd	bd	bd	bd
ACY	bd	bd	bd	bd	bd
ACE	2.340	1.429	7.673	bd	bd
FLU	8.332	bd	12.853	bd	bd
DBT	0.553	0.667	1.714	bd	0.756
PHEN	10.635	11.716	23.919	bd	7.214
ANT	2.927	1.149	92.389	14.343	1.247
2-MP	bd	bd	34.402	bd	bd
1-MP	11.250	bd	7.764	bd	bd
FLT	24.330	13.897	162.888	30.121	34.337
PYR	bd	bd	2267.475	1379.945	8.502
BAA	bd	bd	bd	bd	bd
CHR	bd	bd	. bd	bd	bd
BBF	2.577	0.674	5.381	0.899	1.464
BKF	1.494	0.241	0.414	0.440	0.425
BEP	1.425	0.141	2.312	0.530	2.512
BAP	1.983	bd	2.815	0.043	1.812
PERY	0.932	1.030	3.892	bd	2.455
IND	1.650	0.348	1.981	0.588	7.015
DBA	1.462	bd	1.677	bd	4.293
BGH	2.490	0.431	2.822	0.393	4.410

bd = below LOD (mean blank + 3S.D.)

Table A-21: Concentration in Dissolved Phase of Water, Pennsylvania, (ng/L)

	PW11A*	PW11B*	PW12	PW13	PW14	PW15A*	PW15B*
NAP	bd	bd	bd	bd	bd	bd	bd
ACY	bd	bd	bd	bd	bd	bd	bd
ACE	bd	bd	2.458	2.775	2.186	bd	1.980
FLU	bd	bd	4.234	9.179	bd	bd	1.812
DBT	bd	bd	1.274	bd	bd	bd	bd
PHEN	bd	bd	25.541	5.838	bd	bd	bd
ANT	bd	0.931	4.951	1.052	0.697	bd	1.105
2-MP	bd	bd	10.123	bd	bd	bd	bd
1-MP	bd	1.270	9.975	bd	0.772	bd	3.369
FLT	0.957	1.512	33.394	6.095	4.037	bd	5.878
PYR	6.833	29.909	22.664	bd	bd	bd	27.522
BAA	bd	bd	bd	bd	bd	bd	bd
CHR	bd	bd	bd	bd	bd	bd	bd
BBF	0.290	2.156	1.699	2.763	1.599	bd	3.192
BKF	0.428	0.435	1.499	0.912	bd	bd	1.449
BEP	0.265	0.643	0.444	1.074	1.065	bd	0.531
BAP	bd	0.507	1.644	0.220	3.851	bd	2.227
PERY	0.801	bd	2.669	2.547	0.761	bd	2.794
IND	1.223	0.192	0.324	0.331	bd	0.822	bd
DBA	bd	bd	bd	0.416	bd	2.468	bd
BGH	0.667	bd	bd	bd	bd	bd	bd

bd = below LOD (mean blank + 3S.D.)

* A,B signify duplicate samples.

Table A-22: Concentration on Water Filters, Youngstown Week 1, (ng/L)

	YW12	YW13	YW14	YW15A*	YW15B*
NAP	bd	1.581	0.928	0.681	bd
ACY	bd	0.445	0.232	0.804	bd
ACE	bd	bd	bd	bd	bd
FLU	2.554	1.002	0.789	0.167	bd
DBT	0.560	0.704	0.357	0.581	bd
PHEN	7.720	34.521	15.353	25.600	bd
ANT	1.760	2.037	0.612	2.340	0.087
2-MP	2.777	10.246	3.764	5.834	bd
1-MP	1.560	4.569	1.177	3.631	bd
FLT	15.985	11.481	7.469	12.517	2.253
PYR	48.081	24.039	14.842	29.275	4.116
BAA	25.595	15.583	17.427	21.869	8.670
CHR	12.680	0.985	8.418	16.015	4.205
BBF	42.895	16.012	18.186	43.230	5.527
BKF	3.396	4.060	4.612	12.437	4.316
BEP	4.980	3.815	4.898	10.762	1.838
BAP	8.264	2.037	6.144	16.515	4.315
PERY	3.113	3.135	2.165	4.806	1.060
IND	13.945	8.196	7.960	18.138	4.694
DBA	2.355	1.344	1.245	3.692	0.258
BGH	10.700	9.250	10.055	20.734	5.936

bd = below LOD (mean blank + 3S.D.)
* A,B signify duplicate samples.

Table A-23: Concentration on Water Filters, Meander, (ng/L)

	MW11A*	MW11B*	MW12	MW13	MW14	MW15A*	MW15B*
NAP	0.897	bd	bd	0.837	0.099	bd	bd
ACY	bd	bd	bd	bd	bd	bd	bd
ACE	bd	bd	bd	bd	bd	bd	bd
FLU	0.249	bd	0.097	0.665	bd	bd	bd
DBT	0.199	bd	bd	0.057	0.272	bd	bd
PHEN	17.185	bd	bd	6.757	20.586	bd	bd
ANT	0.549	0.040	0.079	0.477	0.261	0.095	bd
2-MP	2.215	bd	bd	1.099	1.892	bd	bd
1-MP	0.380	0.331	0.548	0.025	1.036	0.324	0.046
FLT	8.383	bd	1.732	2.229	1.482	bd	bd
PYR	22.288	bd	4.360	6.919	3.509	bd	bd
BAA	2.353	0.839	0.771	2.402	0.218	0.459	0.853
CHR	0.828	0.013	0.016	0.133	0.095	0.032	0.027
BBF	1.045	0.382	0.279	bd	0.411	0.321	bd
BKF	0.169	0.047	0.118	0.264	0.488	0.386	0.086
BEP	0.095	bd	0.158	0.229	0.141	0.086	bd
BAP	0.840	bd	bd	bd	bd	1.430	bd
PERY	bd	bd	bd	bd	bd	bd	bd
IND	bd	bd	bd	bd	bd	bd	bd
DBA	0.131	bd	bd	bd	bd	bd	bd
BGH	0.530	bd	bd	bd	bd	bd	bd

bd = below LOD (mean blank + 3S.D.)
* A,B signify duplicate samples.

Table A-24: Concentration on Water Filters, Youngstown Week 2, (ng/L)

	YW21	YW22	YW23	YW24	YW25
NAP	4.156	2.903	4.717	2.674	0.541
ACY	0.928	0.373	0.194	bd	0.175
ACE	0.824	0.629	bd	0.949	bd
FLU	5.666	1.215	2.000	0.992	0.113
DBT	0.566	0.660	0.626	0.416	0.016
PHEN	8.518	34.493	36.542	21.669	0.841
ANT	2.407	1.733	1.295	1.065	0.456
2-MP	7.677	2.580	4.338	4.496	bd
1-MP	2.916	3.003	0.744	1.351	0.238
FLT	6.243	10.616	16.806	15.916	3.775
PYR	17.511	23.941	39.230	31.086	4.655
BAA	20.665	17.467	18.402	18.051	8.386
CHR	10.845	8.289	11.625	12.759	4.512
BBF	21.746	20.384	25.978	25.842	5.941
BKF	5.094	5.907	6.950	6.173	2.922
BEP	6.773	3.671	9.073	7.300	2.292
BAP	8.931	7.419	14.318	12.879	4.953
PERY	2.690	3.372	6.212	5.198	1.281
IND	10.504	9.307	11.092	13.141	5.174
DBA	1.290	0.706	2.046	2.573	0.939
BGH	12.725	10.659	14.751	17.500	6.325

bd = below LOD (mean blank + 3S.D.)

Table A-25: Concentration on Water Filters, Pennsylvania, (ng/L)

	PW11A*	PW11B*	PW12	PW13	PW14	PW15A*	PW15B*
NAP	bd	bd	bd	bd	bd	bd	bd
ACY	bd	bd	bd	bd	bd	bd	0.622
ACE	bd	bd	bd	bd	bd	bd	0.790
FLU	bd	0.053	0.207	0.408	bd	bd	0.210
DBT	0.057	0.101	0.142	0.077	bd	bd	0.010
PHEN	11.876	16.581	11.274	10.818	0.940	bd	bd
ANT	0.071	0.214	0.129	0.957	bd	bd	bd
2-MP	bd	bd	4.118	bd	bd	bd	bd
1-MP	0.281	0.632	1.276	0.211	bd	bd	0.348
FLT	1.035	0.643	2.839	3.417	1.113	bd	bd
PYR	bd	bd	3.813	7.693	bd	bd	bd
BAA	0.187	8.197	1.127	0.802	0.810	0.629	2.092
CHR	bd	0.297	0.900	0.113	0.133	bd	0.633
BBF	bd	bd	1.337	0.702	bd	0.299	1.356
BKF	0.130	0.217	0.252	0.107	0.112	bd	0.343
BEP	0.130	0.294	0.964	0.104	bd	0.114	0.245
BAP	bd	0.303	0.950	bd	bd	0.160	0.758
PERY	0.486	bd	0.351	0.265	bd	bd	0.488
IND	bd	0.317	2.053	bd	bd	bd	bd
DBA	bd	bd	bd	bd	bd	bd	0.345
BGH	bd	bd	1.567	0.338	bd	bd	0.756

bd = below LOD (mean blank + 3S.D.)
* A,B signify duplicate samples.

Table A-26: PAH Data Used in PCA Correlations

Source		Campbell sediment (mg/kg)	Lowellville sediment (mg/kg)		used oil* (g/L)	unused diesel* (g/L)	unused reg. gas* (g/L)
NAP		7.16	6.40		241,216.52	2.33	53,741.39
ACY		nr	nr		7,555.12	2.49	22.57
ACE		nr	nr		21,419.19	57.08	5,472.19
FLU		nr	nr		27,282.31	226.32	4,638.08
DBT		nr	nr		1,866.49	23.00	149.02
PHEN		12.12	nd		53,743.88	613.06	4,171.50
ANT		8.14	nd		30,111.93	101.84	2,788.74
2-MP		nr	nr		117,270.16	1,286.28	6,257.67
1-MP		nr	nr		94,856.94	2,378.21	4,286.89
FLT		nr	124.80		20,008.01	42.18	604.78
PYR		nr	nr		87,492.69	666.45	1,972.64
BAA		76.11	31.15		64,128.85	10.04	1,023.03
CHR		426.31	98.67		28,520.44	22.96	684.53
BBF		561.17	202.04		26,915.47	0.78	265.36
BKF		550.82	307.89		12,781.19	0.31	109.29
BEP		nr	nr		21,253.86	0.59	191.79
BAP		882.02	257.62		27,575.51	0.85	303.43
PERY		nr	nr		8,787.11	0.29	112.30
IND		225.33	85.82		23,687.48	0.40	149.79
DBA		89.74	25.71		7,984.19	0.14	41.78
BGH		163.52	38.00		89,407.49	0.96	429.58
Coronene		nr	nr		nr	nr	nr

nr = not reported

* Values determined in this study.

Table A-26: PAH Data Used in PCA Correlations (cont.)

Source		British Columbia Summer (ng/m3)	Baltimore Tunnel (traffic) (ng/m3)	Brown Coal (mg/kg)	Wood Soot (mg/kg)	Gasoline Soot (mg/kg)	Diesel Soot (mg/kg)	Diesel Particulate (mg/kg)	Diesel Particulate (mg/kg)	Diesel Particulate (mg/kg)	Lake Superior pore water stratified (ng/g)	Lake Superior pore water unstratified (ng/g)
NAP		1.87	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
ACY		2.72	nr	nr	nr	nr	nr	30.00	30.00	nr	nr	nr
ACE		4.23	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
FLU		7.00	nr	0.07	nr	nr	nr	168.00	100.00	166.00	312.00	368.00
DBT		nr	nr	0.10	nr	nr	nr	246.00	129.00	172.00	nr	nr
PHEN		3.84	18.00	3.69	nr	nr	nr	4,883.00	2,186.00	2,821.00	5,461.00	2,694.00
ANT		0.61	2.90	0.60	nr	nr	nr	356.00	224.00	155.00	nr	nr
2-MP		nr	19.00	0.63	nr	nr	nr	1,481.00	1,099.00	1,142.00	nr	nr
1-MP		nr	9.80	nr	nr	nr	nr	nr	nr	nr	nr	nr
FLT		2.11	20.00	5.32	nr	nr	nr	7,321.00	3,399.00	3,748.00	395.00	165.00
PYR		3.33	27.00	3.69	nr	nr	nr	8,002.00	3,652.00	3,532.00	152.00	37.00
BAA		0.34	7.60	1.81	148.00	89.00	85.00	1,076.00	463.00	495.00	58.00	52.00
CHR		0.61	12.00	2.09	193.00	147.00	103.00	1,529.00	657.00	873.00	102.00	47.00
BBF		0.38	10.60	2.08	141.00	91.00	166.00	1,367.00	492.00	680.00	94.00	65.00
BKF		0.16	nr	0.57	73.00	57.00	70.00	1,098.00	421.00	593.00	101.00	50.00
BEP		nr	5.00	nr	80.00	59.00	65.00	289.00	163.00	91.00	50.00	111.00
BAP		0.25	5.80	nr	153.00	189.00	81.00	946.00	510.00	487.00	nr	282.00
PERY		nr	nr	0.12	nr	nr	nr	nr	nr	nr	nr	nr
IND		0.42	4.60	0.54	118.00	129.00	128.00	93.00	30.00	50.00	26.00	27.00
DBA		0.07	nr	0.11	nr	nr	nr	nr	nr	nr	nr	nr
BGH		0.76	8.00	0.41	98.00	454.00	147.00	1,050.00	443.00	661.00	nr	nr
Coronene		nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr

nr = not reported

* Values determined in this study.

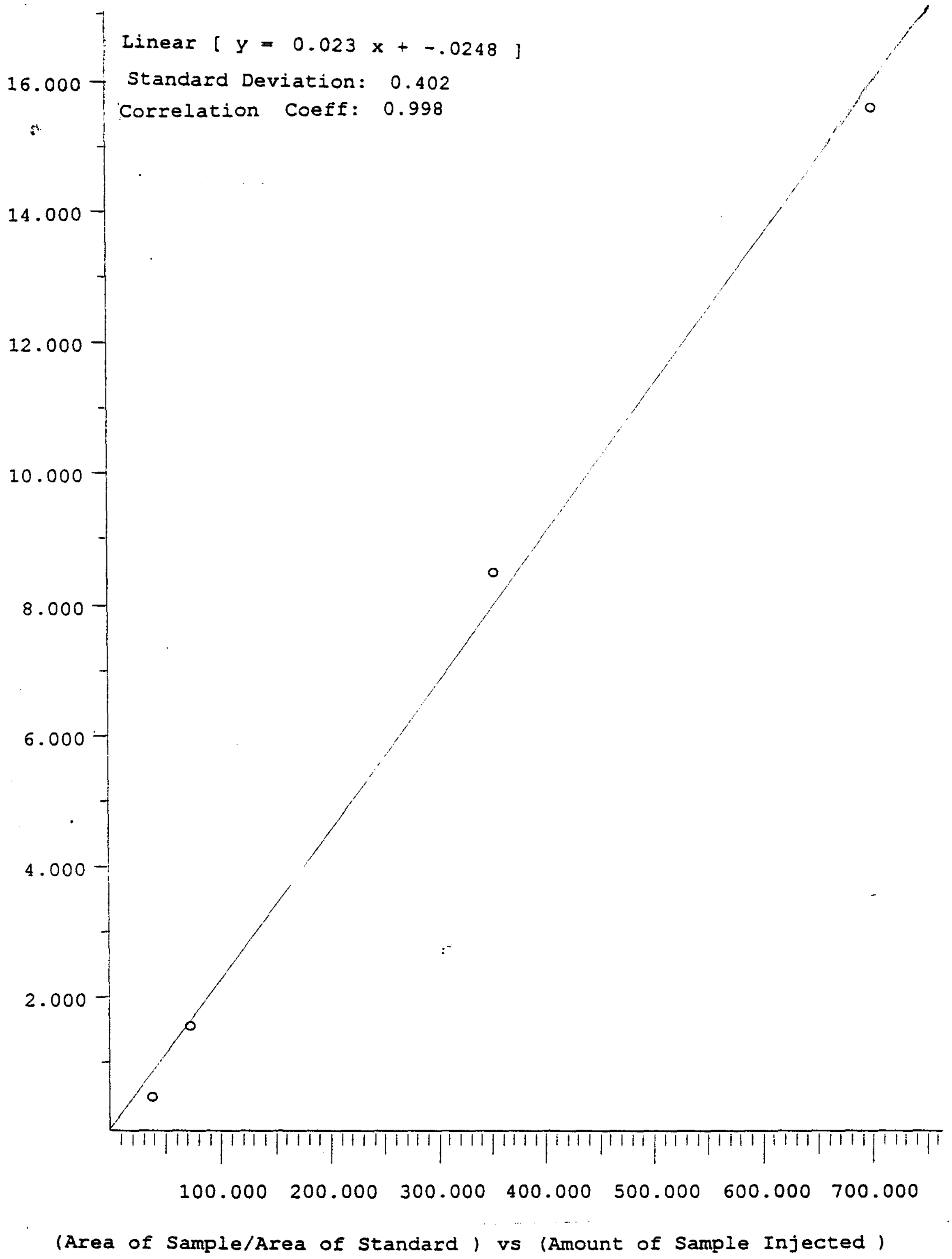

Figure A-1. Standard Calibration Plot of naphthalene-d_8 from GC/MS (4 standards ranging from 0.05 - 1.00 ng/µL).

