Identification and Quantification of Selected PAHs from Soil Samples Collected at Three Industrial Sites Adjacent to the Fraser River

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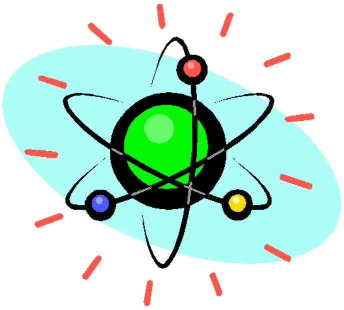

Abstract

The objective of this experiment was to investigate what if any PAHs, were contaminating the soil at an industrial site along the Fraser River in Vancouver, B.C. The sites sampled along the Fraser River have historically been home to industrial plants and commercial manufacturing.

Three different sites were sampled, each sample was analyzed twice for a total of six extractions. Extraction of the PAHs from their soil matrix was carried out with a Soxhlet Extractor using approximately 200 mL of an Organic Solvent, hexane. The resulting solution was concentrated to a volume of 8-12 mL with a macro-distillation apparatus. 1 μL of sample was injected then analyzed with a Hewlett-Packard Gas Chromatograph/Mass Spectrometer. Quantification of the concentrations was carried out through the use of an internal standard. Deutarated Anthracene was injected into the soil sample before the extraction was carried out.

The levels of PAHs in Site 1 were found to exceed the B.C. Ministry of Environment (B.C.M.O.E.) Contaminated Site Regulations for Commercial/Industrial sites for all PAHs analyzed. Many of the PAHs exceeded the regulations by 20 times. In samples from Site 2, only one PAH exceeded the B.C.M.O.E. Regulations for Commercial/Industrial sites. Methyl Anthracene with a concentration of 52 ppm exceeded the regulations of 50 ppm dry weight. In the samples from Site 3, near a rail line, the concentrations of Fluorene, Phenanthrene, Anthracene and Methyl Anthracene exceeded the B.C.M.O.E. Regulations for Commercial/Industrial sites.

This experiment confirmed that site 1 was severely contaminated with PAHs, and that the remediation of the site was justified. While site 2 only exceeded the regulations for Commercial/Industrial for one PAH, the site exceeded the stricter (B.C.M.O.E.) Regulations for Residential/Urban Park for many of the PAHs analyzed. Concentrations of PAHs from site 3 exceeded the regulations for at least four PAHs, and if further sampling and analysis confirmed these results, the site should be remediated.

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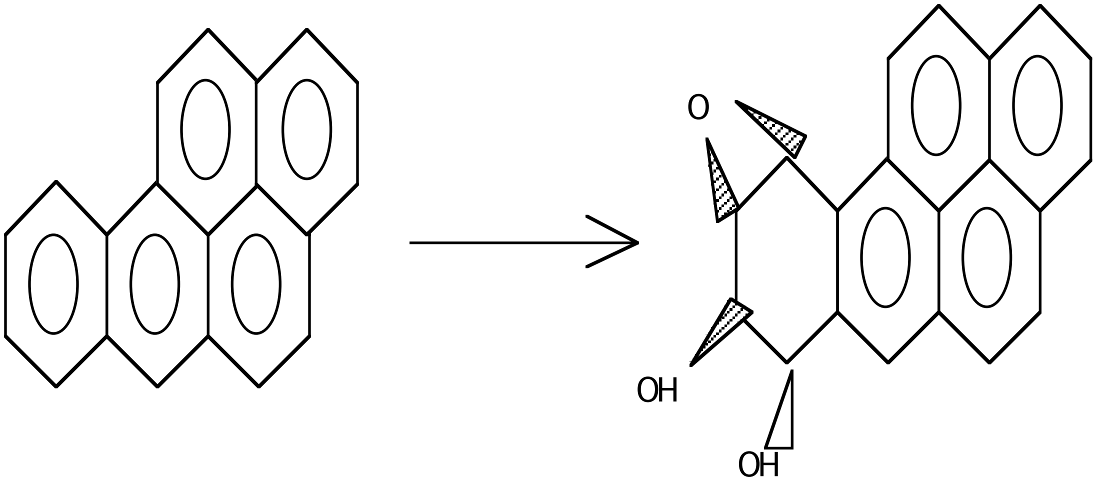
Introduction:

Polycyclic Aromatic Hydrocarbons (PAHs) are Persistent Organic Pollutants (POPs). Due to their chemical structure, PAHs are quite resistant to degradation. In addition to being long lived, PAHs build up within fatty tissue of animals and humans. This bio-accumulation can have health repercussions as many PAHs are either suspected carcinogens or known carcinogens.

PAHs such as Benzo[a]pyrene are not carigenic themselves, but react in the body to form cargigenic compounds. PAHs undergo enzyme-catalyzed oxidation and are changed to a diol epoxide after it enters cells. The oxidized compund is more water soluble and can be eliminated from the cell, but the diol epoxide is carcigenic. Mutations within the cell cuases the cell to lose its ability to control replication, leading to uncintrolled growth.



Benzo[a]pyrene

diol epoxide

Enzyme-Catalyzed Oxidation Reaction of a PAH

(Mechanism taken from Organic Chemistry, Schmid)

