Feasibility of using passive sampling devices to measure polynuclear aromatic hydrocarbon concentrations around Alaskan boat harbors.

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ABSTRACT

The USFWS performed a study in Seward, Alaska, to assess the utility of Passive Sampling Devices (PSDs) for the evaluation of petroleum contamination in and around boat harbors. Low Density Polyethylene Devices (LDPEs) and Semipermeable Membrane Devices (SPMDs) are two different PSDs that can be used to monitor organic contaminants in water or air. In this study, LDPEs and SPMDs were deployed to compare their utility for future studies of risk to Steller's eiders. Both types of devices were deployed within and outside the confines of the harbor. Surface and epibenthic samples were paired to evaluate differences in contaminant concentrations. The data were evaluated to determine whether the location and analyte "fingerprint" of different sources of contamination could be detected, and whether the average water concentrations of PAH analytes could be calculated from the SPMD data. The PSDs were able to identify the chemical source of hydrocarbons to the water column, although specific locations of the contaminant sources were not always identified. The PAH analyte fingerprint at all the locations in this pilot study is suggestive of an uncombusted diesel fuel source. Average water concentrations of most of the 16 priority pollutant PAHs could be calculated from the SPMD data, however, no lab calibration data are available to calculate the concentrations of any of the akylated homologues. Although the exact relationship between PSD data and an assessment of risk to Steller's eiders from harbor-related contamination has yet to be determined, this study shows the devices can be useful tools in the upcoming risk assessment process.

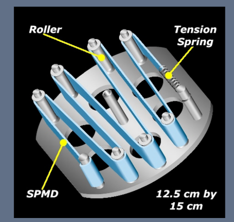

Figure 1. SPMD, "spider" deployment rack

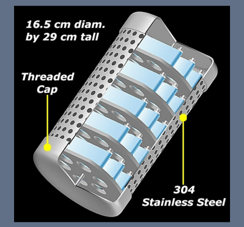

Figure 2. Stainless steel deployment canister for five SPMDs (www.spmds.com)

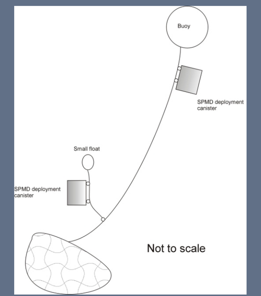

Figure 3. SPMD/LDPE deployment apparatus: Buoy Anchor System. Either rocks or cinder-blocks and chains comprised the anchor. All anchors in Seward were cement blocks and galvanized chain.

INTRODUCTION

Background

The North American breeding population of Steller's eiders (*Polysticta stelleri*) was listed as Threatened under the Endangered Species Act in 1997, due to population declines on breeding grounds. Preferred Steller's eider wintering habitat areas are also favored for harbor development, resulting in a co-location of Steller's eiders and anthropogenic contaminant inputs. Petrogenic hydrocarbons from boating and oil spills can adversely affect Steller's eiders and are cause for concern when they occur in eider habitat. Accurate measurements of contaminant concentrations in the marine environment are required to determine whether eiders are being exposed to contaminants in their wintering areas.

Passive Sampling Devices

SPMDs

Semipermeable membrane devices (SPMDs) are patented devices available from Environmental Sampling Technologies (EST), St Joseph, Missouri. Each standard SPMD consists of a 91.4x2.54 cm (36x1 inch) low-density polyethylene tube filled with one milliliter of high purity (98%) triolein. Organic contaminants diffuse through the polyethylene of the device and are sequestered in the triolein lipid. Permeability performance reference compounds (PRCs) are organic compounds added to the SPMD to permit calculation of an exposure adjustment factor (EAF). The EAF allows the researcher to account for differences in contaminant uptake caused by differences in water velocity, temperature, or biofouling in different SPMDs.

LDPEs

LDPEs have recently been used by the National Oceanic and Atmospheric Administration's (NOAA) Auke Bay Laboratory (ABL). These devices are similar to SPMDs in construction, however, they do not include the triolein. The plastic tubing sequesters organic contaminants from the air or water column. These devices provide a relative measure of different contaminants present in the sampling media. LDPEs cannot be used to quantify contaminant concentrations in water.

GOALS AND OBJECTIVES

How do PSDs compare in terms of cost, ease of use, and utility of data?

Can the location and analytical fingerprint of different sources of contamination can be detected?

Can water concentrations can be calculated using PRC-spiked SPMDs?

Is the analytical data applicable to future assessment of risk to eiders from harbor-related contamination?