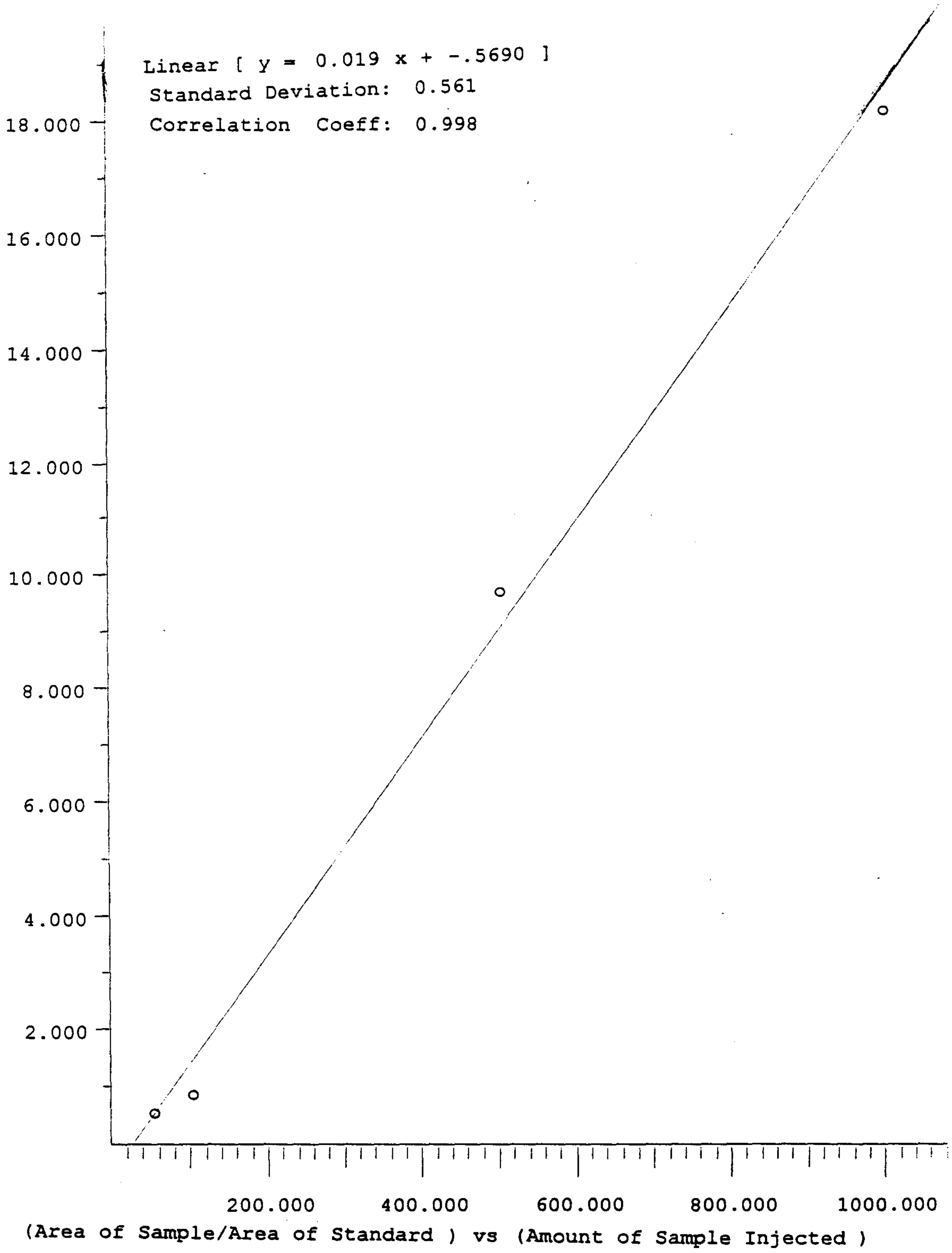

Figure A-2. Standard Calibration Plot of naphthalene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

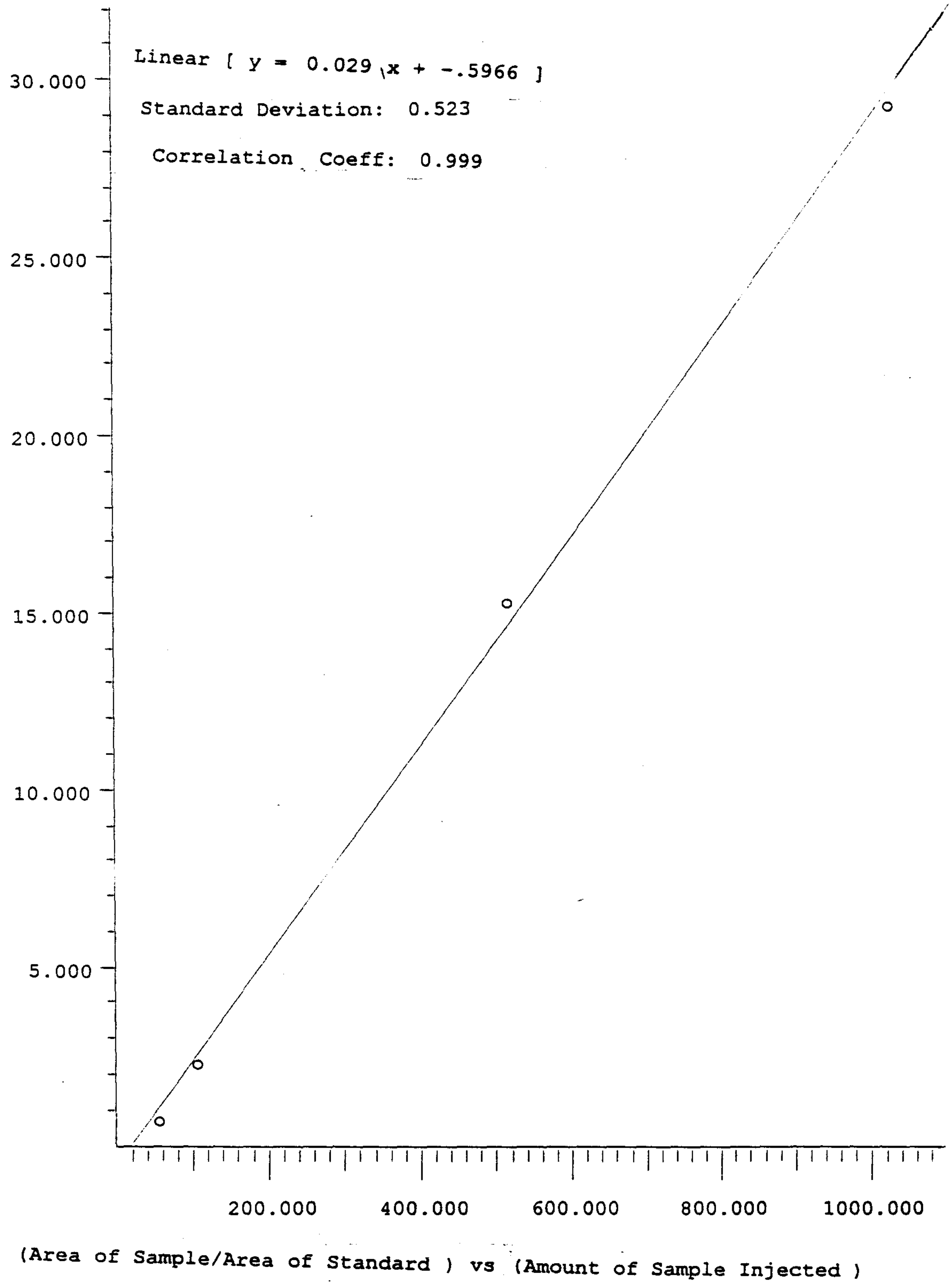

Figure A-3. Standard Calibration Plot of acenaphthylene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

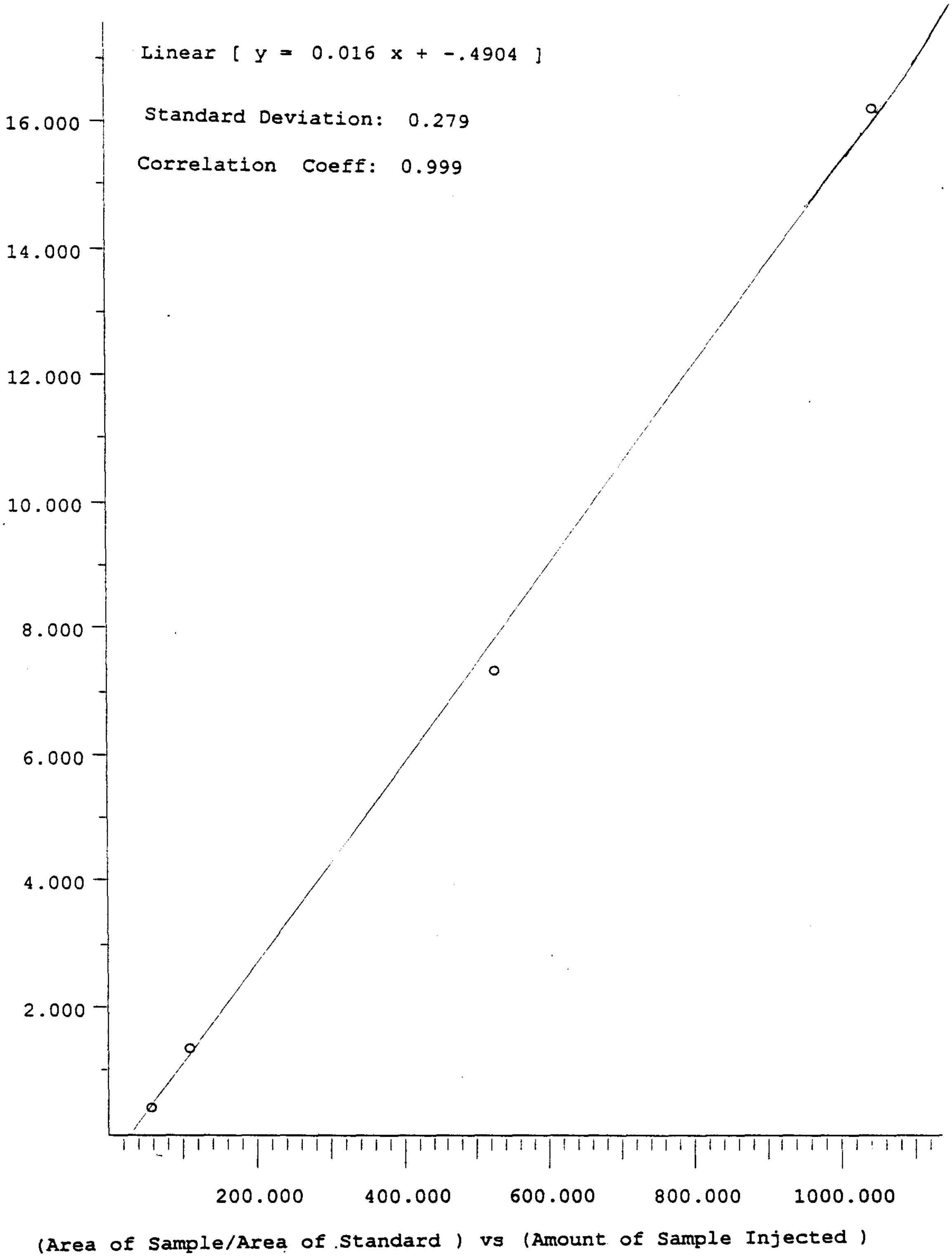

Figure A-4. Standard Calibration Plot of acenaphthene-d_{10} from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

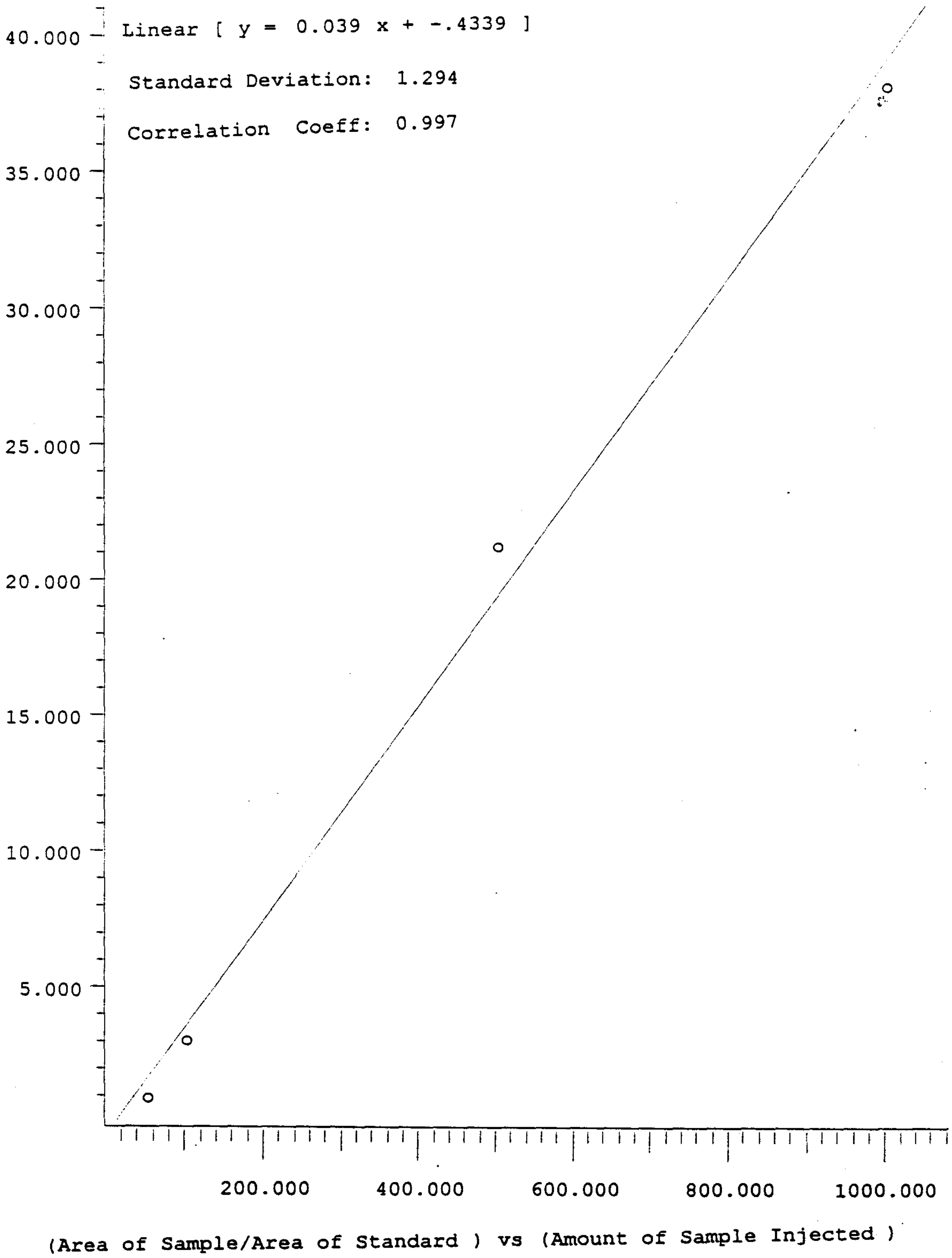

Figure A-5. Standard Calibration Plot of acenaphthene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

