An evaluation of the abundance of polycyclic aromatic hydrocarbons in Glacier Bay, Alaska

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Abstract

Polycyclic aromatic hydrocarbons (PAH) are a widespread pollutant mainly found in soils (Zedeck, 1980). They are primarily formed from the incomplete combustion of carbon-based fuels and have both carcinogenic and mutagenic effects on biology (Zedeck, 1980). Research was performed to evaluate their currently unknown concentration in Glacier Bay, AK. Sampling was accomplished using a combination of sediment cores and grabs. The separation method utilized both gas chromatography with flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC/MS). Samples were also taken in Puget Sound for comparison as well as for a control in the extraction and separation method. Puget Sound samples revealed total PAH concentrations ranging from about 6,464 - 51,212 ng g^{-1} dry sediment, with the highest concentration existing in Pier 61 in Seattle. However after analysis with the GC-FID and GC/MS, it was determined there is no detectable level of the 24 PAH compounds examined in Glacier Bay. After further investigation, this may be due to the time these samples were taken or the depth at which the sediment was sampled.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of hydrocarbons that are present in carbon-based substances such as coal, crude oil, gasoline, and coal-tar (IDPH). They are micro-pollutants, known to be carcinogenic and mutagenic, and have been placed on the US EPA list of priority pollutants (Zedeck, 1980). When these substances are burned, PAHs are released into the air, and the less efficient the burning process will result in more PAHs (IDPH). These compounds can exist in the air, water, and soil, but are primarily found in sediment or oily substrates because of their lipophilic behavior (Zedeck, 1980). Once they accumulate in sediment they can have detrimental effects on the environment and ecosystem (Incardona et al., 2004; Shailaja et al., 2006). A study performed by Incardona et al. found that zebrafish embryos exposed to PAHs developed cardiovascular defects, which were irreversible and could result in sublethal conditions later in the fishes life cycle (Incardona et al., 2004). Biological effects such as these should be of great concern; since much of the early life of many fish involves contact with sediment, these animals cannot escape the effects of PAH contaminated sediment. Many of these compounds are resistant to weathering and biological removal as well, and so continue to build up, creating lasting effects on the habitat (Zedeck, 1980).

This research evaluated the levels of the most common PAHs (Table 2) in Glacier Bay, Alaska. Every year cruise ships make their way to Glacier Bay, where they release thousands of tons of diesel fuel exhaust into the atmosphere (Holland America Line pers. comm., 2008; Princess Cruises pers. comm., 2008; Koehler, 2000). PAHs released from the fuel exhaust eventually rain down into the water where these lipophilic particles adsorb onto phytoplankton and other organic lipids (Zedeck, 1980). From there they eventually sink out and accumulate on the sediment (Zedeck, 1980). Being that fossil fuel combustion is an ever increasing problem in the world today (IPCC, 2007), and that it is main contributing source of PAHs (Zedeck, 1980), Glacier Bay could potentially be facing an environmental risk that has yet to be examined. The information resulting from this research project is not only of present importance, but of future as well.

Historically, research done in Glacier Bay has neglected to focus on sediment chemistry. This project will provide the Parks Department with a general evaluation of the types and concentrations of PAHs present in the sediment. The separation and quantitative analysis of each type of PAH was performed using a gas chromatograph with flame ionization detector (GC-FID) as well as a gas chromatograph-mass spectrometry (GC/MS). Studies that used similar extraction and separation methods have been performed in Korea (Cho et al., 2003) and Mexico (Arce-Ortega et al., 2004) where PAH contamination in sediments was evaluated to determine environmental and health risks. A study done along the Egyptian Coast looking at the sources and distribution of PAHs in marine sediment found that "pyrogenic origins" followed by "atmospheric fall-out" both greatly contributed to the accumulation of PAHs in marine sediment (El Nemr et al., 2007). This leads to the hypothesis that PAH contamination in Glacier Bay is occurring and is exacerbated by heavy diesel-fueled (Holland America Line pers. comm., 2008; Princess Cruises pers. comm., 2008; Koehler, 2000) cruise liner activity. The level of PAHs in Puget Sound were also measured in this study to compare with the levels found in Glacier Bay. Although PAH presence in Glacier Bay is predicted to be significantly lower than in Puget Sound, it is still important to evaluate their concentration considering they are an EPA priority list pollutant and Glacier Bay is an area known to be subjected to frequent diesel-fuel combustion exposure.