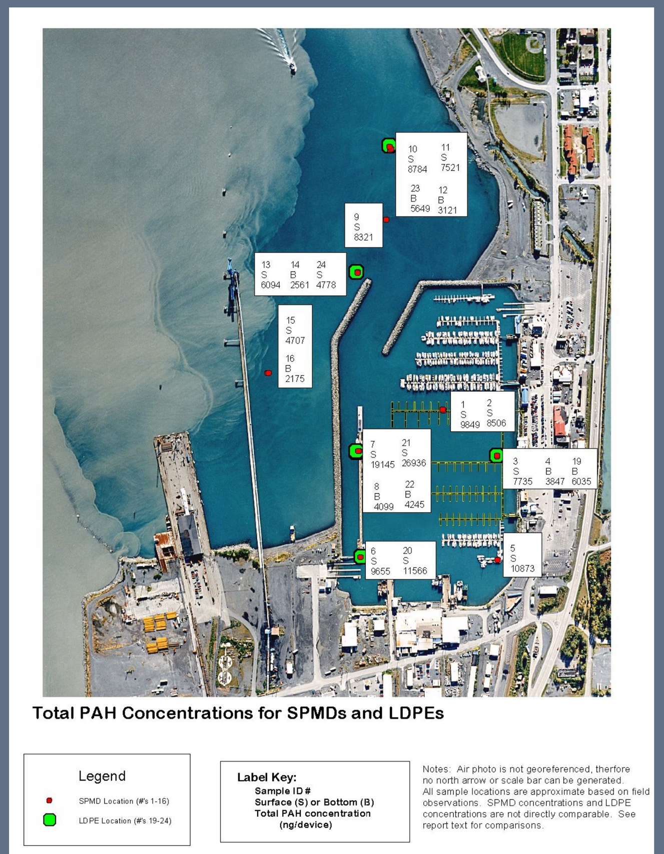

Figure 4. PSD sample locations and PAH concentrations in the Seward Boat Harbor. Input to water at left of the photo is naturally-occurring glacial silt.

Table 1. Water concentrations of different PAH analytes calculated from PRCs in pg l^{-1}

PAHs	201p*	201a	201py	202p	202a	202py	203p	203a	203py	204p	204a	204py	205p	205a	205py	206p	206a	206py
Biofouling	2	2	2	3	3	3	2	2	2	1	1	1	3	3	3	2	2	2
Acenaphthylene	305	305	500	266	266	153	201	20	305	187	187	95	139	139	75	288	288	542
Acenaphthene	230	230	433	371	371	194	335	335	582	1844	1844	2979	480	480	714	1011	1011	2185
Fluorene	413	413	972	529	529	888	499	499	1086	853	936	1891	428	428	797	562	562	1519
Phenanthrene	1786	1786	3794	1933	1933	2928	1866	1866	3665	2262	2426	4425	1749	1749	2936	2072	2072	5053
Anthracene	239	239	772	72	72	167	75	75	225	197	219	657	166	166	423	250	250	927
Fluoranthene	1267	1490	12293	1408	1632	9632	1498	1745	13059	884	1112	10076	2054	2333	14595	2849	3289	30721
Pyrene	788	925	7508	797	922	5355	947	1101	8111	545	685	6086	1656	1878	11567	2062	2375	21837
Benz[a]anthracene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chrysene	97	43	963	37	48	762	46	59	1174	155	106	764	100	127	2043	124	158	3919
Benzo[b]fluoranthene	69	45	692	19	13	139	22	5	213	59	40	289	76	22	714	152	36	1875
Benzo[k]fluoranthene	18	11	175	15	10	111	18	12	176	27	19	134	44	29	413	107	72	1318
Benzo[a]pyrene	3	2	30	0	0	0	3	2	32	16	11	80	9	6	85	47	32	581
Indeno[1,2,3-cd]pyrene	17	11	172	0	0	0	0	0	0	0	0	0	0	0	0	19	13	240
Dibenzo[a,h]anthracene	25	16	248	6	4	42	0	0	0	0	0	0	0	0	0	0	0	0
Benzo[g,h,I]perylene	25	16	246	12	8	86	11	7	104	0	0	0	29	19	273	55	36	673