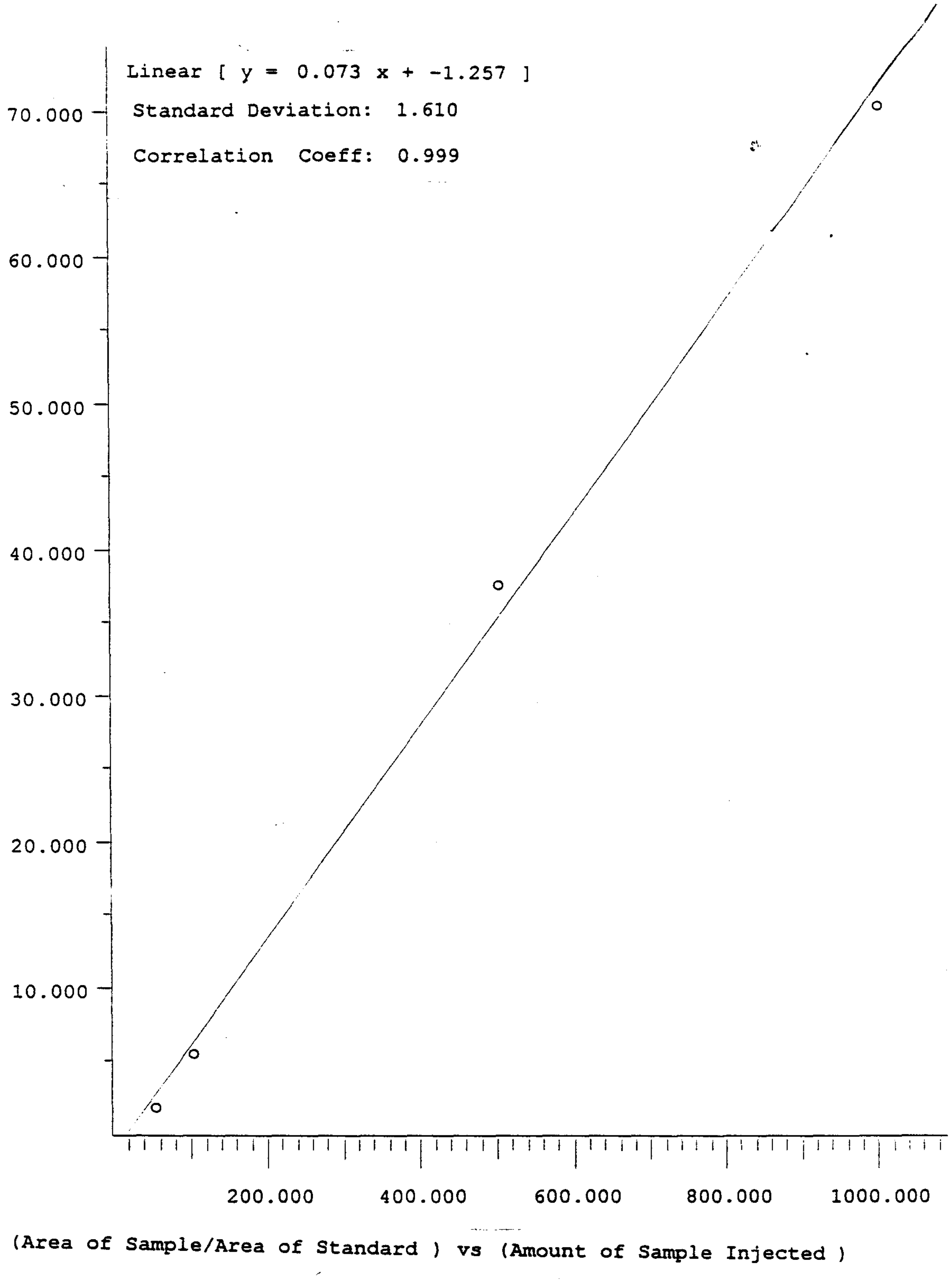

Figure A-6. Standard Calibration Plot of dibenzothiophene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

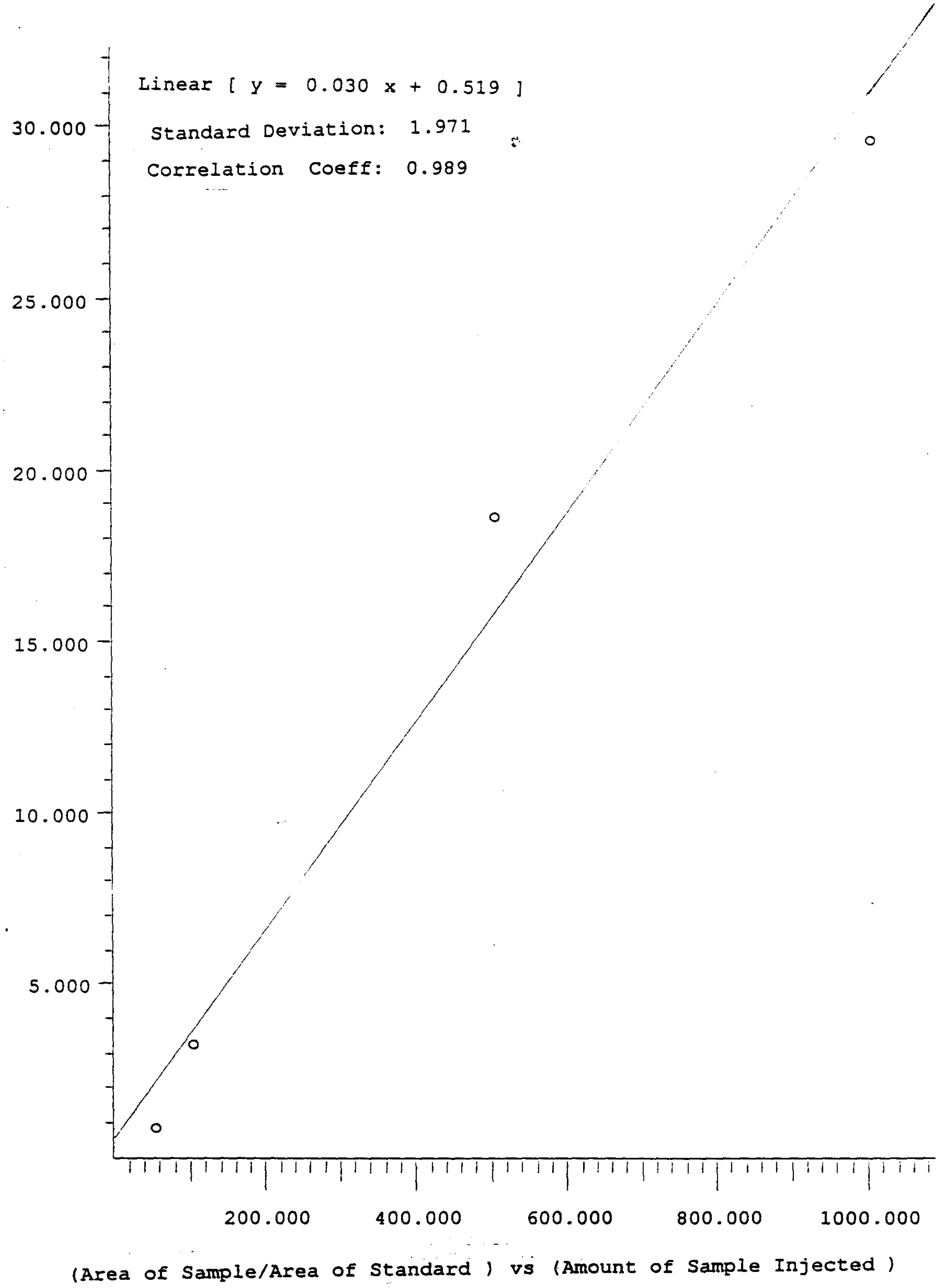

Figure A-7. Standard Calibration Plot of phenanthrene-d_{10} from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

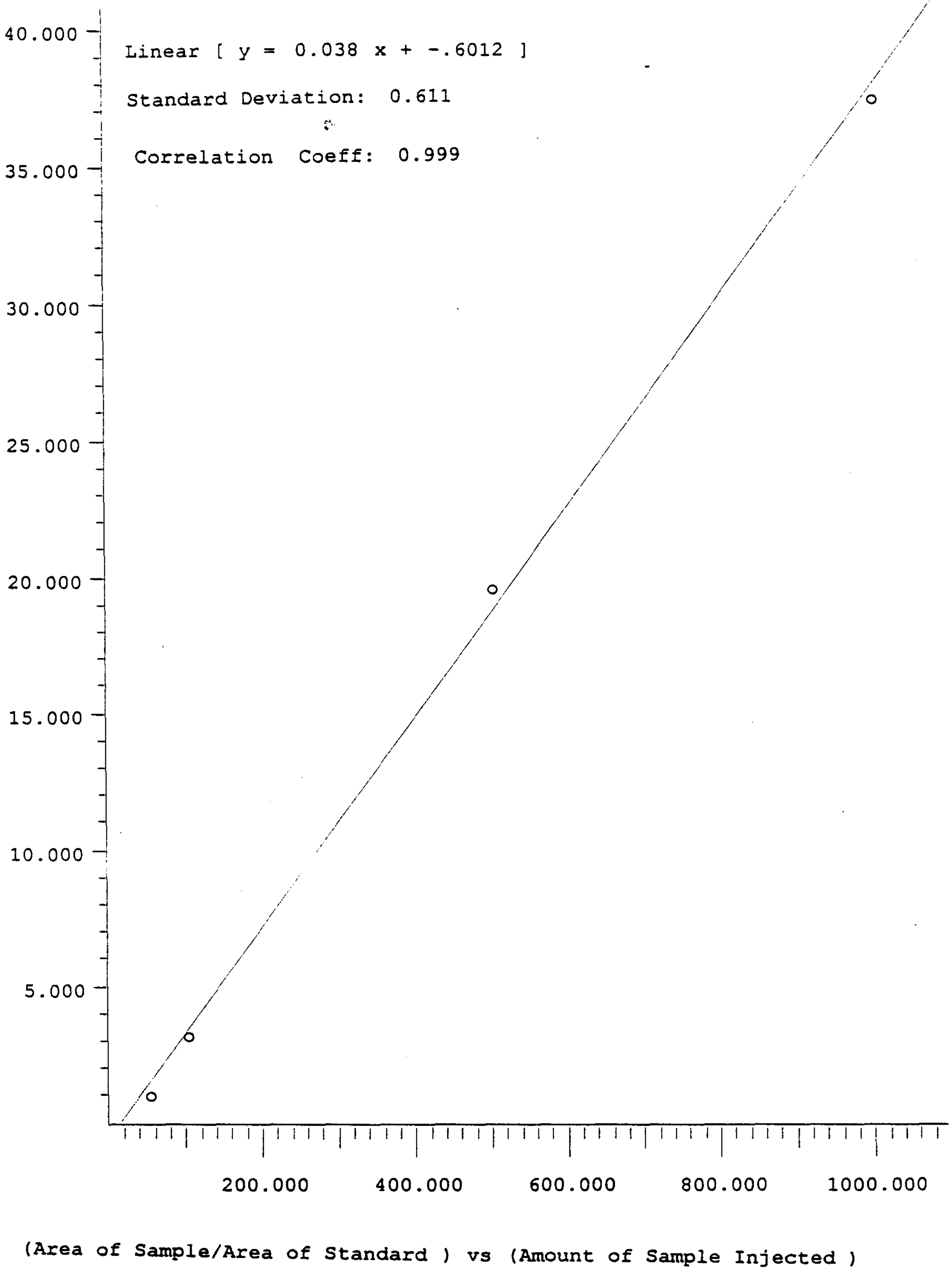

Figure A-8. Standard Calibration Plot of phenanthrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

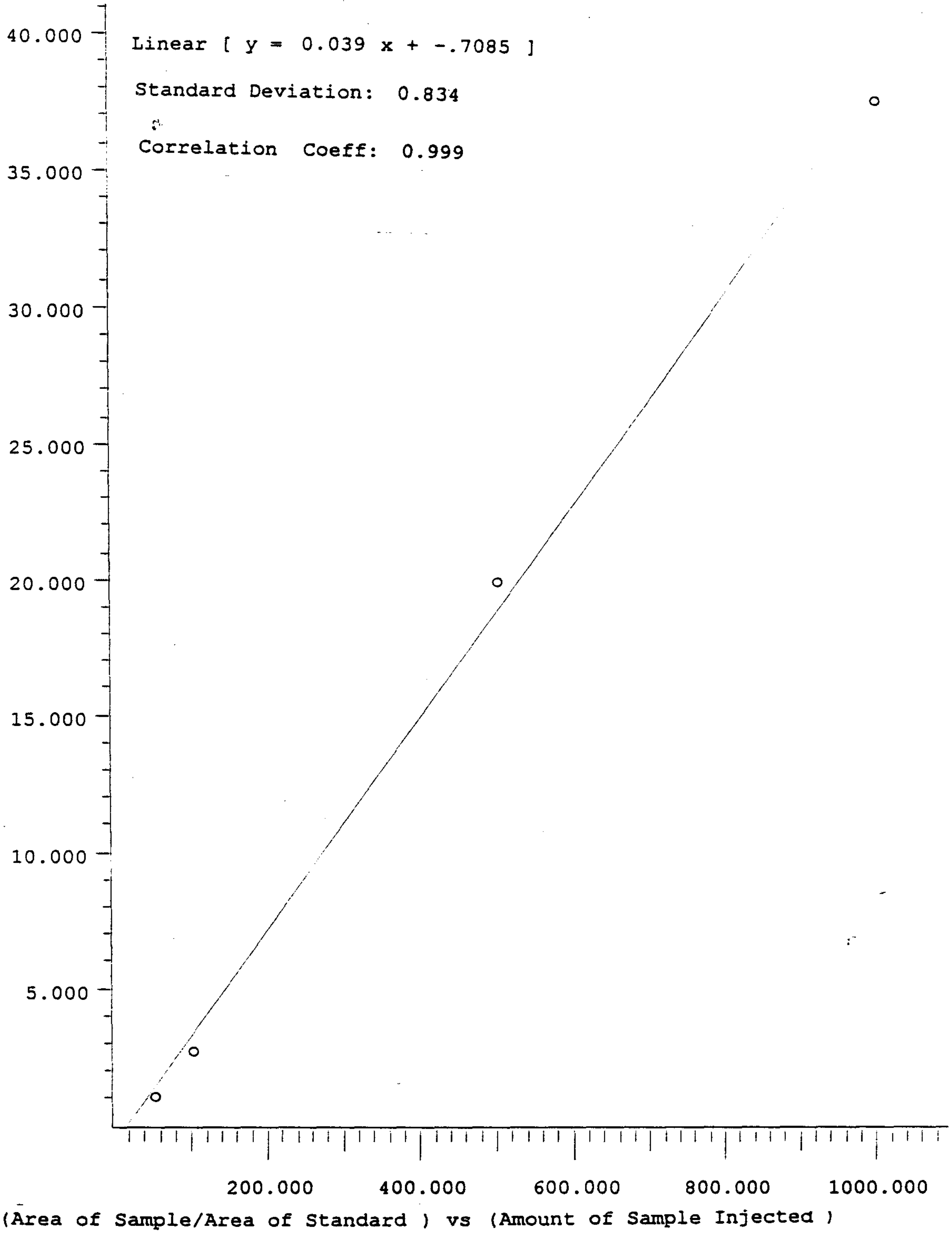

Figure A-9. Standard Calibration Plot of anthracene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