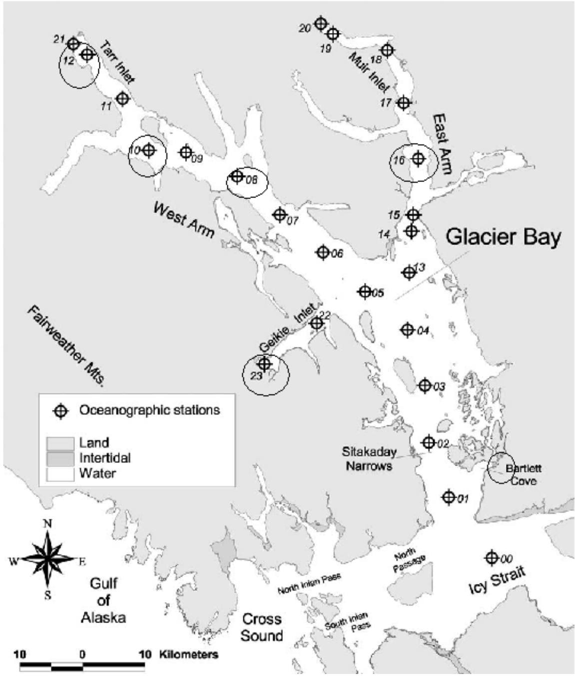
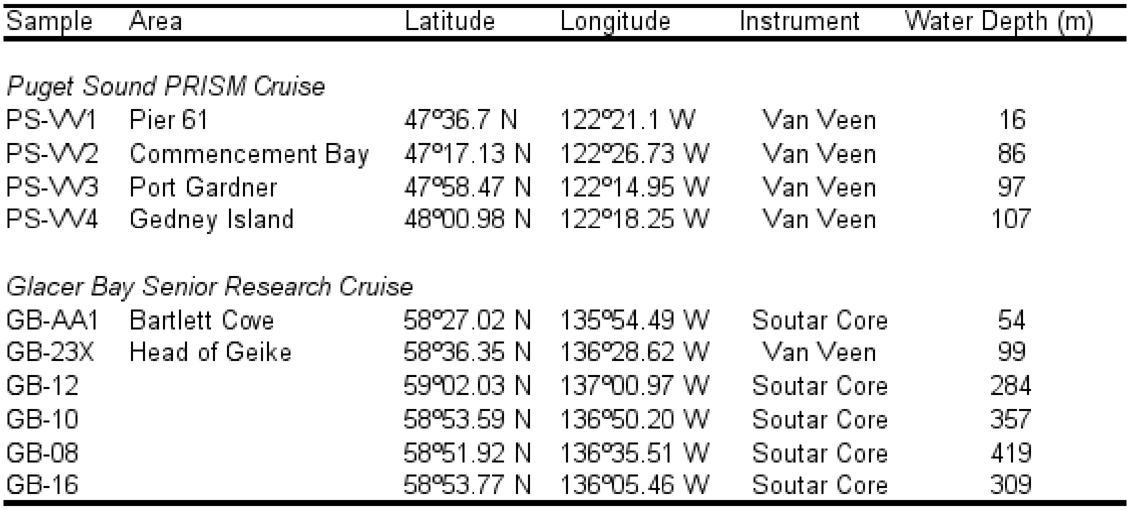


Figure 1: Glacier Bay, Alaska USGS stations; stations sampled are circled (taken from Hooge and Hooge, 2002)

Method

Puget Sound sediment samples were taken during the PRISM cruise between February 6-8 2008 using a Van Veen sediment grab (Table 1). Glacier Bay, Alaska (Fig. 1) sediment samples were taken during the UW senior thesis cruise between March 14-26 2008 using a combination of Van Veen grabs and Soutar cores (Table 1). With each sediment core and grab, about 50-100



Sample	Area	Latitude	Longitude	Instrument	Water Depth (m)
Puget Sound PRISM Cruise					
PS-VV1	Pier 61	47°36.7 N	122°21.1 W	Van Veen	16
PS-VV2	Commencement Bay	47°17.13 N	122°26.73 W	Van Veen	86
PS-VV3	Port Gardner	47°58.47 N	122°14.95 W	Van Veen	97
PS-VV4	Gedney Island	48°00.98 N	122°18.25 W	Van Veen	107
Glacer Bay Senior Research Cruise					
GB-AA1	Bartlett Cove	58°27.02 N	135°54.49 W	Soutar Core	54
GB-23X	Head of Geike	58°36.35 N	136°28.62 W	Van Veen	99
GB-12		59°02.03 N	137°00.97 W	Soutar Core	284
GB-10		58°53.59 N	136°50.20 W	Soutar Core	357
GB-08		58°51.92 N	136°35.51 W	Soutar Core	419
GB-16		58°53.77 N	136°05.46 W	Soutar Core	309

Table 1: Sample station locations and descriptions.

grams of the top five centimeters of sediment was extracted and stored in doubled plastic bags. The samples were stored in a -20 °C freezer on the ship.