PAHs	207p	207a	207py	208p	208a	208py	209p	209a	209py	210p	210a	210py	211p	211a	211py
Biofouling	3	3	3	3	3	3	2	2	2	2	2	2	3	3	3
Acenaphthylene	122	122	66	244	244	124	303	303	303	928	928	859	189	189	175
Acenaphthene	142	142	211	1865	1865	3016	401	401	401	431	431	386	360	360	322
Fluorene	554	554	1027	706	706	1427	603	603	544	735	735	615	531	531	443
Phenanthrene	2470	2470	4132	2476	2476	4519	2022	2022	1869	2548	2548	2206	1953	1953	1687
Anthracene	114	114	291	204	231	640	144	144	117	151	151	111	113	113	83
Fluoranthene	1367	1512	9295	884	1096	8952	1643	2005	1065	1651	1973	3626	1593	1815	3311
Pyrene	1172	1293	7832	525	649	5207	945	1147	614	930	1108	2005	884	1005	1806
Benz[a]anthracene	0	0	0	75	50	445	42	12	94	48	11	120	45	13	133
Chrysene	55	68	1051	113	28	675	33	44	153	31	43	199	28	36	165
Benzo[b]fluoranthene	75	25	785	19	13	115	26	8	58	36	9	90	25	8	74
Benzo[k]fluoranthene	25	17	258	15	10	89	7	4	15	9	5	23	7	4	19
Benzo[a]pyrene	4	3	40	8	5	45	5	3	11	1	1	3	5	3	14
Indeno[1,2,3-cd]pyrene	4	3	45	0	0	0	0	0	0	0	0	0	0	0	0
Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Benzo[g,h,I]perylene	15	11	160	0	0	0	0	0	0	0	0	0	0	0	0

PAHs	212p	212a	212py	213p	213a	213py	214p	214a	214py	215p	215a	215py	216p	216a	216py	Log Kow
Biofouling	1	1	1	2	2	2	2	2	2	2	2	2	1	1	1	
Acenaphthylene	313	313	684	151	151	151	90	90	57	134	134	134	85	85	58	4.08
Acenaphthene	1736	1736	4361	275	275	275	231	231	135	249	249	249	200	200	125	4.22
Fluorene	1038	1113	3496	443	443	443	235	235	118	359	359	324	226	226	123	4.38
Phenanthrene	2787	2787	7904	1693	1693	1693	986	986	531	1495	1495	1381	883	883	514	4.46
Anthracene	222	258	1111	63	63	58	46	46	89	69	69	56	35	35	60	4.54
Fluoranthene	669	846	11076	1160	1431	974	517	609	2957	942	1083	620	382	455	2043	5.2
Pyrene	262	330	4250	586	719	493	296	348	1661	527	605	348	212	253	1115	5.3
Benz[a]anthracene	105	69	894	0	0	0	0	0	0	0	0	0	0	0	0	5.91
Chrysene	114	74	967	21	29	66	9	12	148	16	20	74	22	9	111	5.61
Benzo[b]fluoranthene	70	46	598	21	7	31	0	0	0	0	0	0	0	0	0	5.78
Benzo[k]fluoranthene	21	14	182	6	4	9	0	0	0	0	0	0	0	0	0	6.2
Benzo[a]pyrene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6.35
Indeno[1,2,3-cd]pyrene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6.75
Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6.51
Benzo[g,h,I]perylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6.9

Table 1. Notes:
Biofouling 1=light;2=medium; 3=heavy
Each distinct number is an individual SPMD.
p=phenanthrene, a=anthracene, py=pyrene.

MATERIALS & METHODS

Deployment and Retrieval

Standard SPMDs and associated hardware were obtained from Environmental Sampling Technologies (EST), St Joseph, Missouri. Each standard SPMD consisted of a 91.4x2.54 cm (36x1 inch) low-density polyethylene tube filled with one milliliter of high purity (98%) triolein. Each SPMD was mounted on a separate standard "spider" deployment rack by the manufacturer under "clean" laboratory conditions (Figures 1 and 2).

The LDPEs and associated deployment hardware were obtained from NOAA's Auke Bay Lab (ABL). Each LDPE consisted of 2, 5 cm x 50 cm low density polyethylene plastic strips, with a total of 500 cm^2 surface area. The LDPEs were pre-mounted in deployment cages at ABL.

Exposure to air was minimized for all SPMDs and LDPEs, and air exposure times were recorded.

PSDs were deployed in paired samples; one unit was within one meter of the water's surface and one was within one meter of the water/sediment interface (Figure 3). Epibenthic devices were only deployed at depths of <10 meters, which is consistent with Steller's eider foraging depths.

Devices were secured at locations both inside and outside of the Seward small boat harbor using either an anchor/buoy combination or an existing fixed or floating structure (pilings or floating docks).

For in-harbor petroleum source identification, PSDs were located near potential source areas, such as the fuel dock, storm water outfalls, the boat loading ramp, and debris collection areas.