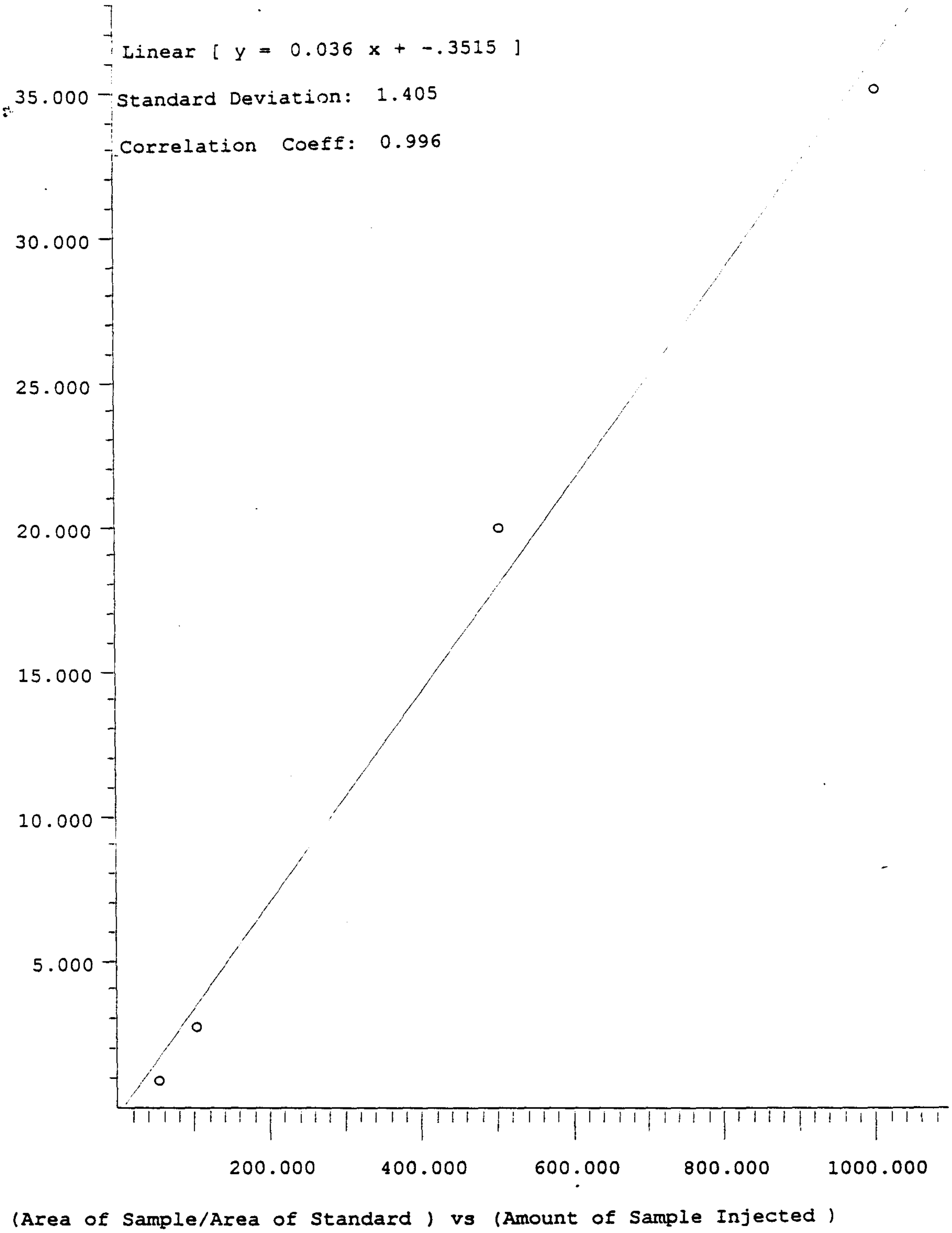

Figure A-10. Standard Calibration Plot of 2-methylphenanthrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

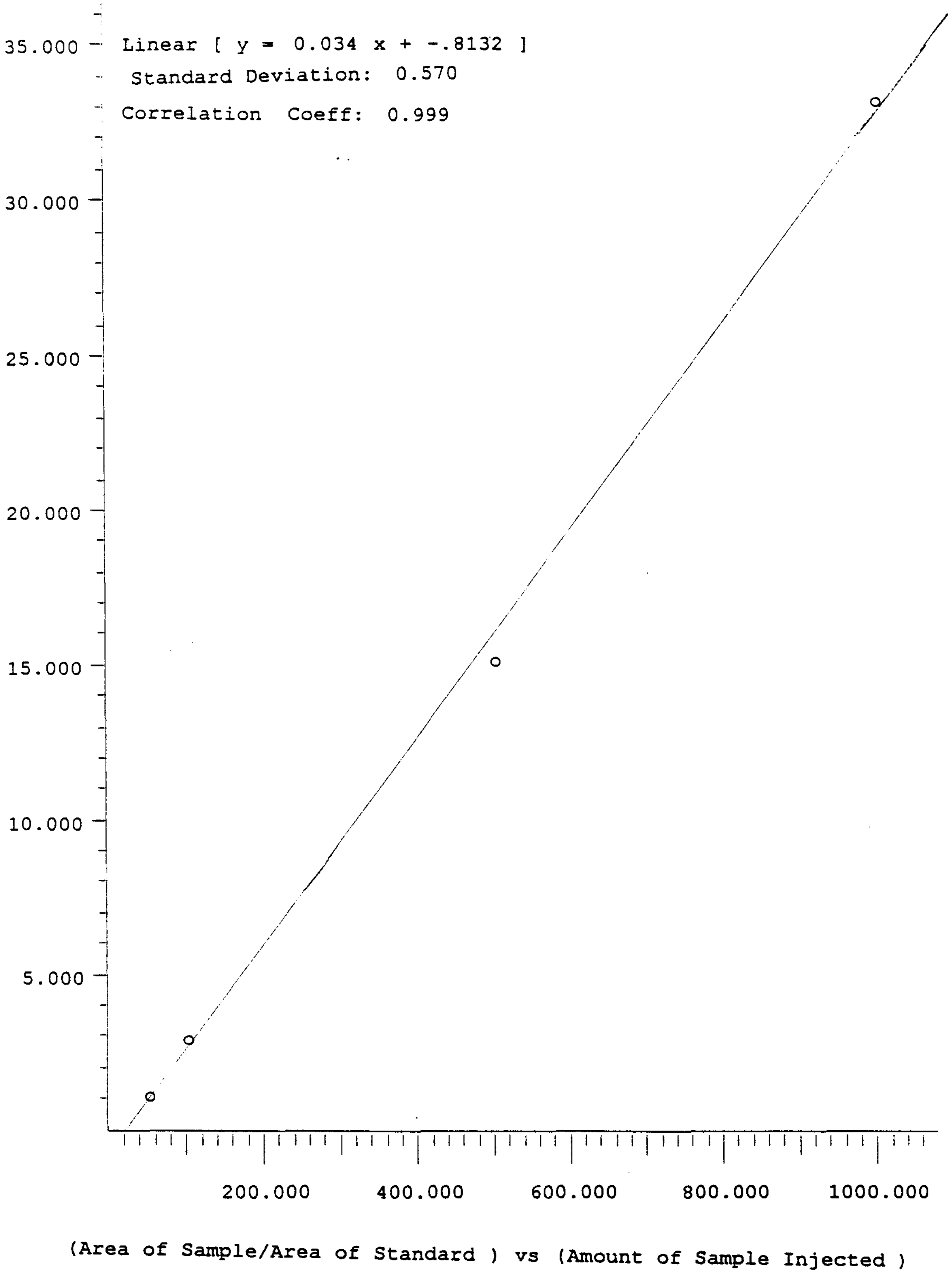

Figure A-11. Standard Calibration Plot of 1-methylphenanthrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

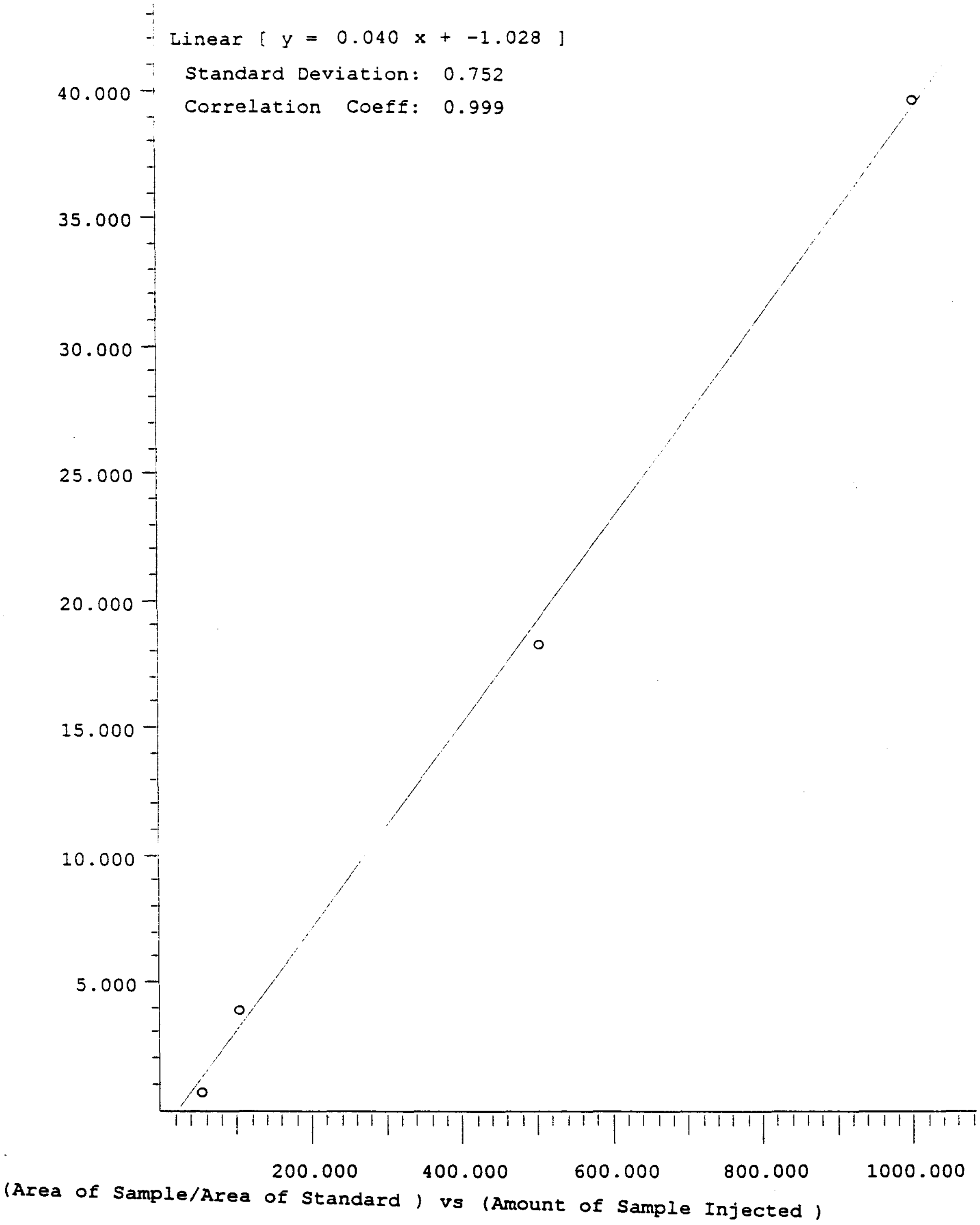

Figure A-12. Standard Calibration Plot of pyrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

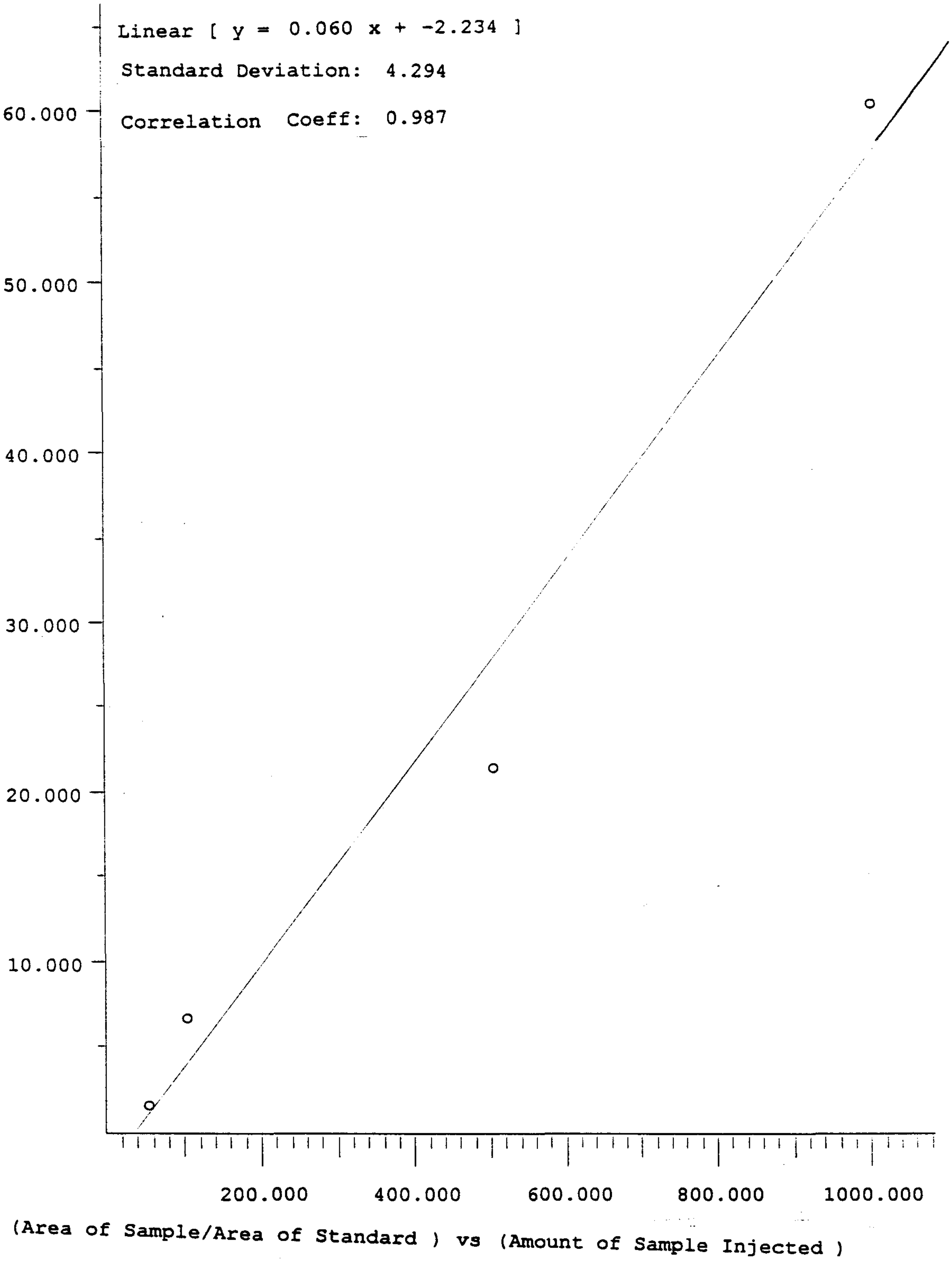

Figure A-13. Standard Calibration Plot of benzo(a)anthracene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/µL).