Analysis of these samples was performed in the Aquatic Organic Geochemistry Lab in the ocean sciences building at the University of Washington (http://depts.washington.edu/aog) . Once in the lab, the samples were centrifuged, decanted, and placed in a freeze dryer for two days. For hydrocarbon extraction, a modified version of the Bligh-Dyer method (Bligh et al., 1959) was performed; the modification being the addition of a fourth solvent, 10% acetone in hexane. The extraction method consisted of three washes with 15 ml of four solvents (methanol, 50% methanol/50% dichloromethane, 100% dichloromethane, and 10% acetone in hexane). With each wash, the mixture was shaken in a vortex until homogenized, sonicated for 15 minutes, and then centrifuged at 2000 rpm for 10 minutes. After every centrifuge the solvent extract was transferred with a pipette to a glass vial. Once the washes were complete, the extract mixture was dried down to about 5 ml using the Turbovap II and transferred to a 10 ml glass vile. This mixture was then dried down completely, and then resuspended to 4 ml, where a 2 ml split was taken and stored away for another students project. With the remaining 2 ml a silica-gel column clean-up step was performed, based on the Metro King County method (King County, 2004). The mixture was once more dried down, resuspended with 500 ul of dichloromethane, and 100 ul of the sample was transferred to a GC vile. All ten samples were treated in this manner. The stock solution including 24 PAH standards (AccuStandard Neat SET [Z-001-SET]) was also transferred into a GC vile.

Once in the GC-FID (which used a DB-1 column) 1 ul of each sample and of the standard were injected. PAH peaks (indicators of the compounds) present in the chromatograms of the samples were identified based on the peaks in the PAH standard chromatogram and matching retention times. Concentrations of PAHs found in the samples were calculated using a ratio based on the peak areas of the compounds in the samples and in the standard stock solution and the known concentration (5 ug ml^{-1}) of standard used. The amounts were converted to ng/g of dry sediment. At the end of the quantification process half of the samples (PS-VV1, PS-VV3, GB-BC, GB-10, GB-16) along with the standard solution were run in the GC/MS, using a DB-5 column. Identification of compounds in the GC-FID chromatogram was accomplished by running separate GC vials containing a single PAH compound and comparing the resulting peak and retention time to the complete PAH standard chromatogram. Identification of compounds in the GC/MS chromatogram was accomplished by examining the main target ion in each peak (which is the molecular weight of a particular PAH compound).

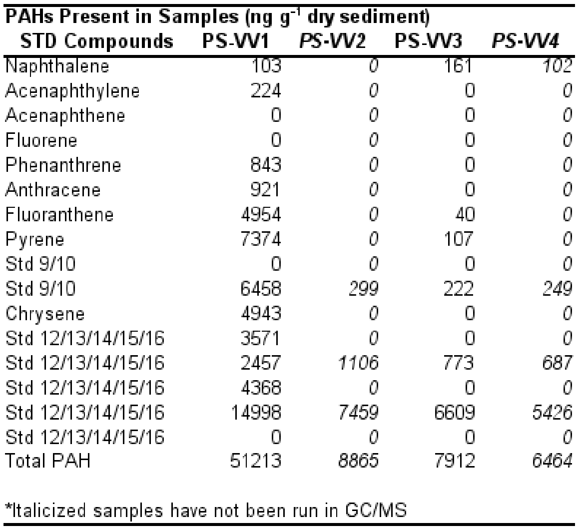
Results

PAH Standards

The standard chromatogram from the GC-FID (Fig. 2) revealed 16 of the 24 standards listed in the stock solution. A few of the standard peaks were difficult to categorize as a PAH because they were shoulder peaks of another peak (Fig. 3). Here two different compounds were considered to be present with retention times of about 47.08 minutes and 47.15 minutes (Fig. 3). The process for identifying PAH standard compounds required running solutions in the GC-FID that contained just one particular standard. Instead of continuing with this method after identifying five of the compounds, the decision was made to examine the standard stock solution in the GC/MS. The standard chromatogram from the GC/MS (Fig. 4) revealed 22 of the 24 standards listed in the stock solution (Table 2), 6 more than were revealed using the GC-FID.

Samples

PAH compounds with higher retention times were revealed after using the more sensitive GC/MS, but since they were not detected in the FID, they were not quantified. PAH compound presence was evaluated for all stations (Table 3), however quantification of compounds only includes Puget Sound stations (Table 4). Sample PS-VV1 (Pier 61 in Seattle; Fig. 5) contained the greatest number of PAHs. The concentration of PAHs present in PS-VV1 ranged from about 100-15,000 ng g^{-1} dry sediment; the total PAH concentration was 15,212 ng g^{-1}. The other three Puget Sound samples contained fewer types of PAHs, and the concentrations found in PS-VV3 are comparatively less than in PS-VV1. After running half of the Glacier Bay samples in the GC/MS, it was determined that the compounds that were repeatedly seen in all six samples were not PAHs but some other type of compound. The result is that there were no detectable PAHs found in Glacier Bay.