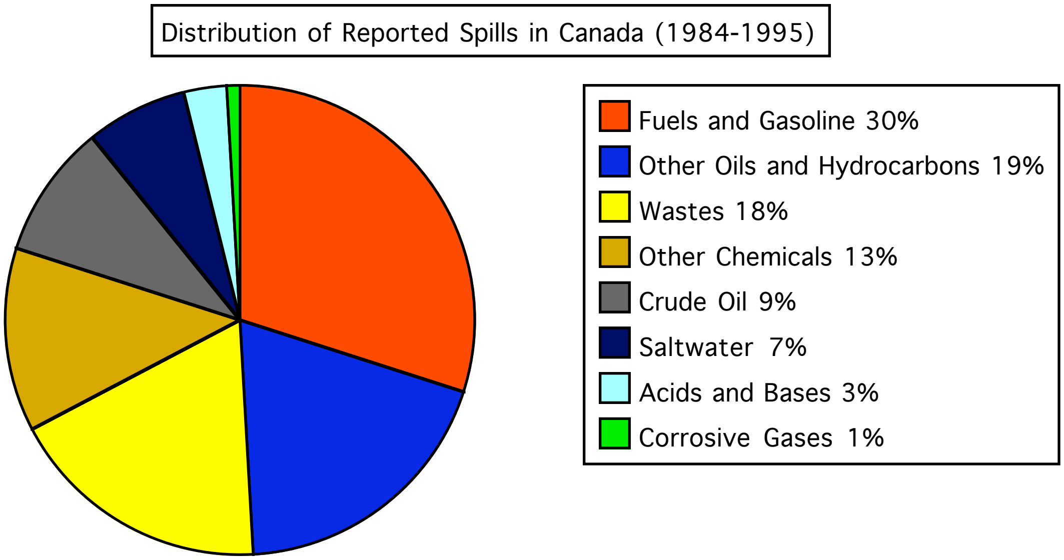
PAHs have been connected with liver lesions in English Sole by two studies conducted in Washington State: Malins et al. 1984 and Myers et al 1987. In a study by Environment Canada these findings were confirmed. 75% of mature English Sole from the Port Moody Arm had either pre-cancerous or cancerous liver lesions. The liver lesions were strongly correlated with levels of PAHs in the river sediment. Elevated concentrations of PAHs have been found in Vancouver Harbour and in the Fraser River near the Oak St. Bridge. Results published by Environment Canada in Water Quality in the Fraser River Estuary January 1993 to March 1994 found concentrations of Pyrene and Benzo[a]pyrene of 20-140 ppm at the Oak St. Bridge. Concentrations of Phenanthrene, in that same study was found to be 300-370 ppm. (The State of Canada's Environment)

PAHs bio-accumulate because they are fat soluble. Once absorbed into an organism the PAHs build up with in the the fatty tissue. The accumulation in smaller organisms may be small, but are magnified up the food chain. Bio-magnification occurs when larger organisms/animals ingest smaller organisms/animals, who themselves are contaminated. The contaminants are passed up the food chain. (MacKenzie Basin Impact Study)

While PAHs do occur naturally as a by-product of biological activity, the most worrying PAHs are generated by humans. Once released into the environment, PAHs do not readily degrade. The resonance that comes from the structure of the benzene rings that are characteristic to PAHs means that the compounds are relatively stable. Also the low volatility and low aqueous solubility make PAHs very persistent pollutants. (Some aspects of the Distribution and Fate of Polycyclic aromatic Hydrocarbon Contamination in the Kitamat Fjord System)

Primarily PAHs enter the environment in two ways, petroleum spills and incomplete combustion of hydrocarbons. PAHs can enter river systems or sediment through either run off, leaching and disposal of refinery effluents. In the period between 1984-1995 94,000 spills were reported in Canada releasing 11,000,000 tonnes of pollutants into the environment. 58% of the spills (by weight) were of petroleum products.

Total Number of Spills Reported in Canada Between 1984-1995	Total Reported Amount of Contaminants Spilled in Canada (tonnes)
94,000	11,000,000



The above data is from Environment Canada's Summary of Spill Events in Canada. The data is only for those spills that were reported through a voluntary reporting system. Data from Alberta was not available from 1991 on.

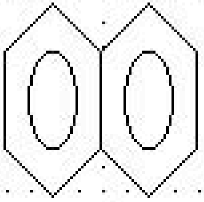
While Environment Canada doesn't keep figures for the amount of incompletely combusted petroleum products released in Canada, it does believe that pollution from highly publicized cases of pollution account for only a small minority of this form of pollution. For 16 days, from February 12-28, 1990 a used tire dump burned uncontrollably in Hagersville Ontario. The intensity of the fire meant that firefighters could not put the fire out, but could only contain the blaze. An estimated 12.6 million tires burned releasing 12,000-15,000 litres of oil into the local water table. The company, Trye King, that owned the dump was able to avoid environmental protection laws that were enacted a couple years earlier. These laws would have lowered the chance that a small fire could spread into a large fire. This is an example were laws to protect the environment are on the books are not always enforced. (Summary of Spills Events in Canada)

The importance of having a healthy Fraser River has been recognized by the B.C. government. The Fraser River is 1400 km long, and supports 80% of the economic activity in B.C. 44% of the farm land in B.C. is in the boundaries of the Fraser River Drainage Basin. Two- thirds of B.C. 2.9 million population live within the Basins boundaries. (Water Quality Trends in the Fraser River Basin)

Chemical Structures of Selected PAHs

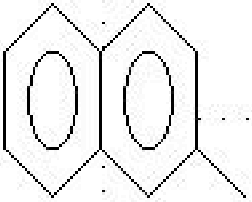
Naphthalene:

MW =128g/mol
B.P. = 178 ^{O}C



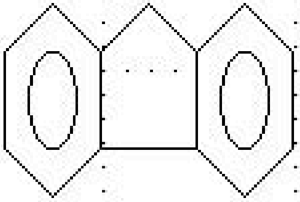
Methyl Naphthalene:

MW = 142 g/mol



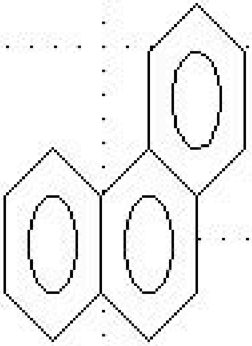
Fluorene:

MW = 166 g/mol
B.P. = 294 ^{O}C



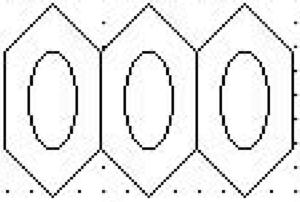
Phenanthrene:

MW = 178 g/mol
B.P. = 340 ^{O}C



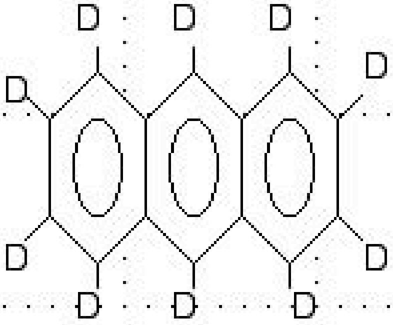
Anthracene:

MW = 178 g/mol
B.P. = 342 ^{O}C



D-10-Anthracene:

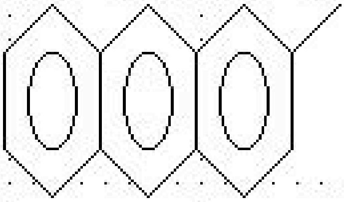
MW = 188 g/mol



Chemical Structures of Selected PAHs Cont'd

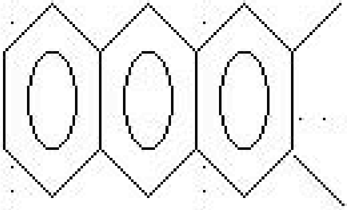
Methyl Anthracene:

MW = 192 g/mol



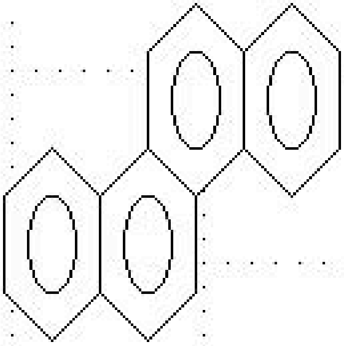
Dimethyl Anthracene:

MW = 206 g/mol



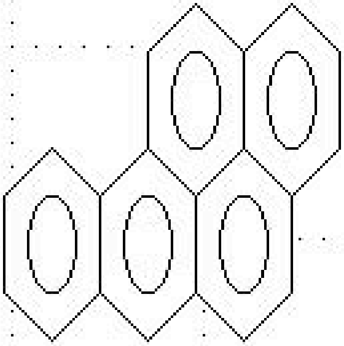
Chrysene:

MW = 228 g/mol
B.P. = 448 ^{O}C



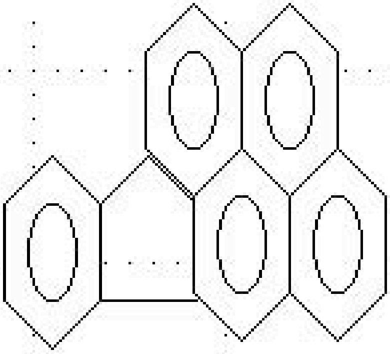
Benzo[a]pyrene:

MW = 252 g/mol
B.P. = 475 ^{O}C

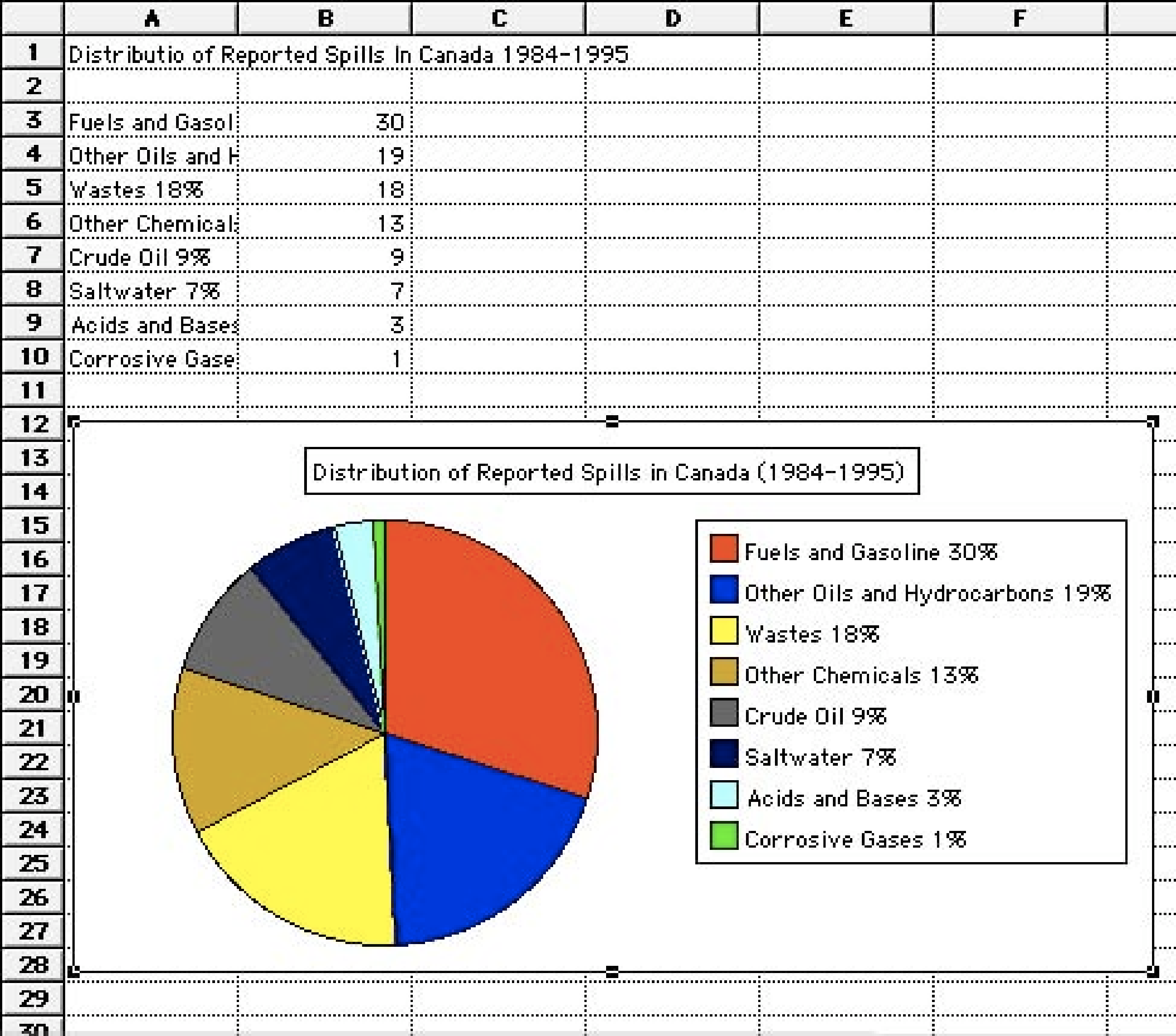


Indeno[1,2,3-cd]pyrene:

MW = 276 g/mol
B.P. = n/a ^{O}C



The above information was taken from Analysis of Polycyclic Aromatic Hydrocarbons by Chemical Ionization Ion Trap Mass Spectrometry



	A	B	C	D	E	F
1	Distributio of Reported Spills In Canada 1984-1995					
2						
3	Fuels and Gasol	30				
4	Other Oils and H	19				
5	Wastes 18%	18				
6	Other Chemical:	13				
7	Crude Oil 9%	9				
8	Saltwater 7%	7				
9	Acids and Bases	3				
10	Corrosive Gase	1				

B.C. Ministry of Enviroment Lands and Parks
Contaiminated Sites Regulations

Polycyclic Aromatic Hydrocarbon	Maximum Concentration for Agricultural Land Use (ppm)	Maximum Concentration for Urban Park/Residential Land Use (ppm)	Maximum Concentration for Commercial/Industrial Land Use (ppm)
Naphthalene	0.1	5	50
Fluorene	0.1	5	50
Phenanthrene	0.1	5	50
Anthracene	0.1	5	50
Benzo[c]phenanthrene			
Benz[a]-anthracene	0.1	1	10
Chrysene	0.1	1	10
Triphenylene			
Tetracene (naphthacene)			
Benzo[b]fluoranthene	0.1	1	10
Benzo[k]fluoranthene	0.1	1	10
Benzo[e]pyrene			
Benzo[a]pyrene	0.1	1	10
Perylene			
Indeno[1,2,3-cd]-pyrene	0.1	5	50
Benzo[ghi]perylene			

Chemicals for no value is presented were not listed in the regulations.

Experimental:

Sample Collection:

Both Site 1 and Site 2 were previously sampled. Collected in 1997 from two industrial sites adjacent to each other, the two samples have been stored in a cool, 5-10 ^{O}C, dry and dark room, since then. The two samples were collected with a stainless steel trowel. To avoid contamination, the trowel was cleaned with detergent then rinsed with de-ionized water, before it was used. Approximately one foot of top soil was removed before the sample was collected. Approximately one litre of soil was collected.

Site 3 was sampled from along side railway tracks close to sites 1 & 2 on march 10, 2001. The stainless steel trowel was used and cleaned as noted above before use and after cleaning away surface gravel and soil. Approximately six inches of surface gravel and soil was removed. Approximately one litre of sample was collected.

Sample Preparation:

Two sub-samples weighing approximately 10.0 g where taken from each of the original samples. When the 10.0 g was taken for each sub-sample gravel and large pieces of organic material were excluded. These 10.0 g sub-samples were dried with approximately 2.0 g (20% by mass) of Sodium Sulphate. The Sodium Sulphate (powder) was added to the soil and the two where mixed together with a stainless steel spatula.

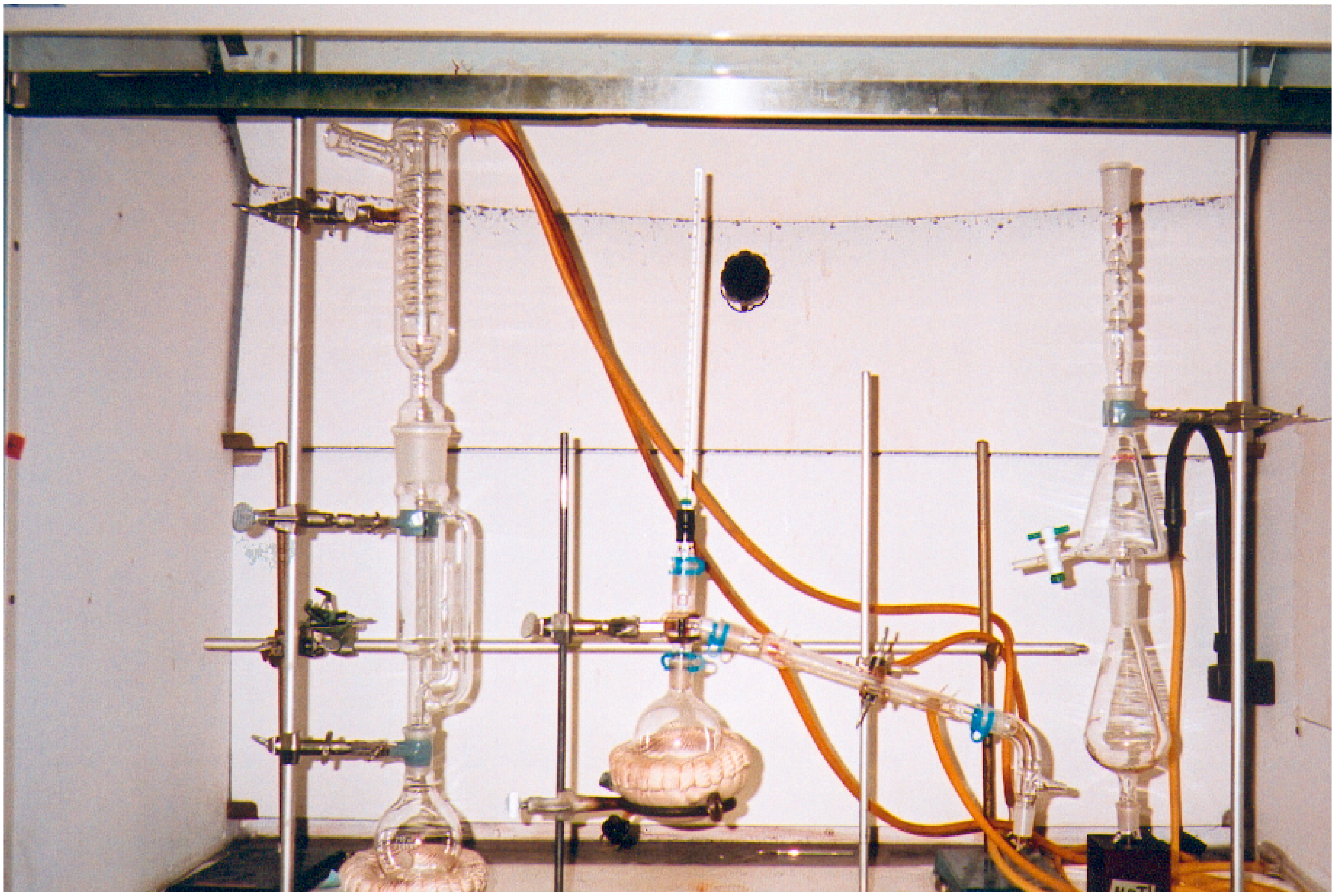
The sample was transferred to a thimble for use in a Soxhlet Extractor. Each sample was then spiked with 100 μL of Deutarated Anthracene, as an internal standard. 200 mL of N-Hexane was used as the organic solvent to extract the PAHs from the soil. The extraction was carried out for four hours on each sub-sample. The average time for the Soxhlet Extractor to flush was 20 minutes, meaning that each sub-sample was extracted approximately twelve times. Sample 1A was placed in a Kudurna-Dansh Concentrator to decrease the volume of the sample, but the Kudurna-Dansh Concentrator was found not to be an efficient apparatus to do so. For the rest of the samples a macro-distillation apparatus was used. The volume was decreased to 8-12 mL. All glassware from beakers to the