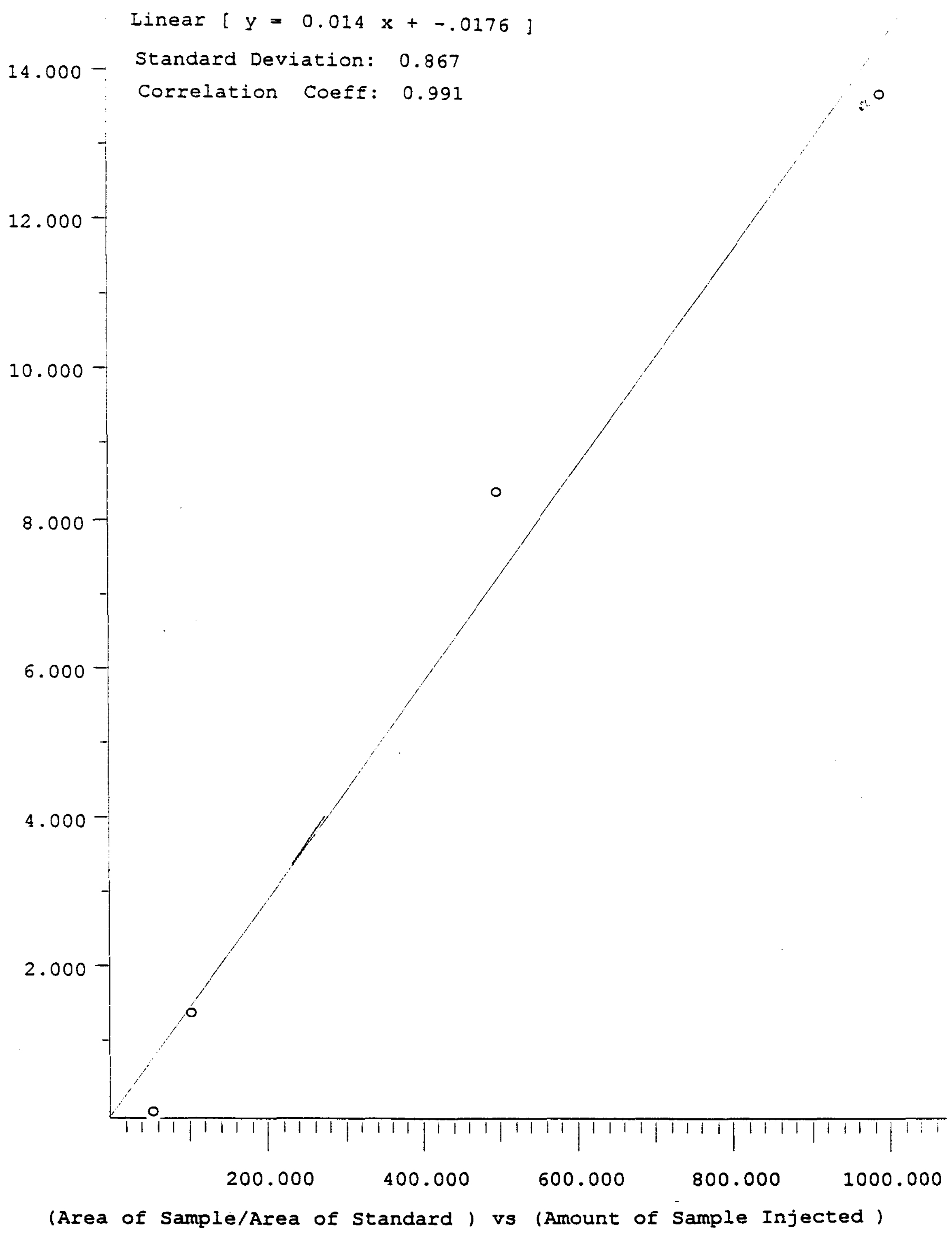

Figure A-14. Standard Calibration Plot of chrysene-d_{12} from GC/MS (4 standards ranging from 0.05 - 1.00 ng/µL).

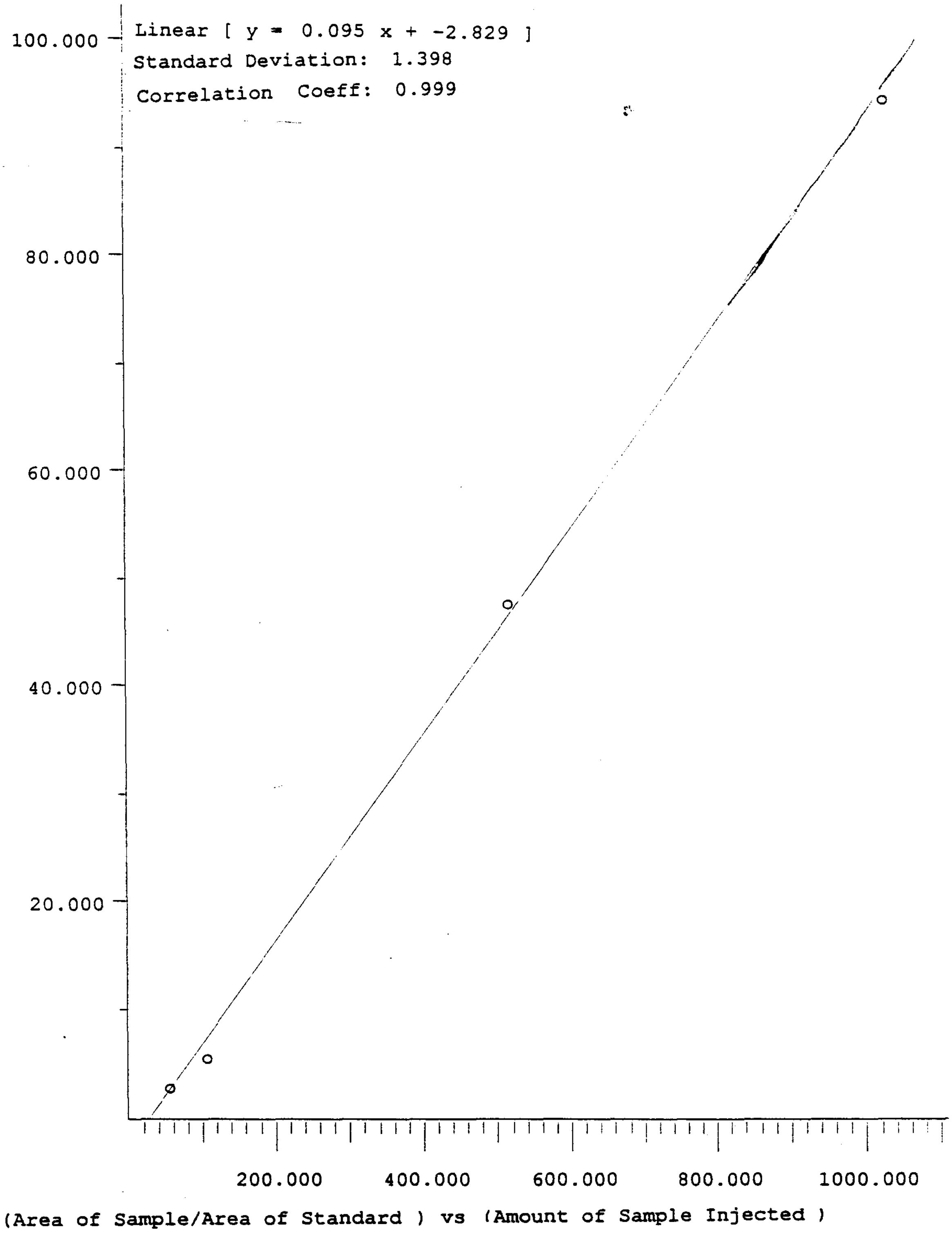

Figure A-15. Standard Calibration Plot of chrysene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

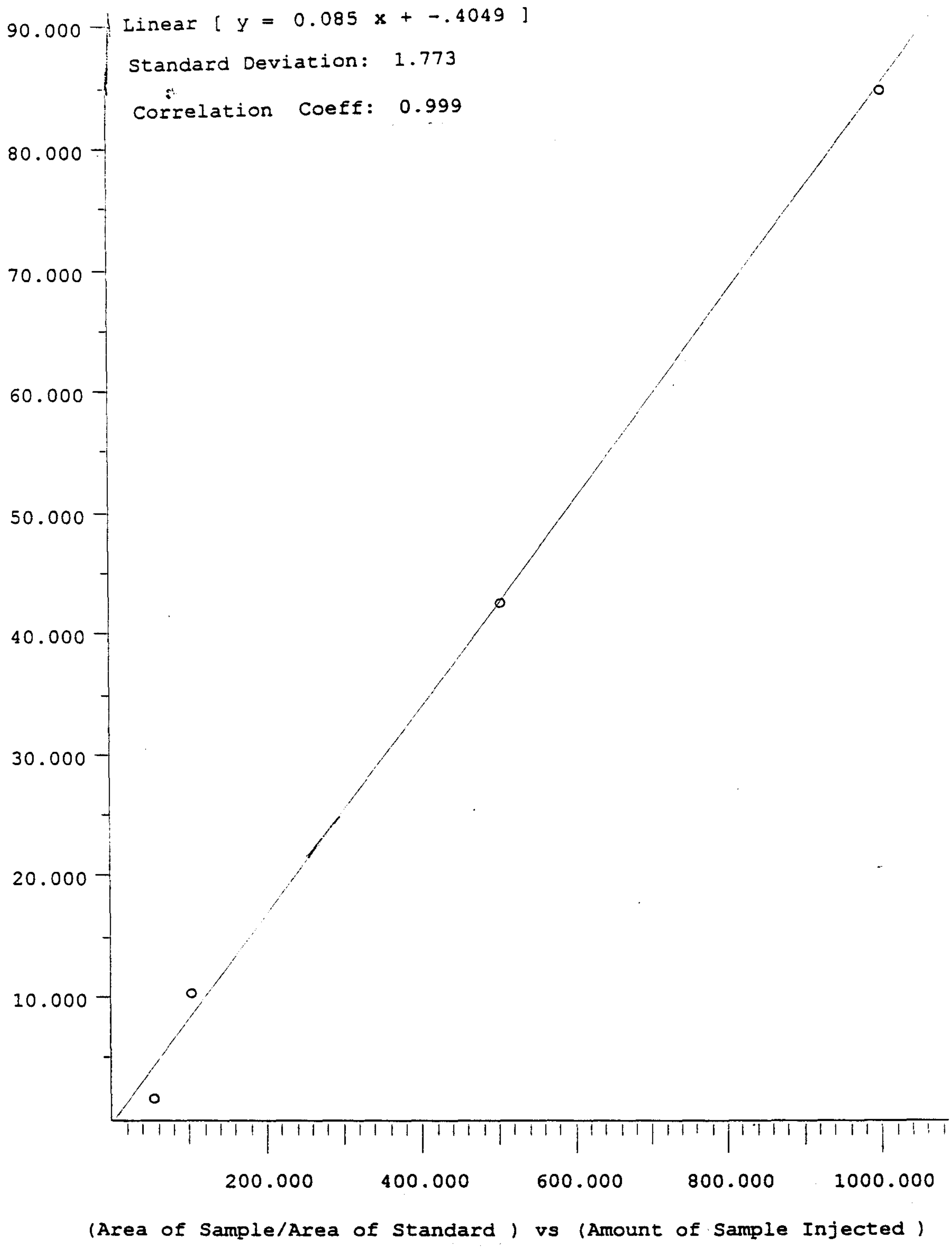

Figure A-16. Standard Calibration Plot of benzo(b)fluoranthene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/µL).

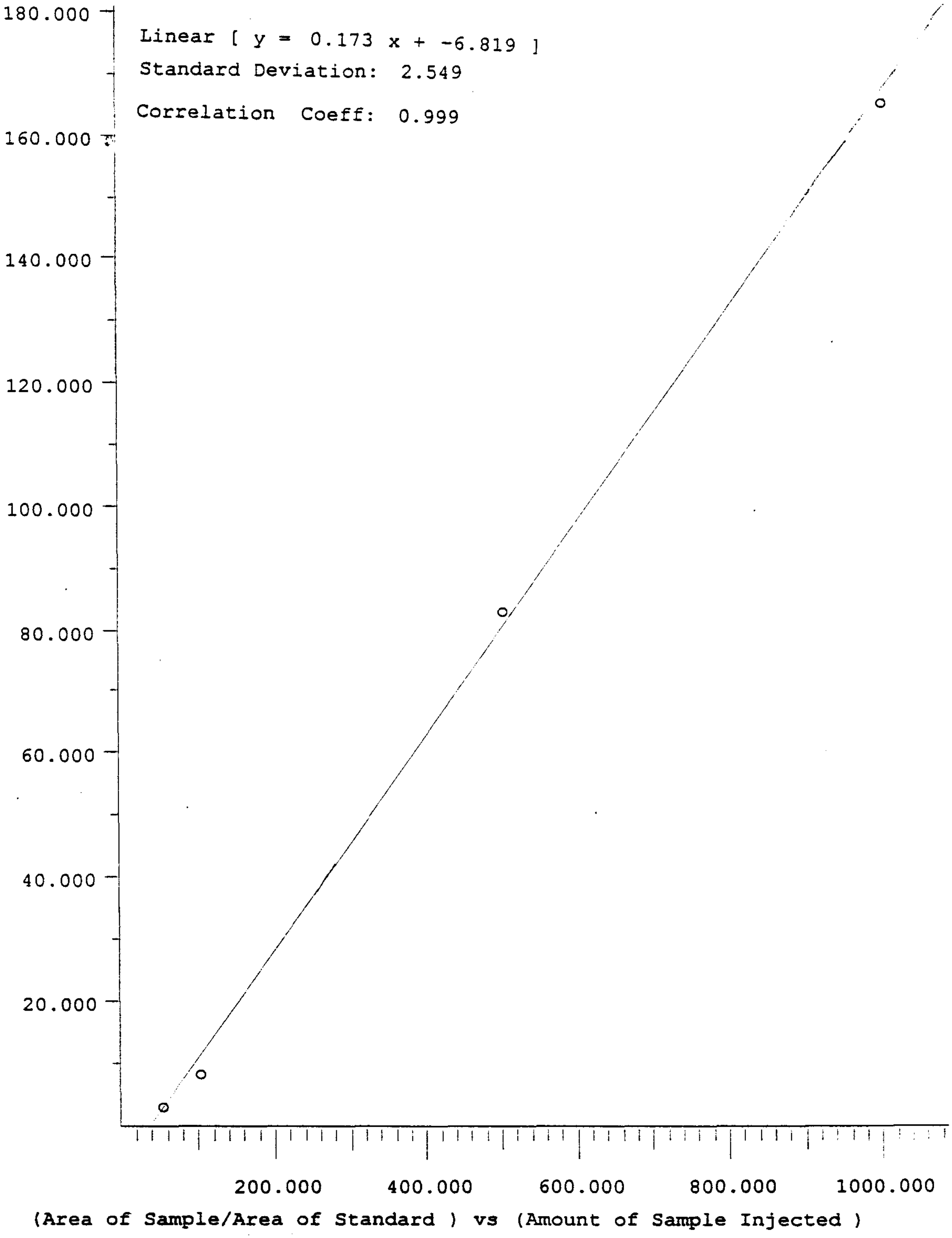

Figure A-17. Standard Calibration Plot of benzo(k)fluoranthene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