PAHs Present in Samples (ng g^{-1} dry sediment)

STD Compounds	PS-VV1	*PS-VV2*	PS-VV3	*PS-VV4*
Naphthalene	103	*0*	161	*102*
Acenaphthylene	224	*0*	0	*0*
Acenaphthene	0	*0*	0	*0*
Fluorene	0	*0*	0	*0*
Phenanthrene	843	*0*	0	*0*
Anthracene	921	*0*	0	*0*
Fluoranthene	4954	*0*	40	*0*
Pyrene	7374	*0*	107	*0*
Std 9/10	0	*0*	0	*0*
Std 9/10	6458	*299*	222	*249*
Chrysene	4943	*0*	0	*0*
Std 12/13/14/15/16	3571	*0*	0	*0*
Std 12/13/14/15/16	2457	*1106*	773	*687*
Std 12/13/14/15/16	4368	*0*	0	*0*
Std 12/13/14/15/16	14998	*7459*	6609	*5426*
Std 12/13/14/15/16	0	*0*	0	*0*
Total PAH	51213	*8865*	7912	*6464*

*Italicized samples have not been run in GC/MS

Table 4: Quantification of Puget Sound PAHs based on GF-FID work.

Discussion

After using the GC-FID and quantifying my results I was under the impression that there were 2-3 PAH compounds present in Glacier Bay. However after using the more sensitive GC/MS it was determined that the compounds were not in fact PAHs, but some other type of compound. I have only run three of the Glacier Bay samples in the GC/MS, however all six of the samples showed small peaks at the same retention in the FID; peaks which when analyzed

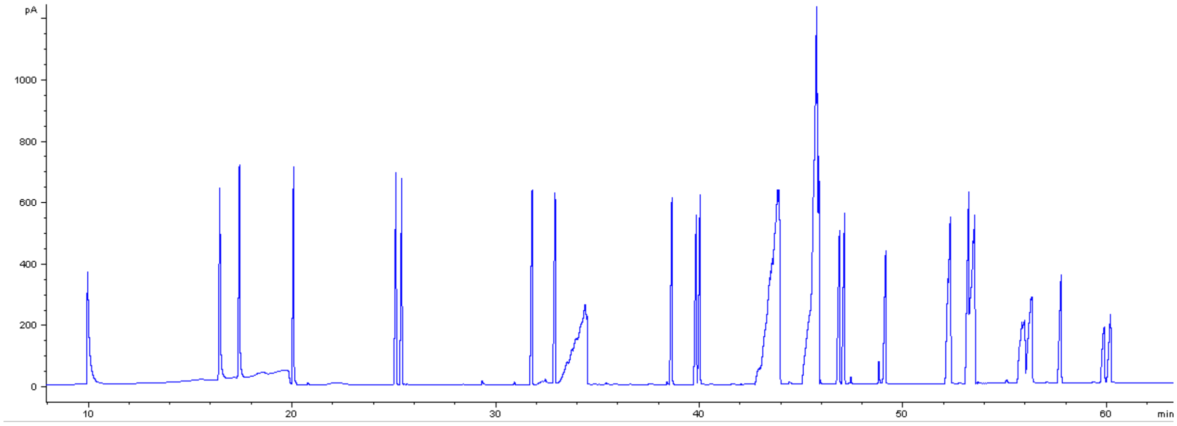


Figure 2: PAH standard chromatogram from the GC-FID.

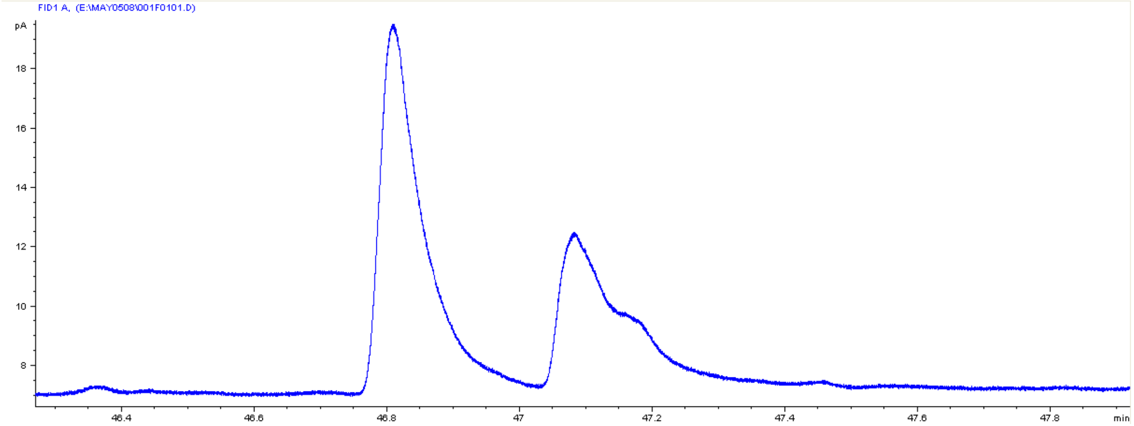


Figure 3: Indistinct peaks around 47 minutes.