A total of nine near-surface sample locations, two near-surface replicates, and five epibenthic sample locations were used.

Twenty-seven days after deployment, the SPMDs were recovered, removed from their deployment devices, placed in sealed canisters, and frozen for shipment.

Analytical Methods

All SPMDs (sample devices, replicates and trip blank) underwent sample clean-up and recovery procedures at EST using standard SPMD methodology (McCarthy and Gale 1999; www.spmds.com). Chemical analysis was done at ABL for all SPMD and LDPE samples. Analysis was done using gas chromatography/mass spectrometry (GC/MS) using an HP6890 gas chromatograph with a 5973 mass selective detector in selected ion monitoring mode.

Analytes: 16 priority pollutant PAHs and their akylated homologues, reported in ng $device^{-1}$, unless otherwise noted.

Quality Control: Two replicate samples, a trip blank, and NIST standard 1491

Data Analysis

Water concentrations were calculated from three different PRCs (phenanthrene, anthracene, and pyrene) by the methods of Huckins *et al* 2002.

Spatial trends in the PAH data were examined by cluster analysis. A dissimilarity matrix relating the hydrocarbon compositions of samples from the various locations was constructed by calculating the Aitichison distance metric (Aitchison, 1992) between each pair of SPMDs and each pair of LDPEs. The Aitchison distance is a quantitative multivariate metric of dissimilarity between two compositional patterns. This metric has advantageous statistical properties, including scale invariance, symmetry, non-negativity, and the property that the dist (u, u) = 0. The hierarchical structure of the resulting matrix was determined from the agglomerative "average" clustering method,, using the Cluster procedure in SAS, version 8. The structure was visualized by constructing dendrograms, which were inspected for evidence of spatial coherence among clusters. The cluster analysis was run for all data, then for the SPMD data without the LDPE data.

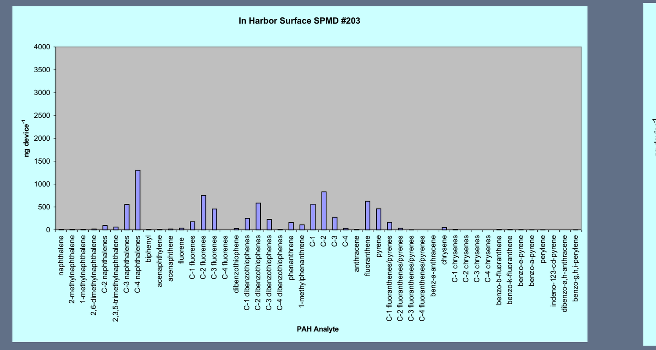

Figure 11. Analyte chart of a representative in-harbor surface

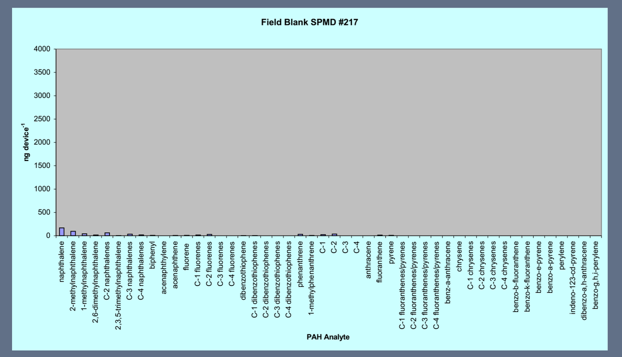

Figure 7. Analyte chart of the field blank

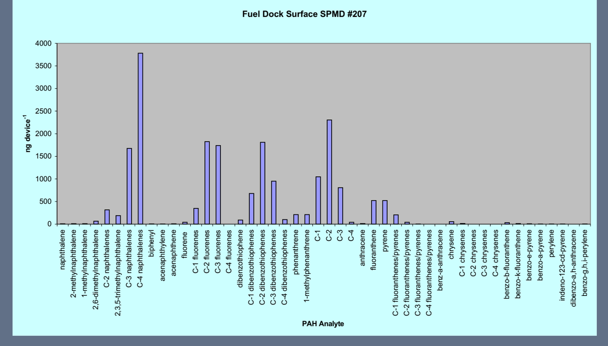

Figure 6. Analyte chart of the surface fuel dock SPMD

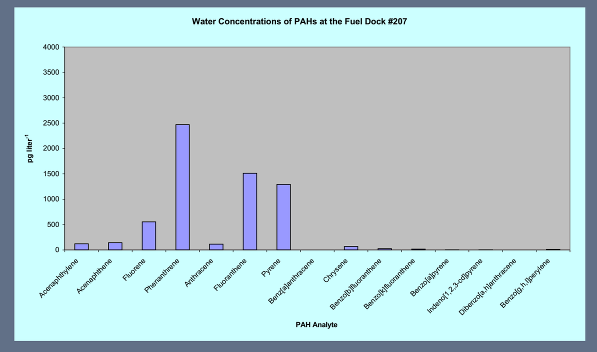

Figure 16. PRC-calculated water concentrations at the fuel dock. Note how total PAH concenrtrations are less than the loading ramp sample in Figure 14.