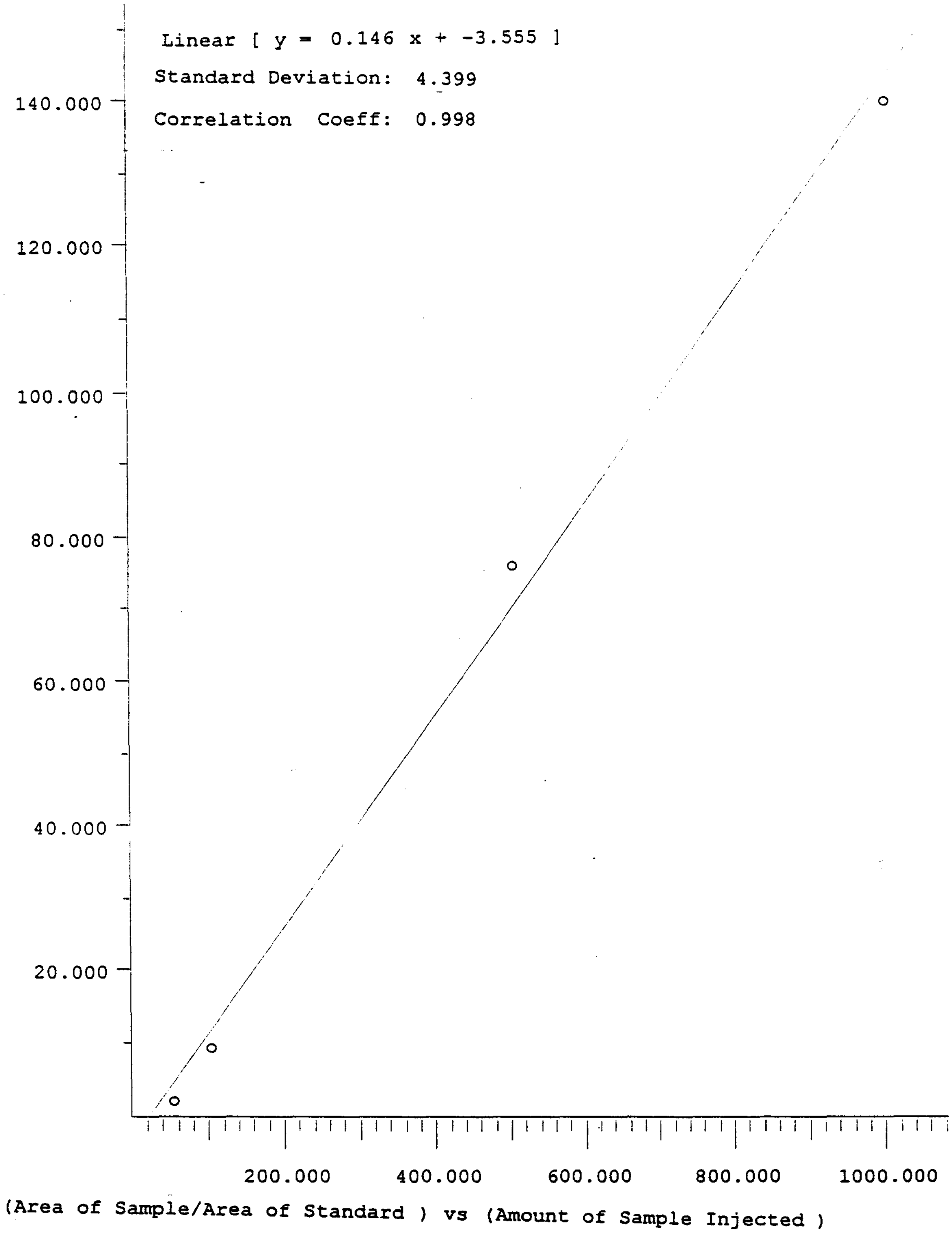

Figure A-18. Standard Calibration Plot of benzo(e)pyrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

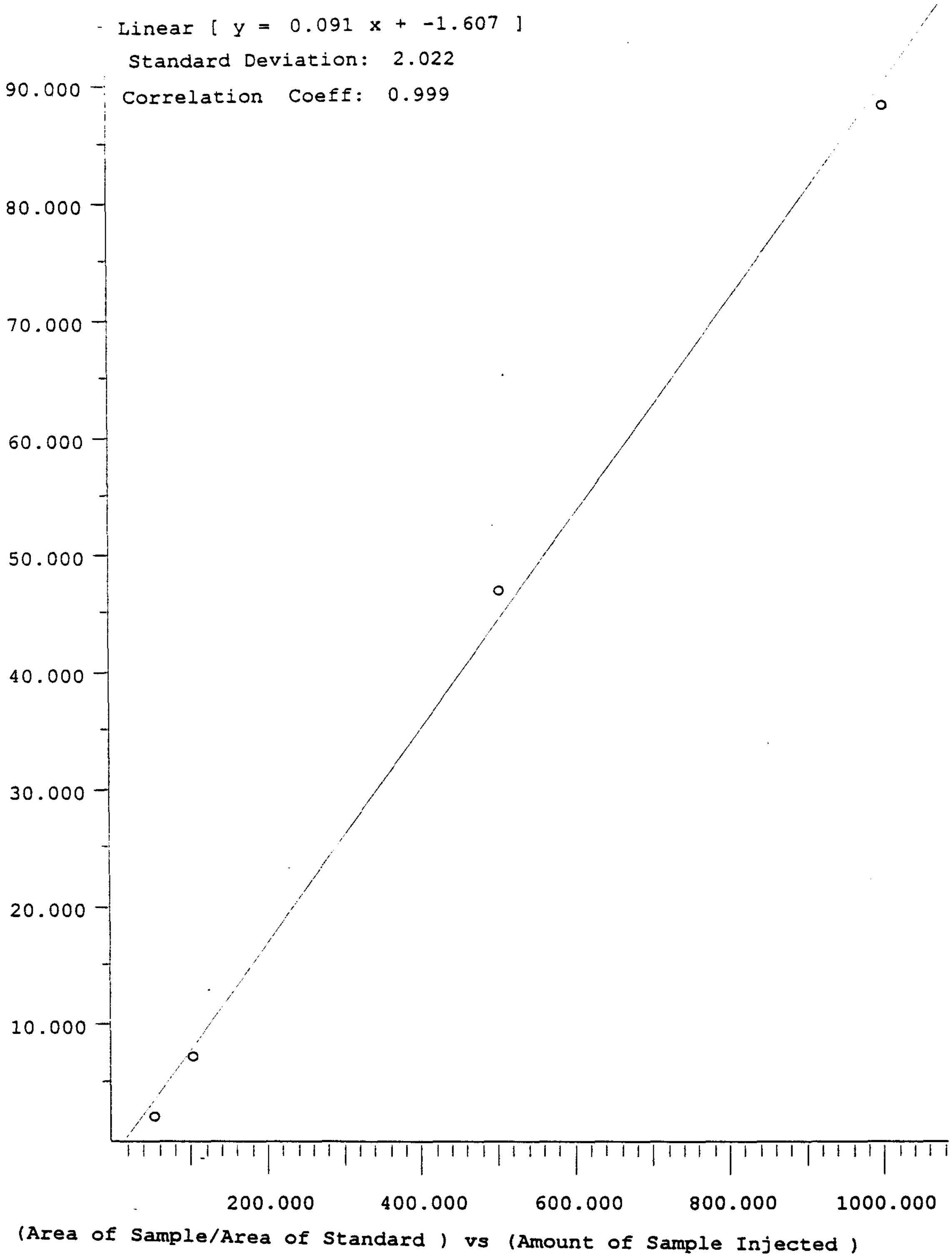

Figure A-19. Standard Calibration Plot of benzo(a)pyrene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

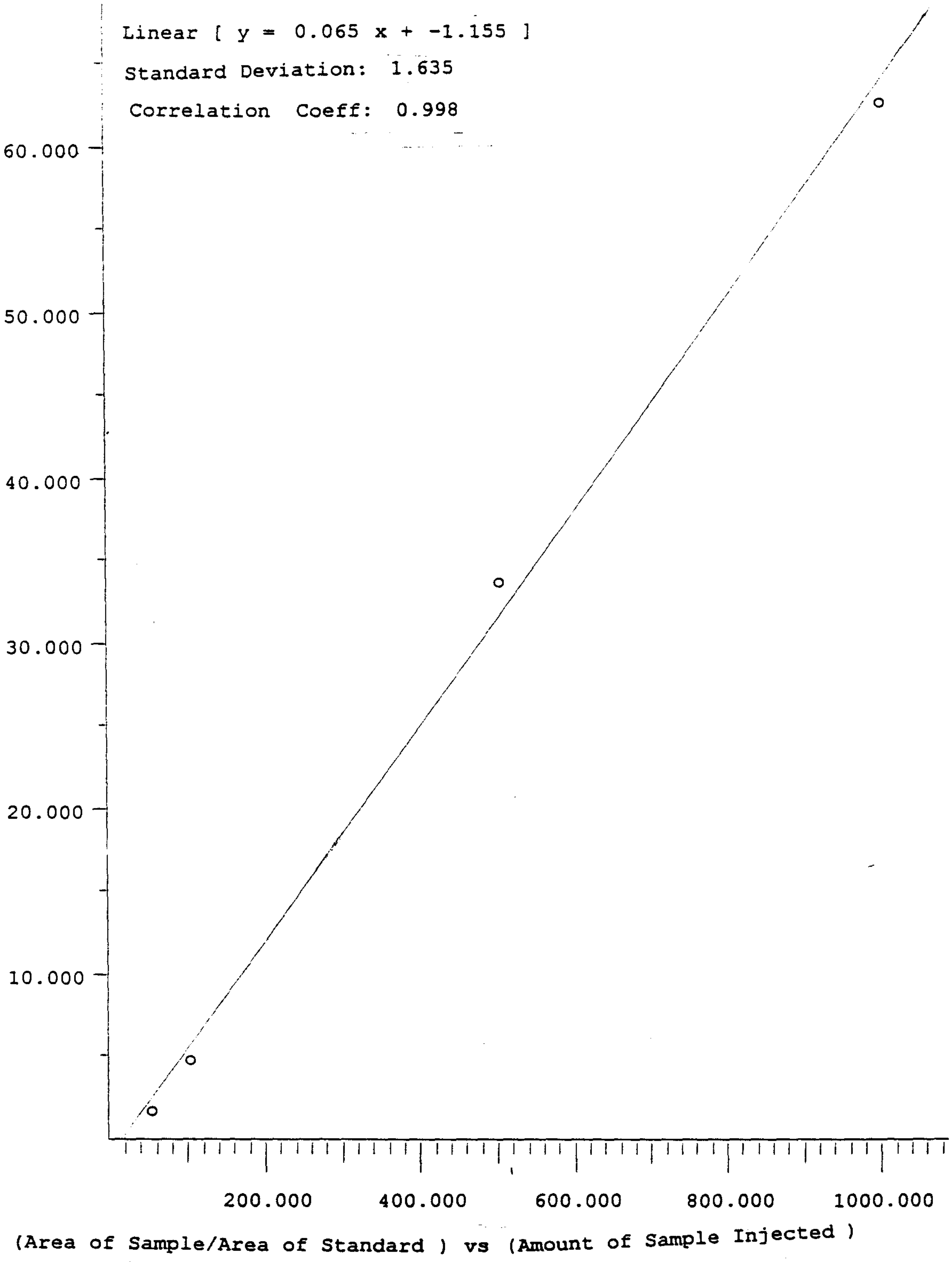

Figure A-20. Standard Calibration Plot of perylene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/µL).

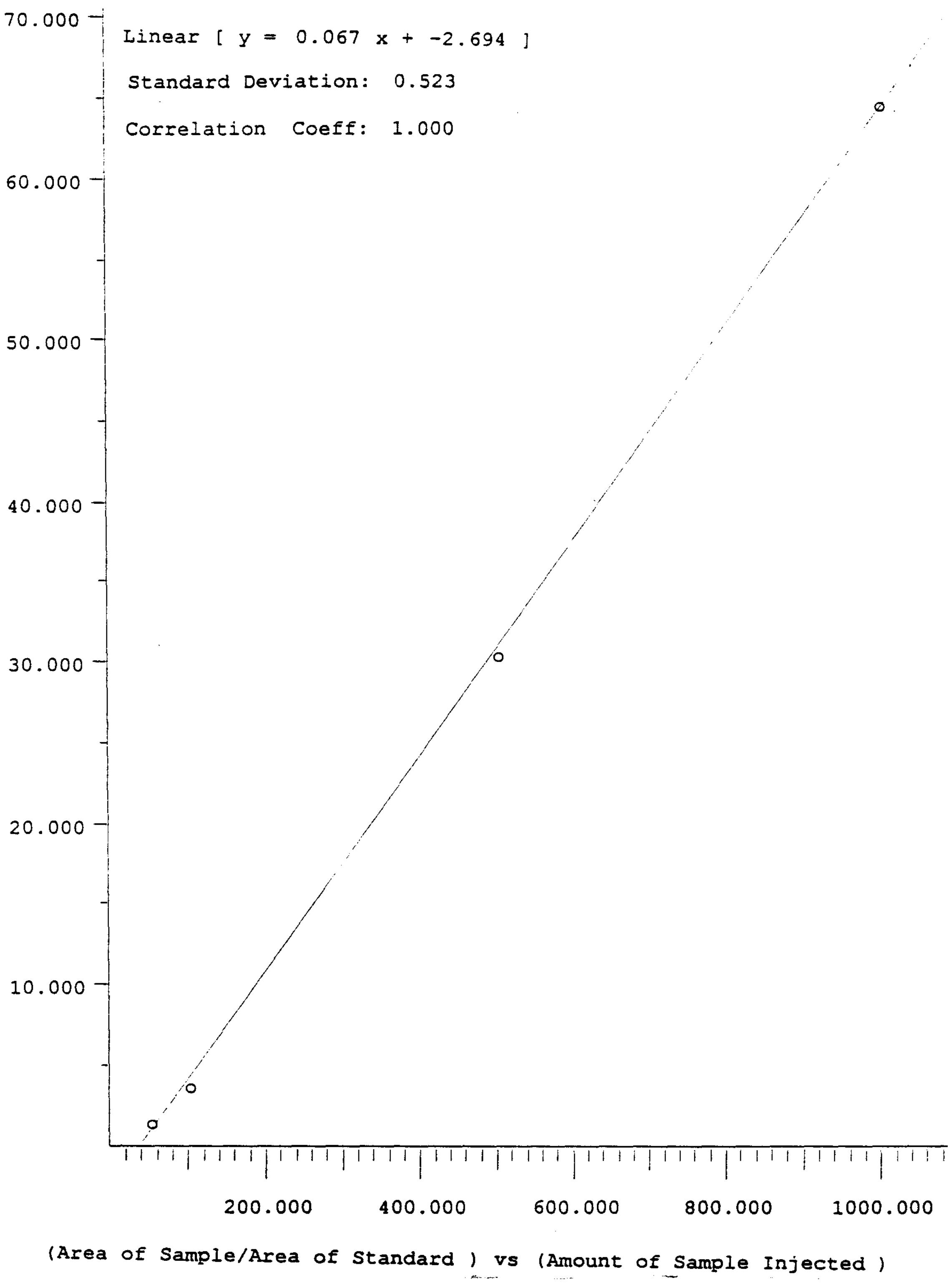

Figure A-21. Standard Calibration Plot of dibenzo(ah)anthracene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