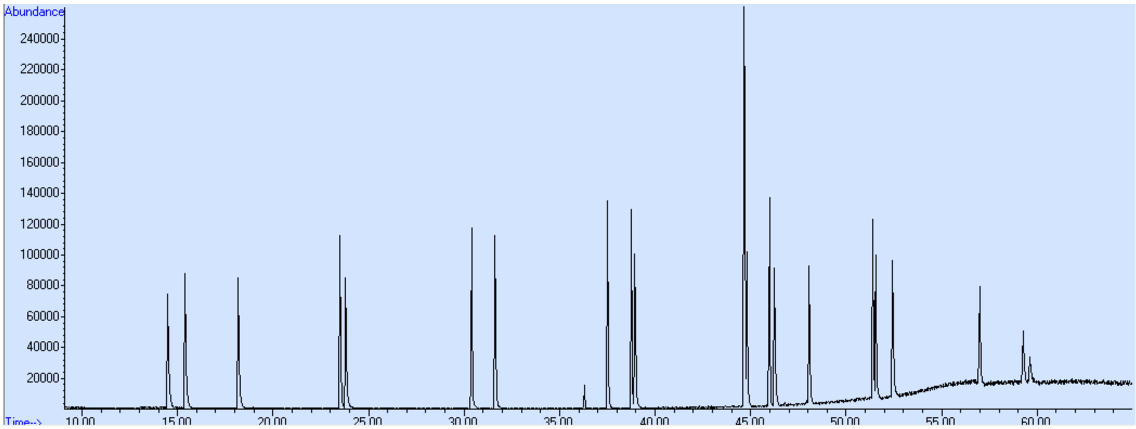
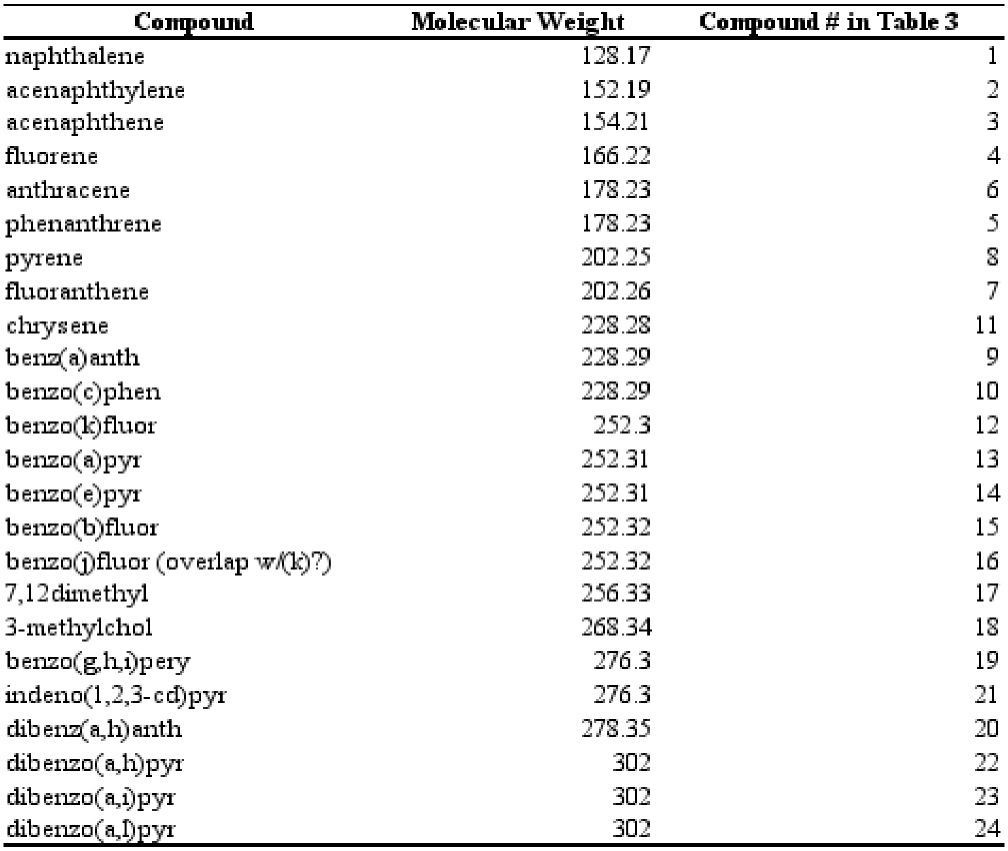


Figure 4: Standard chromatogram from the GC/MS.