Soxhlet Extractor and the Kudurna-Dansh Concentrator were thoroughly cleaned with acetone, cleaned with detergent, rinsed twice with tap water, then rinsed twice with De-ionized water.

GC/MS:

1 μL of the final solution was then injected into a Hewlett-Packard Gas Chromatograph/Mass Spectrometer through a splitless injection. The method run on the GC/MS to separate the out compounds had an initial temperature of 100 ^{O}C, and increased by 15 ^{O}C every minute to a final temperature of 300 ^{O}C was reached. A solvent delay of three minutes was used to spare the GC/MS from unnecessary wear. The results of the GC/MS were then analyzed using software that came with the instrument. A chromatograph of a standard containing sixteen PAHs was used to determine the retention times of the PAHs. The internal standard (D-10-Anthracene) was used to quantify those PAHs that showed large concentrations.

Extraction and Concentration Apparatus



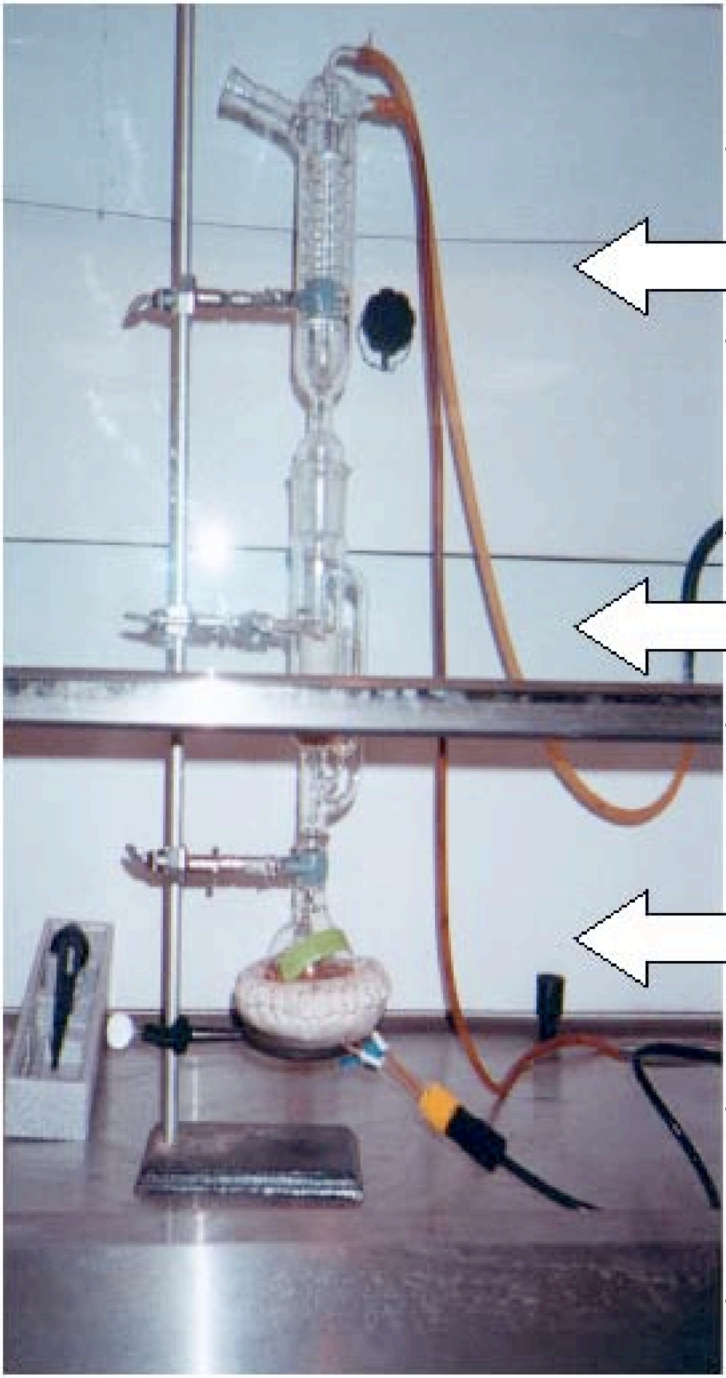
1 2 3

1.) The Soxhlet extractor is an efficient way to separate compounds that are soluble in an organic solvent such as Hexane.

2.) A macro-scale Simple Distillation apparatus was used as the volume of solvent to be concentrated was approximately 200 mL.

3.) While the Kurdurna-Danish concentrator was not used it can be an effective tool to concentrate volatile liquids.