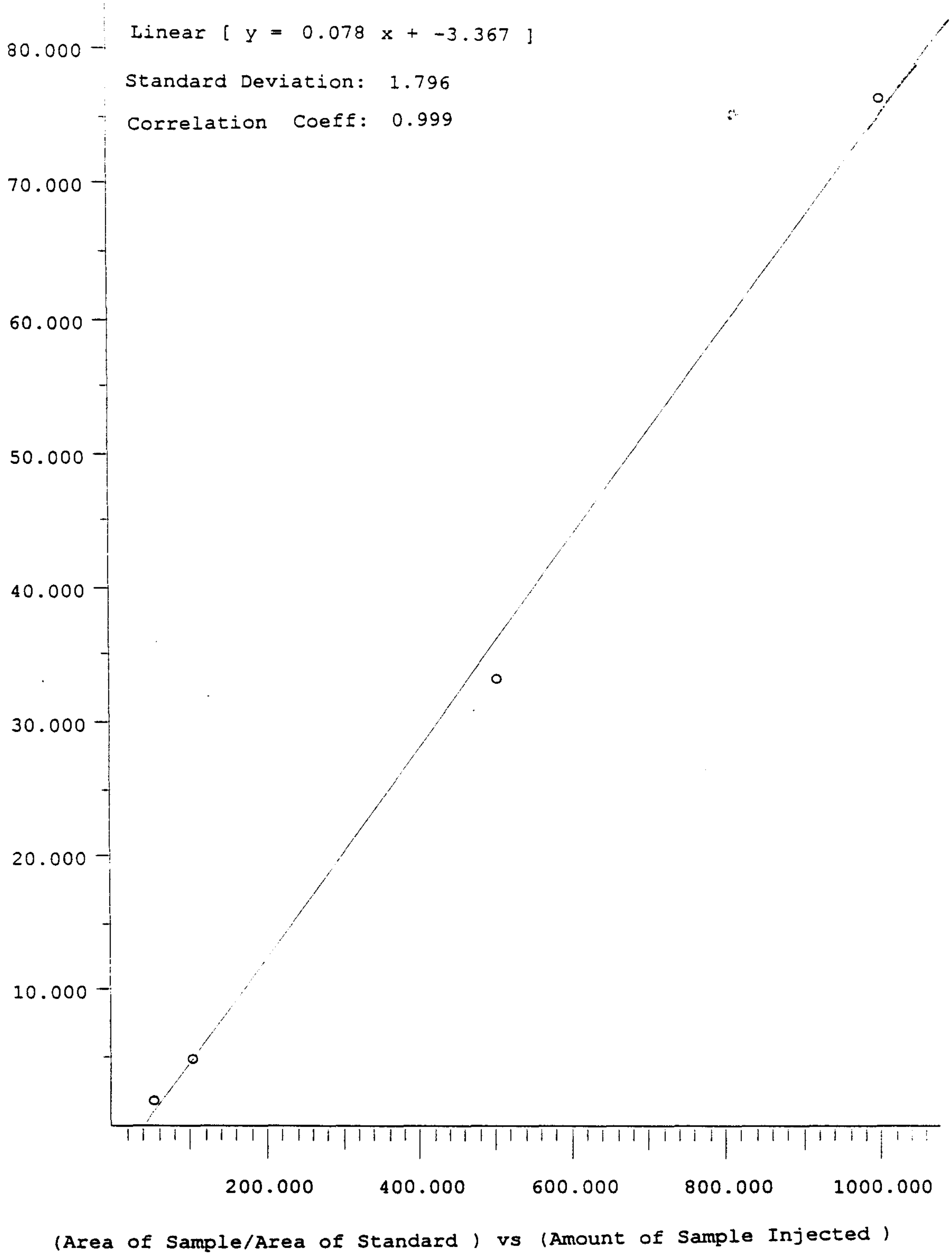

Figure A-22. Standard Calibration Plot of benzo(ghi)perylene from GC/MS (4 standards ranging from 0.05 - 1.00 ng/μL).

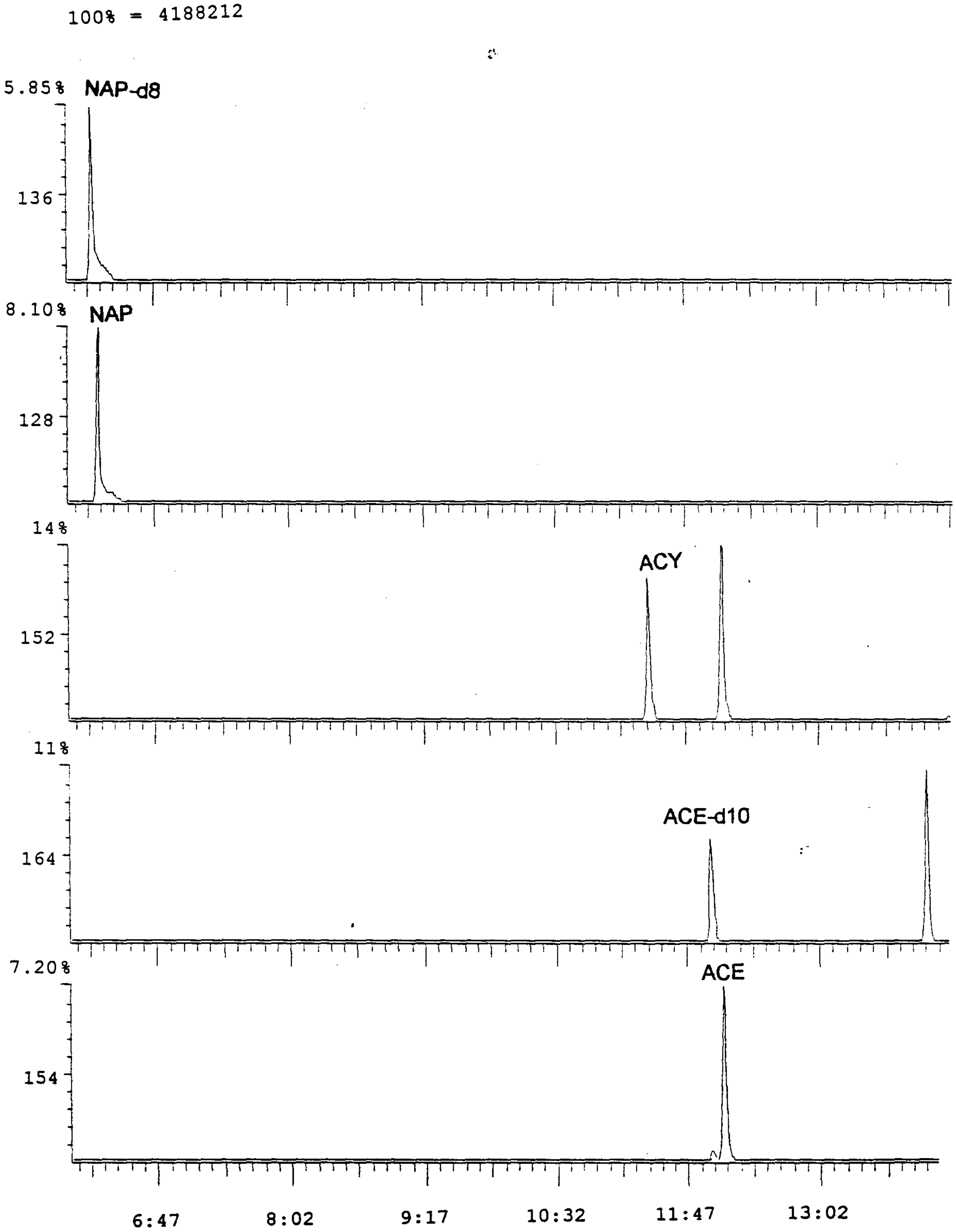

Figure A-23. Ion Chromatograms (SIM) of PAHs determined in this study.

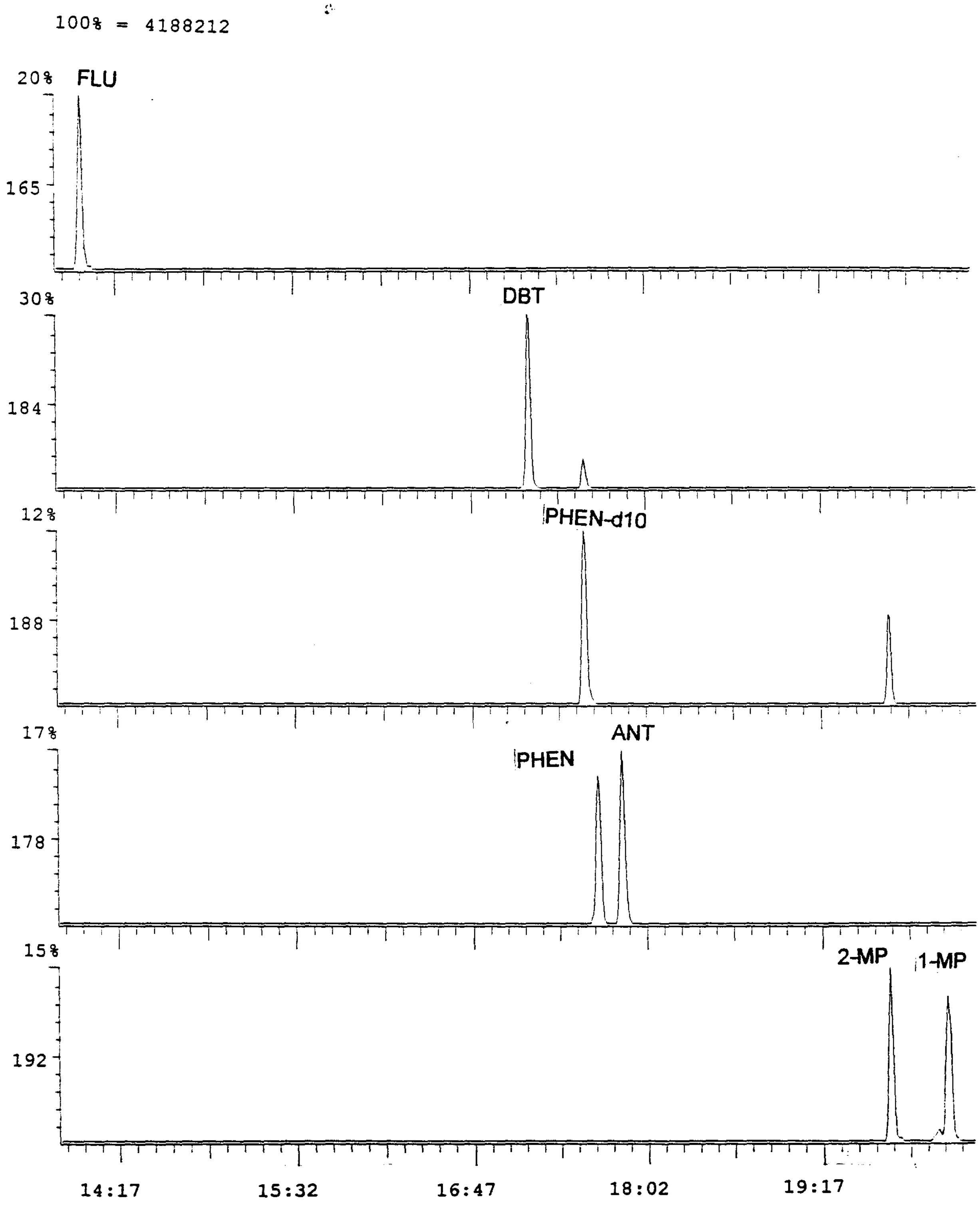

Figure A-23. Ion Chromatograms (SIM) of PAHs determined in this study. (cont.)

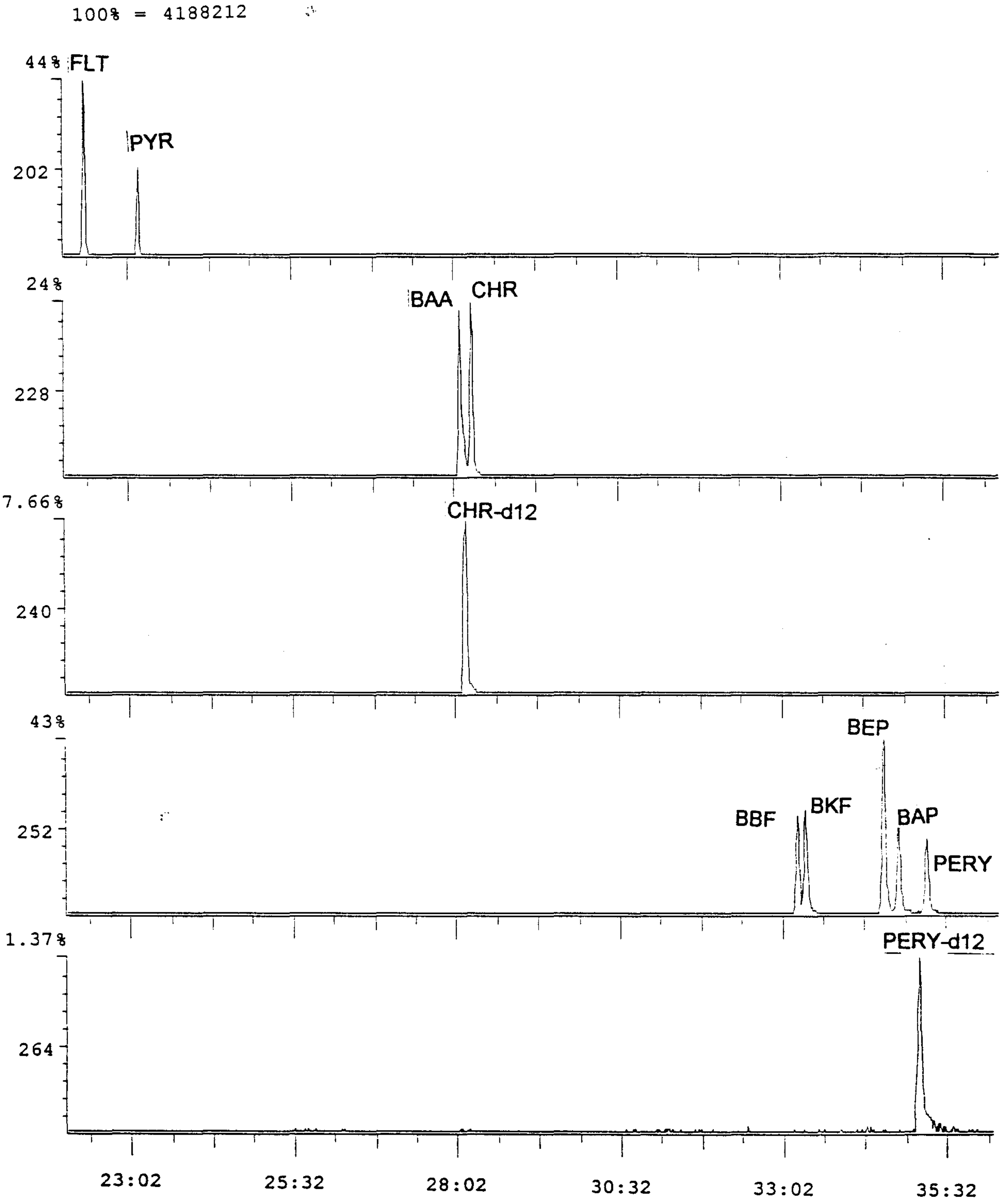

Figure A-23. Ion Chromatograms (SIM) of PAHs determined in this study. (cont.)