Compound	Molecular Weight	Compound # in Table 3
naphthalene	128.17	1
acenaphthylene	152.19	2
acenaphthene	154.21	3
fluorene	166.22	4
anthracene	178.23	6
phenanthrene	178.23	5
pyrene	202.25	8
fluoranthene	202.26	7
chrysene	228.28	11
benz(a)anth	228.29	9
benzo(c)phen	228.29	10
benzo(k)fluor	252.3	12
benzo(a)pyr	252.31	13
benzo(e)pyr	252.31	14
benzo(b)fluor	252.32	15
benzo(j)fluor (overlap w/(k)?)	252.32	16
7,12dimethyl	256.33	17
3-methylchol	268.34	18
benzo(g,h,i)pery	276.3	19
indeno(1,2,3-cd)pyr	276.3	21
dibenz(a,h)anth	278.35	20
dibenzo(a,h)pyr	302	22
dibenzo(a,i)pyr	302	23
dibenzo(a,l)pyr	302	24

Table 2: Complete list of PAHs examined.

in the MS turned out to be something other than the PAH compounds in my standard. Thus, through the two gas chromatography methods, I have determined that there are no detectable PAHs present in the Glacier Bay samples I collected. For future research involving PAH analysis, I would highly recommend using a GC/MS as a means for compound separation and identification; instead of primarily using the FID and treating the MS as a check, I would first utilize the MS and if desired the FID.

The fact that I found a significant amount of PAHs in my Puget Sound samples is validation that the extraction method worked and can be used again in other studies. Presence of these compounds in Puget Sound is also an example of what a contaminated area looks like. The degree of PAH contamination in the sediment is high in comparison to a study done by Prahl et al. (1983) along the coast of Washington (Table 5). Of my four Puget Sound sites, Pier 61 in Seattle had by far the greatest concentration (51,212 ng g^{-1}), which makes sense since it receives heavy pollution input from both land and marine sources. Because of the fact that Pier 61 is extreme in comparison to the three other open-water Puget Sound sites, a separate row in Table 5 was established that removed Pier 61 from the calculations. This results in the mean for Puget Sound samples dropping by almost 11,000 ng g^{-1}. This modified Puget Sound mean is still higher in comparison to the Washington Coast study, but there are a few things to keep in mind: 1) there are now only three sites being included in the calculation for the mean concentration Puget Sound, and all of those sites were specifically targeted because they are known to be contaminated, and 2) the

Compound	PS-VV1	PS-VV2	PS-VV3	PS-VV4	GB-BC	GB-08	GB-10	GB-12	GB-16	GB-23
Naphthalene	■	-	■	▓	NP	-	NP	-	NP	-
Acenaphthylene	■	-	NP	-	NP	-	NP	-	NP	-
Acenaphthene	NP	-	NP	-	NP	-	NP	-	NP	-
Fluorene	NP	-	NP	-	NP	-	NP	-	NP	-
Phenanthrene	■	-	NP	-	NP	-	NP	-	NP	-
Anthracene	■	-	NP	-	NP	-	NP	-	NP	-
Fluoranthene	■	-	■	-	NP	-	NP	-	NP	-
Pyrene	■	-	■	-	NP	-	NP	-	NP	-
Std 9/10	▒	-	NP	-	NP	-	NP	-	NP	-
Std 9/10	■	▓	■	▓	░	▓	░	▓	░	▓
Chrysene	■	-	▒	-	NP	-	NP	-	NP	-
Std 12/13/14/15/16	■	-	▒	-	NP	-	NP	-	NP	-
Std 12/13/14/15/16	■	▓	■	▓	NP	-	NP	-	░	▓
Std 12/13/14/15/16	■	-	▒	-	NP	-	NP	-	NP	-
Std 12/13/14/15/16	■	▓	■	▓	░	▓	░	▓	░	▓
Std 12/13/14/15/16	NP	-	NP	-	NP	-	NP	-	NP	-
7,12-dimethylbenz(a)anthracene	NP	-	NP	-	NP	-	NP	-	NP	-
3-methylcholanthrene	NP	-	NP	-	NP	-	NP	-	NP	-
Benzo(g,h,j)perylene	▒	-	NP	-	NP	-	NP	-	NP	-
Dibenz(a,h)anthracene	▒	-	NP	-	NP	-	NP	-	NP	-
Indeno(1,2,3-cd)pyrene	▒	-	NP	-	NP	-	NP	-	NP	-
Std 22/23/24	NP	-	▒	-	NP	-	NP	-	NP	-
Std 22/23/24	NP	-	NP	-	NP	-	NP	-	NP	-
Std 22/23/24	NP	-	NP	-	NP	-	NP	-	NP	-

■	present (seen in FID and MS)
▒	present (seen in MS)
░	not present (seen in FID but not in MS)
▓	unverified (seen in FID – sample not run in MS)
NP	not present (not seen in FID or MS)
-	unverified (not seen in FID – sample not run in MS)

Table 3: PAH presence based on GC-FID and GC/MS work.