A Closer look at a Soxhlet Extractor



Water- Cooled Condensor- The solvent vapours travel up the apparatus then condense and drip down to the Sample Chamber

Sample Chamber- The sediment sample, in a thimble, is bathed in solvent, extracting soluble compounds.

Solvent Bulb- The solvent is heated with a heating mantle to its boiling point. N-Hexane was usedas the solvent (b.p. 69 ^{O}C).

Aerial Photo of Sample Site

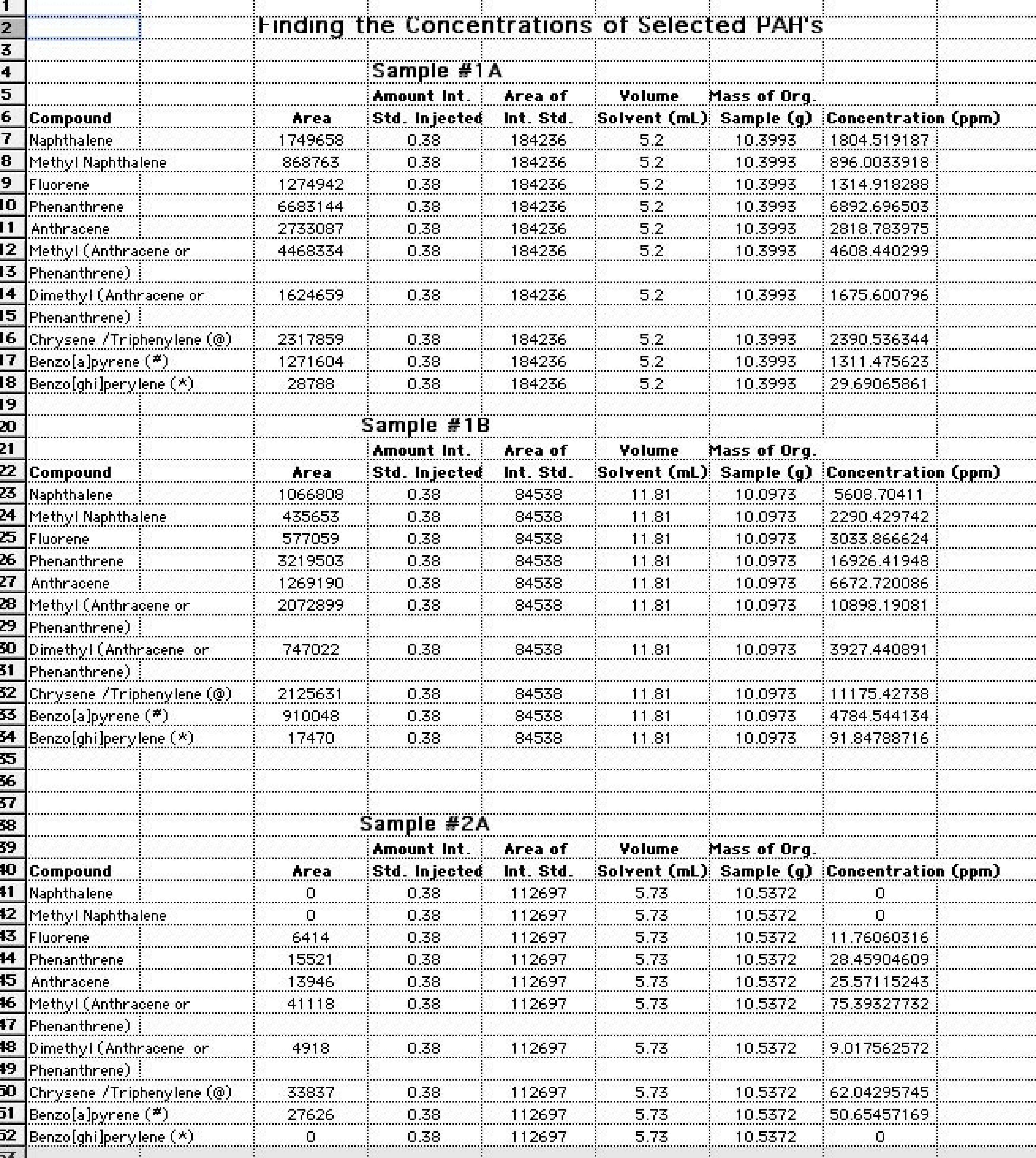
Sample Sites
(Beneath the Oak St. Bridge)

Data:

Masses of soil and sodium Sulfate added to each sample.

Sample Id.	1A	1B	2A	2B	3B	3D
Mass of Soil (g)	10.3993	10.0973	10.5372	9.6393	10.0690	9.5279
Mass of Sodium Sulfate (g)	2.1221	2.0788	2.1000	1.9418	2.0473	2.0754
Final Concentrated Volume (mL)	5.20	11.81	5.73	6.43	8.41	12.34