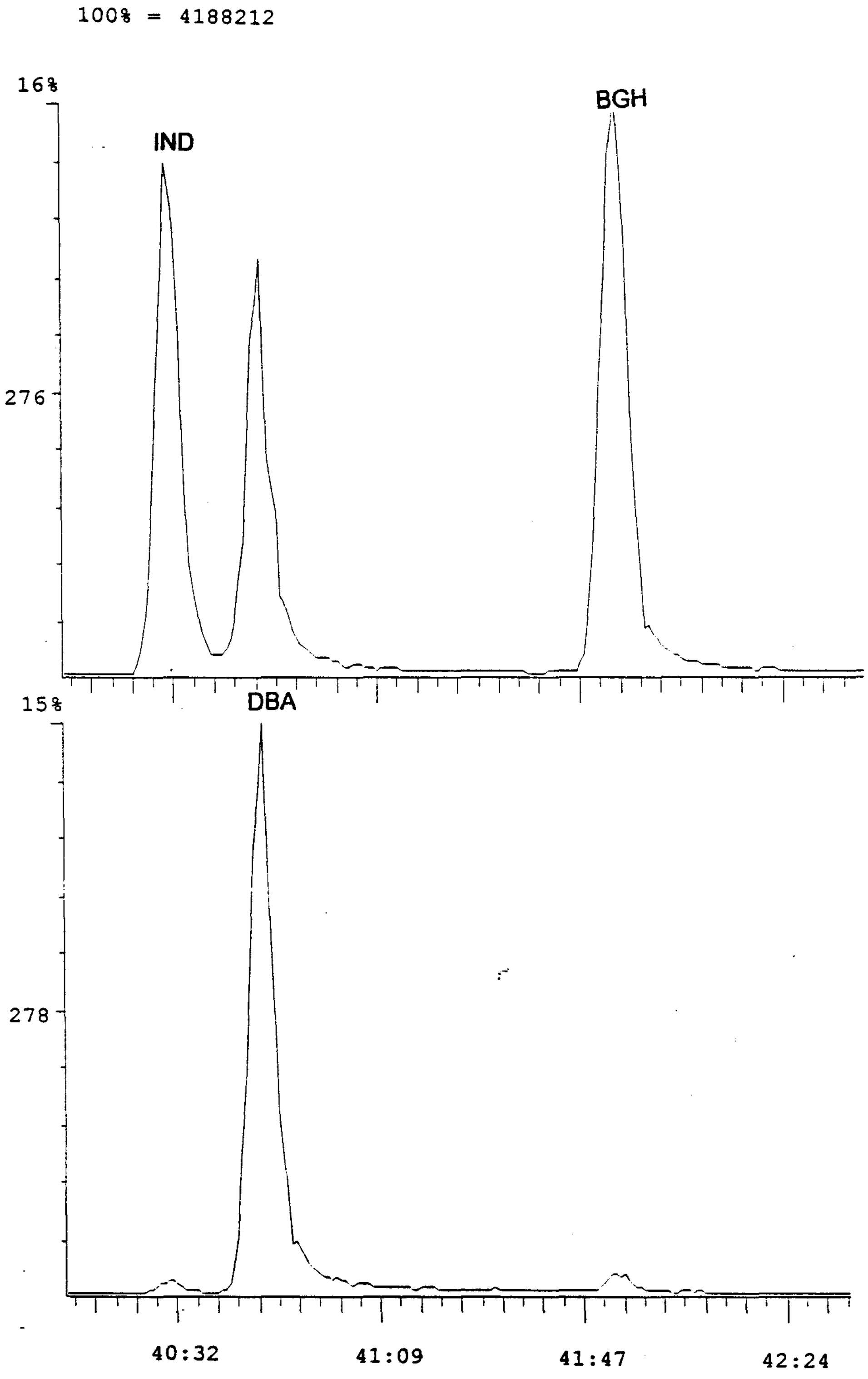

Figure A-23. Ion Chromatograms (SIM) of PAHs determined in this study. (cont.)

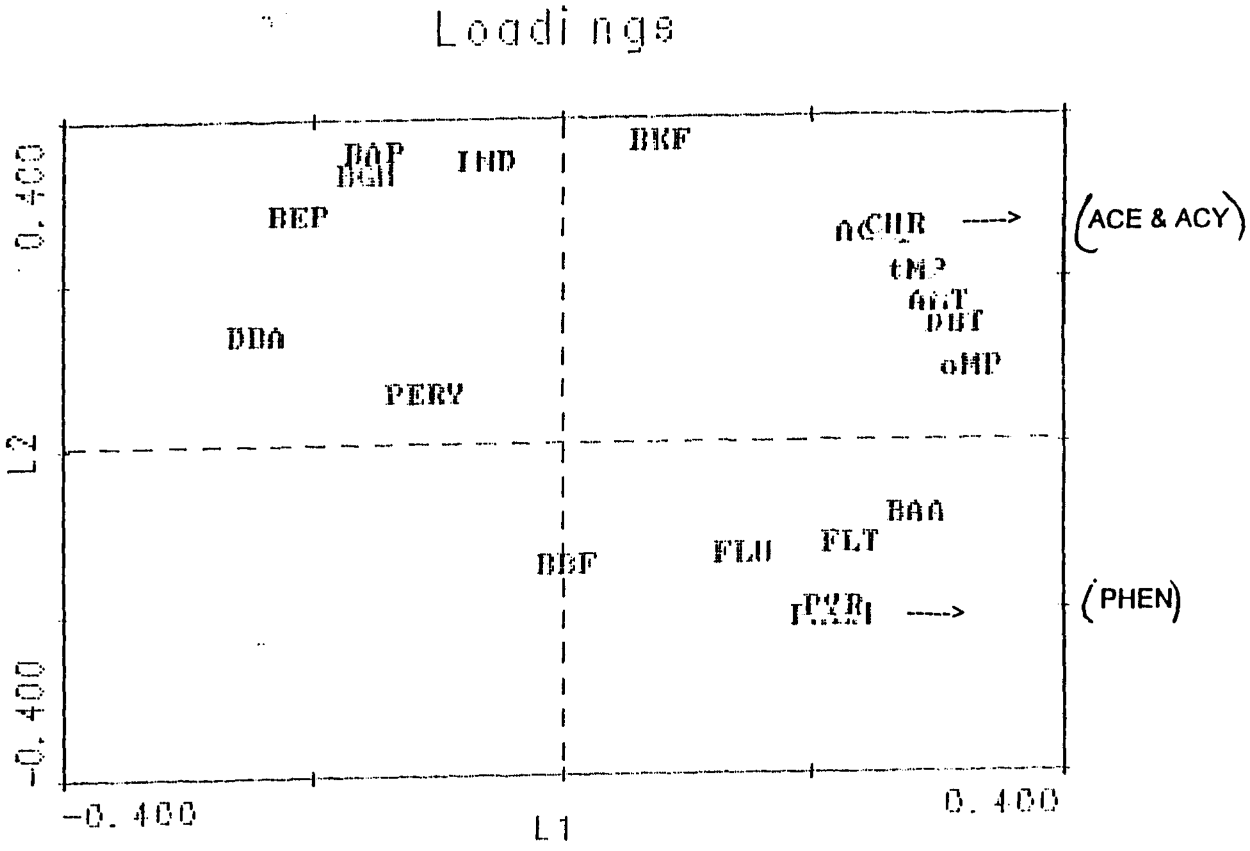

Figure A-24. A typical loadings plot from Einsight PCA program.

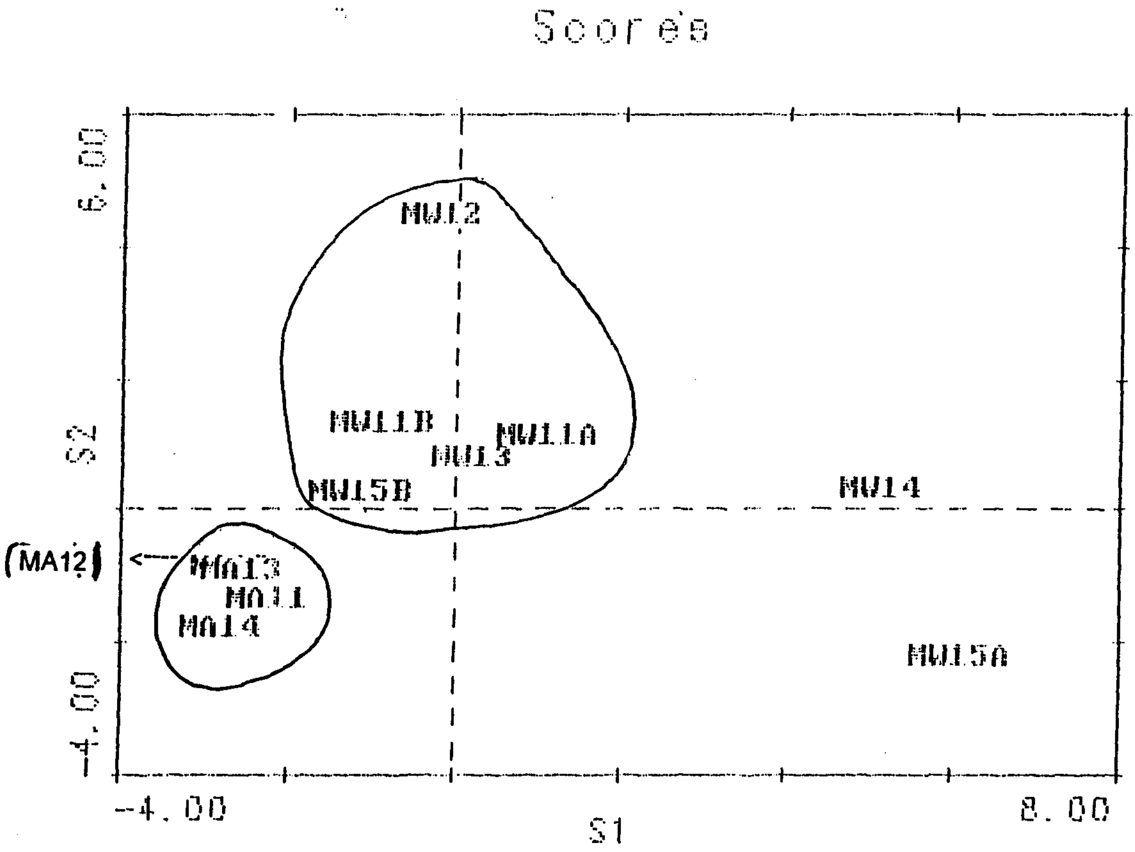

Figure A-25. PCA plot of Meander Air vs. Meander Water Scores showing the lack of correlation for most samples.

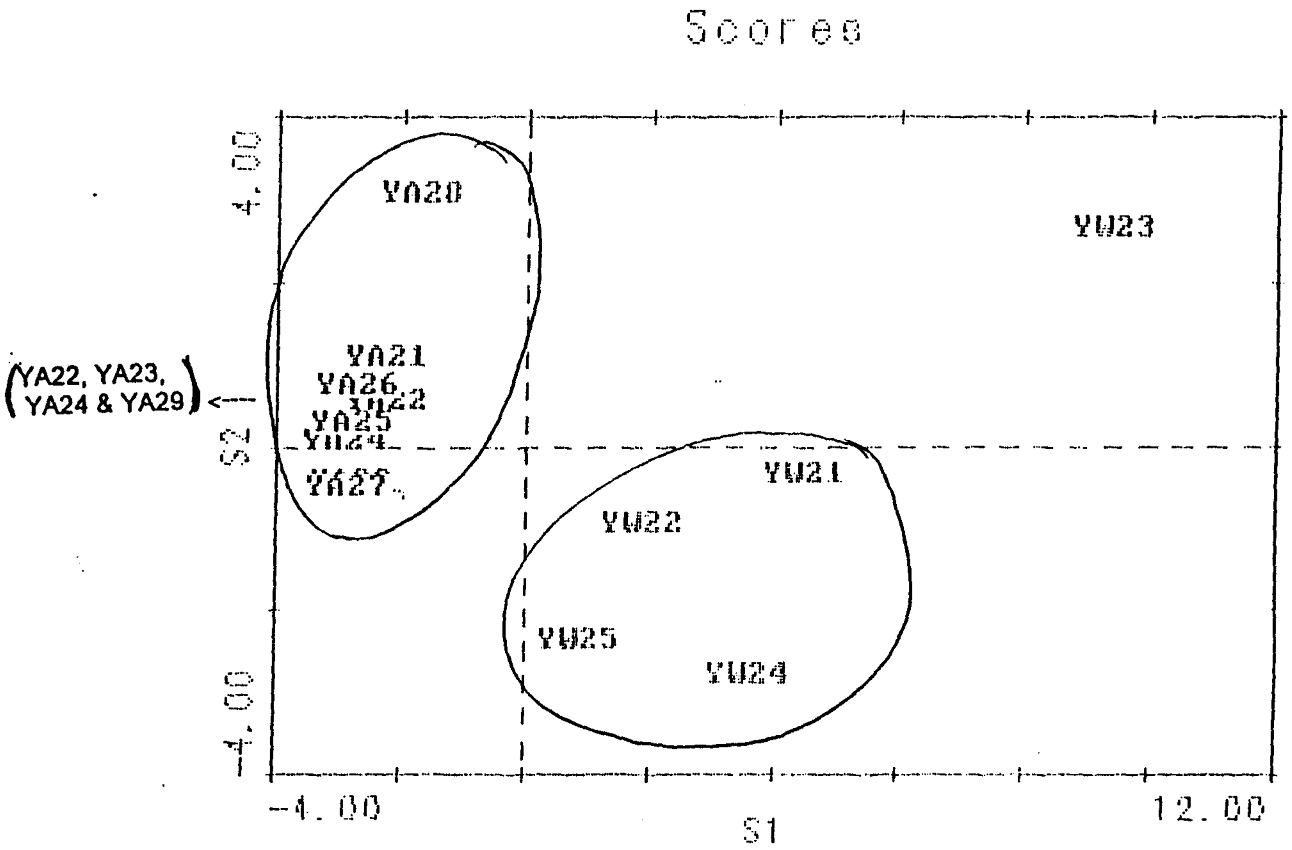

Figure A-26. PCA plot of Youngstown Air vs. Youngstown Water (Both Week 2) Scores showing the lack of correlation for most samples.

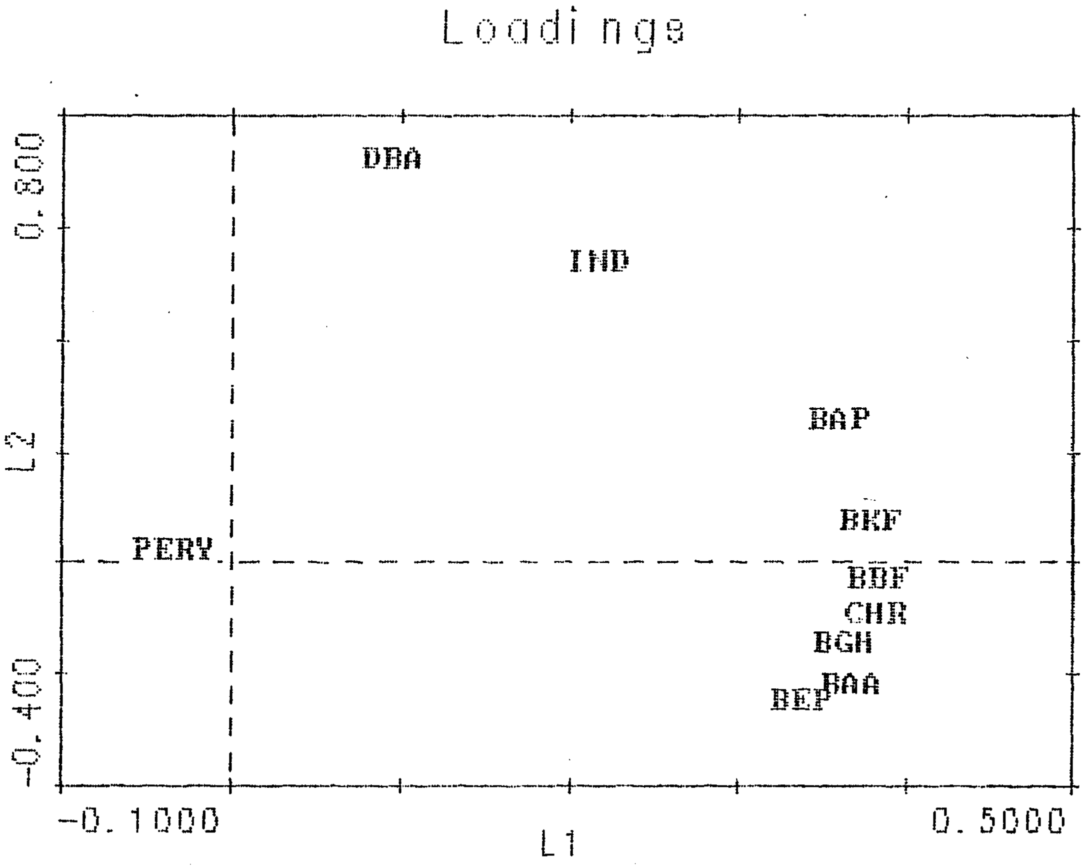

Figure A-27. Loadings plot (PCA) for Air/Water vs. Sources (Einsight).