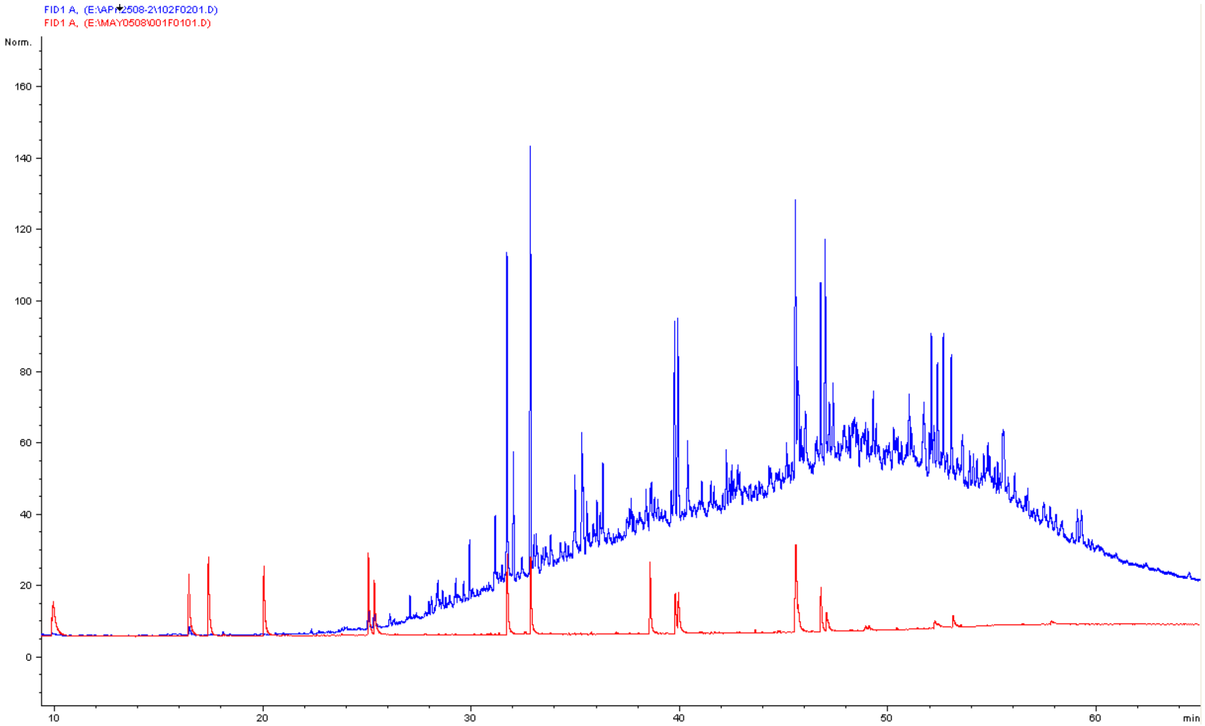


Figure 5: Sample PS-VV1 (in blue and exhibiting trademark PAH hump) with standard (in red) overlaid.

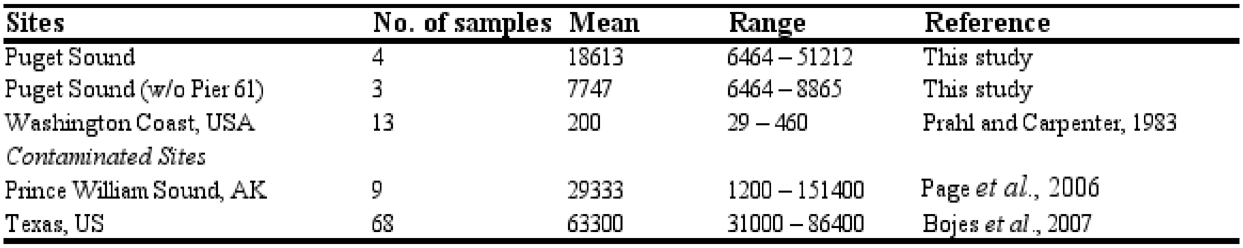
Washington coast receives significantly less direct (spills) and indirect (air-transported) input of pollution. The Puget Sound mean concentrations, especially the unmodified value, are much more comparable to the concentrations of the known contaminated sties (Table 5). The Page et al. (2006) study looked at the effects from the Exxon Valdez spill in 1989, and the Bojes et al. (2007) dealt with contaminated oil exploration and production sites. The unmodified Puget Sound mean concentration (18, 613 ng g^{-1}) is close to being 90 times the mean concentration on the Washington coast, where as it's only about 1.5-3.5 times less than the mean concentrations found at established contaminated sites. The areas I sampled in Puget Sound are exactly what should not happen in Glacier Bay, but with the ever-increasing cruise ship visitations (Sharman, 2008, pers. comm.) it is a concern that should be continually monitored.