Mass of D-10-Anthracene used to make internal standard...........0.0038 g



Finding the Concentrations of Selected PAH's

Sample #1A

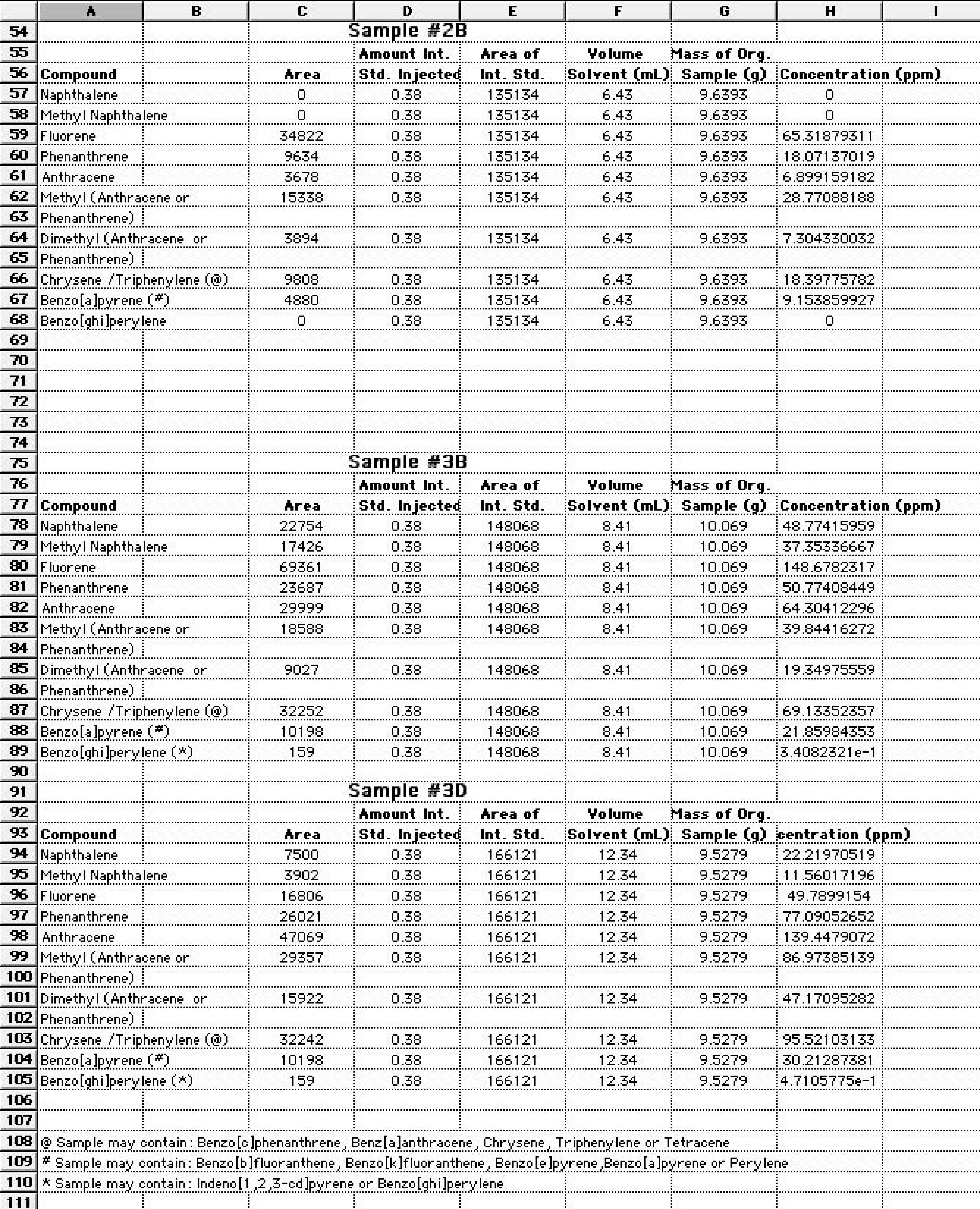
Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	Concentration (ppm)
Naphthalene	1749658	0.38	184236	5.2	10.3993	1804.519187
Methyl Naphthalene	868763	0.38	184236	5.2	10.3993	896.0033918
Fluorene	1274942	0.38	184236	5.2	10.3993	1314.918288
Phenanthrene	6683144	0.38	184236	5.2	10.3993	6892.696503
Anthracene	2733087	0.38	184236	5.2	10.3993	2818.783975
Methyl (Anthracene or Phenanthrene)	4468334	0.38	184236	5.2	10.3993	4608.440299
Dimethyl (Anthracene or Phenanthrene)	1624659	0.38	184236	5.2	10.3993	1675.600796
Chrysene /Triphenylene (@)	2317859	0.38	184236	5.2	10.3993	2390.536344
Benzo[a]pyrene (#)	1271604	0.38	184236	5.2	10.3993	1311.475623
Benzo[ghi]perylene (*)	28788	0.38	184236	5.2	10.3993	29.69065861

Sample #1B

Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	Concentration (ppm)
Naphthalene	1066808	0.38	84538	11.81	10.0973	5608.70411
Methyl Naphthalene	435653	0.38	84538	11.81	10.0973	2290.429742
Fluorene	577059	0.38	84538	11.81	10.0973	3033.866624
Phenanthrene	3219503	0.38	84538	11.81	10.0973	16926.41948
Anthracene	1269190	0.38	84538	11.81	10.0973	6672.720086
Methyl (Anthracene or Phenanthrene)	2072899	0.38	84538	11.81	10.0973	10898.19081
Dimethyl (Anthracene or Phenanthrene)	747022	0.38	84538	11.81	10.0973	3927.440891
Chrysene /Triphenylene (@)	2125631	0.38	84538	11.81	10.0973	11175.42738
Benzo[a]pyrene (#)	910048	0.38	84538	11.81	10.0973	4784.544134
Benzo[ghi]perylene (*)	17470	0.38	84538	11.81	10.0973	91.84788716

Sample #2A

Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	Concentration (ppm)
Naphthalene	0	0.38	112697	5.73	10.5372	0
Methyl Naphthalene	0	0.38	112697	5.73	10.5372	0
Fluorene	6414	0.38	112697	5.73	10.5372	11.76060316
Phenanthrene	15521	0.38	112697	5.73	10.5372	28.45904609
Anthracene	13946	0.38	112697	5.73	10.5372	25.57115243
Methyl (Anthracene or Phenanthrene)	41118	0.38	112697	5.73	10.5372	75.39327732
Dimethyl (Anthracene or Phenanthrene)	4918	0.38	112697	5.73	10.5372	9.017562572
Chrysene /Triphenylene (@)	33837	0.38	112697	5.73	10.5372	62.04295745
Benzo[a]pyrene (#)	27626	0.38	112697	5.73	10.5372	50.65457169
Benzo[ghi]perylene (*)	0	0.38	112697	5.73	10.5372	0