The lack of PAHs in Glacier Bay is good news for the environment, but may also be somewhat expected. A rough calculation can give an idea of what sort of PAH levels to expect right now:

$$[PAH] \sim \left(\frac{N_{SD} \times L_T \times F_E}{A_{GB} \times S_R}\right) \tag{1}$$

Where N_{SD} is the number of days cruise ships spent in Glacier Bay in the year 2007; a total of 225 ships entered the bay, and spent a cumulative 86.68 days there (Sharman, 2008, pers. comm.). N_{SD} is multiplied by L_T (1yr/365d) to convert to years. F_E is the flux of hydrocarbons to the atmosphere due to cruise ship engines, which is $4x10^8$ g HC yr^{-1} (EPA, 1998). A_{GB} is the approximate area of Glacier Bay (10^9 m^2). S_R is the sedimentation rate (Biladeau, 2008), of which I have for station 08 and station 21 (which I will use to estimate concentrations for 12 since they are so close). For station 08, with a sedimentation rate of 421.1 g m^{-2} yr^{-1}, the estimated level of hydrocarbons should be around 225,580 ng g^{-1} dry sediment. As for station 12, based on station 21's sedimentation rate of 18,225.5 g m^{-2} yr^{-1}, the estimated concentration of hydrocarbons should be around 5,212 ng g^{-1} dry sediment. These results seem extremely high, but they are also for the total hydrocarbon count, not strictly PAHs. They are also assuming that all of the exhaust emitted by the ships sinks out to the bottom of the bay. To make these estimations a bit more reasonable, I will assume that only 10% of the hydrocarbons are PAHs – the exact 24 compounds in my standard stock solution – and also that only 10% of that resulting amount makes it to the sediment at the bottom of the bay. Of these two assumption, more importance lies in the fact that these compounds get released into the air where they are free to disperse and able to travel with the winds and clouds, so that by time they get deposited, they could be miles from the point they were originally released. An estimation of 10% may therefore be a bit of an overestimate. With these new assumptions, the PAH concentration should be about 2,256 ng g^{-1} and 52 ng g^{-1} at station 08 and 12, respectively. The concentration at station 08 should definitely be detectable on both the FID and MS, whereas station 12's concentration of 52 ng g^{-1} may be too small to see on the FID. However both estimated concentrations are still higher than what was observed in Glacier Bay.

To investigate the disparity between actual and estimated concentrations even further, the time the samples were taken and what is needed for these compounds to be deposited in the sediment should be examined. The cruise took place during mid to late March, which is before or right at the beginning of cruise ship season (Sharman, 2008, personal comm.). This means that the air was fairly clear of cruise ship induced hydrocarbons. The time we arrived was also before the Spring bloom, so there were low levels of phytoplankton in the water (Hannam, 2008). Without the abundance of plankton and other organic lipid in the surface water, the PAHs that have fallen out of the atmosphere have little to adsorb to, and to eventually transport them to the bottom where they can



Sites	No. of samples	Mean	Range	Reference
Puget Sound	4	18613	6464 – 51212	This study
Puget Sound (w/o Pier 61)	3	7747	6464 – 8865	This study
Washington Coast, USA	13	200	29 – 460	Prahl and Carpenter, 1983
Contaminated Sites				
Prince William Sound, AK	9	29333	1200 – 151400	Page *et al.*, 2006
Texas, US	68	63300	31000 – 86400	Bojes *et al.*, 2007

Table 5: Comparison of sediment PAH concentration (ng g^{-1} dry sed) measured in this study and others.

accumulate. An even more important factor is that Glacier Bay has some of the fastest sedimentation rates in the world (Biladeau, 2008). This means that unless there has been recent PAH deposition activity, sampling just the top 5 cm (which is what was done in this study) will not yield any compounds.

The estimations produced from the equation are extremely rough because of just how much variability exists with the values needed to calculate what PAH concentrations *should* look like; it may be pointless to even attempt at an estimation. Depending on the engine, what the exact content of the substance being burned is, and how efficient the engine is are all contributing factors as to how many and what types of PAHs are released into the atmosphere. During the Glacier Bay cruise, a sample of the *R/V Thompson* exhaust was collected on a filter for a recorded amount of time. After determining whether the extraction method worked with my sediment samples, I had planned to extract the filter paper, but unfortunately ran out of time. Had the filter been analyzed, the exact flux of PAHs from the engine could have been calculated and used in this equation, further eliminating uncertainty.

Although my study did not reveal there to be any, or at least a detectable amount of, PAHs, this could be due to the timing of the research cruise and possibly the depth at which the sediment was sampled. I think it would therefore be interesting to go back to Glacier Bay when cruise ship season is in full swing and just after the Spring bloom, because a significant amount of hydrocarbons will have been emitted by the ships and it will also have given any PAHs present to not only adsorb to the plankton, but sink out and collect at the bottom of the bay.

Conclusions

- There was no detectable amount of PAHs present in Glacier Bay
- Pier 61 in Seattle was the most contaminated of the Puget Sound samples
- A PAH separation method that uses a GC/MS is highly recommended
- Performing this same research in July/August may be a better time to test the effect of cruise ships in PAH accumulation and reveal different results than the ones in this study

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