Sample #2B

Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	Concentration (ppm)
Naphthalene	0	0.38	135134	6.43	9.6393	0
Methyl Naphthalene	0	0.38	135134	6.43	9.6393	0
Fluorene	34822	0.38	135134	6.43	9.6393	65.31879311
Phenanthrene	9634	0.38	135134	6.43	9.6393	18.07137019
Anthracene	3678	0.38	135134	6.43	9.6393	6.899159182
Methyl (Anthracene or Phenanthrene)	15338	0.38	135134	6.43	9.6393	28.77088188
Dimethyl (Anthracene or Phenanthrene)	3894	0.38	135134	6.43	9.6393	7.304330032
Chrysene /Triphenylene (@)	9808	0.38	135134	6.43	9.6393	18.39775782
Benzo[a]pyrene (#)	4880	0.38	135134	6.43	9.6393	9.153859927
Benzo[ghi]perylene	0	0.38	135134	6.43	9.6393	0

Sample #3B

Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	Concentration (ppm)
Naphthalene	22754	0.38	148068	8.41	10.069	48.77415959
Methyl Naphthalene	17426	0.38	148068	8.41	10.069	37.35336667
Fluorene	69361	0.38	148068	8.41	10.069	148.6782317
Phenanthrene	23687	0.38	148068	8.41	10.069	50.77408449
Anthracene	29999	0.38	148068	8.41	10.069	64.30412296
Methyl (Anthracene or Phenanthrene)	18588	0.38	148068	8.41	10.069	39.84416272
Dimethyl (Anthracene or Phenanthrene)	9027	0.38	148068	8.41	10.069	19.34975559
Chrysene /Triphenylene (@)	32252	0.38	148068	8.41	10.069	69.13352357
Benzo[a]pyrene (#)	10198	0.38	148068	8.41	10.069	21.85984353
Benzo[ghi]perylene (*)	159	0.38	148068	8.41	10.069	3.4082321e-1

Sample #3D

Compound	Area	Amount Int. Std. Injected	Area of Int. Std.	Volume Solvent (mL)	Mass of Org. Sample (g)	centration (ppm)
Naphthalene	7500	0.38	166121	12.34	9.5279	22.21970519
Methyl Naphthalene	3902	0.38	166121	12.34	9.5279	11.56017196
Fluorene	16806	0.38	166121	12.34	9.5279	49.7899154
Phenanthrene	26021	0.38	166121	12.34	9.5279	77.09052652
Anthracene	47069	0.38	166121	12.34	9.5279	139.4479072
Methyl (Anthracene or Phenanthrene)	29357	0.38	166121	12.34	9.5279	86.97385139
Dimethyl (Anthracene or Phenanthrene)	15922	0.38	166121	12.34	9.5279	47.17095282
Chrysene /Triphenylene (@)	32242	0.38	166121	12.34	9.5279	95.52103133
Benzo[a]pyrene (#)	10198	0.38	166121	12.34	9.5279	30.21287381
Benzo[ghi]perylene (*)	159	0.38	166121	12.34	9.5279	4.7105775e-1

@ Sample may contain: Benzo[c]phenanthrene, Benz[a]anthracene, Chrysene, Triphenylene or Tetracene

Sample may contain: Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene ,Benzo[a]pyrene or Perylene

* Sample may contain: Indeno[1,2,3-cd]pyrene or Benzo[ghi]perylene

Results and Discussion:

Results from site 1 were found exceed the B.C. Ministry of the Environment (B.C.M.O.E) Contaminated Sites Guidelines for Industrial/Commercial sites. Many of the PAHs that were tested for exceeded the guidelines by twenty times. Remediation of site 1 has taken place since the sample was collected. It appears as though remediation was justified. The extreme levels of all of the PAHs most likely are a by-product of the decades of Industrial use that has taken place on the site. A Paper Mill and an Oil Refinery were situated closely to where the sample was collected. These are possibly responsible for the contamination on the site.

Results from site 2 where within the B.C.M.O.E. Contaminated Sites Regulations for Industrial/Commercial sites, with the exception of the 52 ppm concentration of Methyl Anthracene that was above the 50 ppm allowable concentration. However, this site would not be suitable for Residential/Urban Park usage, as Fluorene, Phenanthrene, Anthracene, Methyl Anthracene and Dimethyl Anthracene were all well above the applicable regulations. Remediation of this site would be necessary before it were to be re-zoned.

Results from site 3, perhaps the most interesting because the sample was recently obtained, exceeded the B.C.M.O.E. Contaminated Site Regulations for Commercial/Industrial sites for four PAHs. Fluorene, Phenanthrene, Anthracene, Methyl Anthracene all exceeded the regulations. Site 3 was chosen because of its proximity to a railway line. That railway line is a possible source of contamination. The locomotives that drove the trains in the past have been powered by coal, and more recently the fuel for the locomotives has been diesel. Either way a fossil fuel was used as a fuel. If uncomplete combustion occurred in the locomotives PAHs could have been released. In addition to the fossil fuel sources used to power the trains, the train track ties were treated with creosote. The creosote was applied as a wood preservative to make them more resistant to degradation by the environment. Creosote is a tar like petroleum product that would likely contain PAHs. Lastly the railway lines spray herbicides along the sides of the track to kill weeds. Many of these industrial herbicides are extremely powerful and with study found to be carcinogenic.

Summary of Concentrations Found in Sediment Samples (ppm)

Compound	Sample 1A	Sample 1B	Sample 2A	Sample 2B	Sample 3B	Sample 3D
Naphthalene	1,805	5,608	0	0	49	22
Methyl Naphthalene	896	2,290	0	0	37	12
Fluorene	1,315	3,033	12	65	149	50
Phenanthrene	6,893	16,926	28	18	51	77
Anthracene	2,819	6,672	26	7	64	139
Methyl Anthracene	4,608	10,898	75	29	40	87
Dimethyl Anthracene	1,676	3,927	9	7	19	47
Benz[a]anthracene @	2,391	11,175	62	18	69	96
Benzo[a]pyrene #	1,311	4,786	51	9	22	30
Benzo[ghi]perylene *	30	92	0	0	.3	.5

@ Sample may contain any of: Benzo[c]phenanthrene, Benz[a]anthracene, Chrysene, Triphenylene or Tetracene.

Sample may contain any of: Benzo[b]fluoranthene, Benzo[k]Fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene or Perylene.

* Sample may contain: Indeno[1,2,3-cd]pyrene or Benzo[ghi]perylene.

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