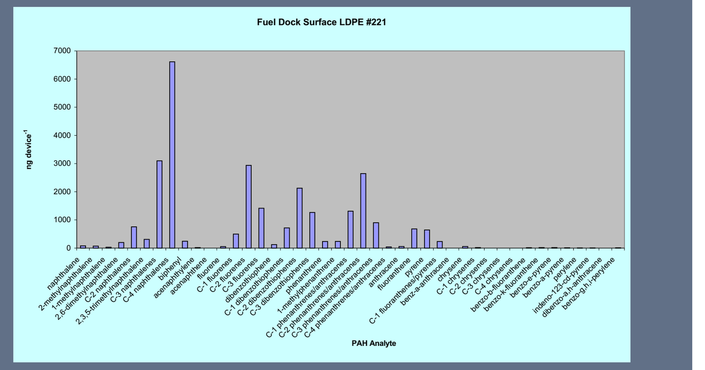

Figure 8. Analyte chart of the surface LDPE at the fuel dock, note analyte pattern similarities to surface SPMD at the Fuel Dock (Figure 7) although the scales differ.

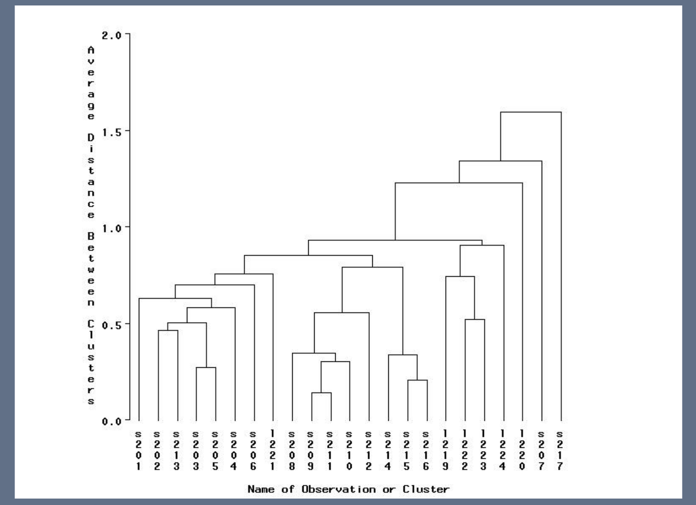

Figure 5. Dendrogram from the agglomerative cluster analysis, including all PSDs.

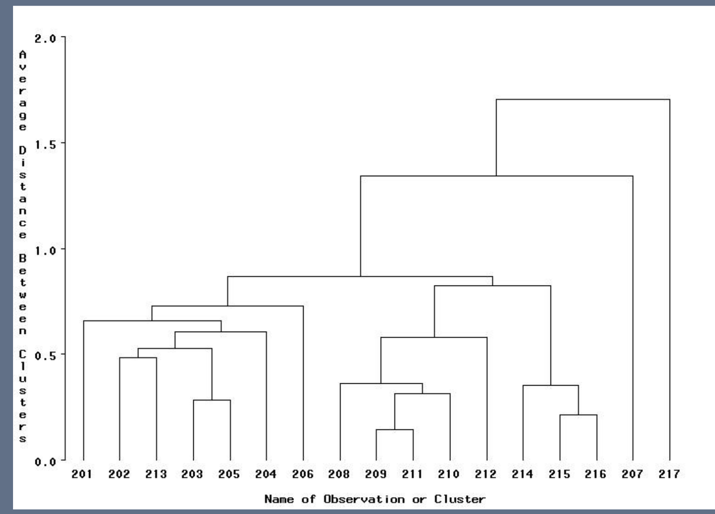

Figure 9. Dendrogram from the agglomerative cluster analysis, including only SPMDs

Figure 10. SPMD sample locations. Points marked with a similar symbol were placed into the same cluster in the cluster analysis, indicating that these points had similar PAH analyte signatures.

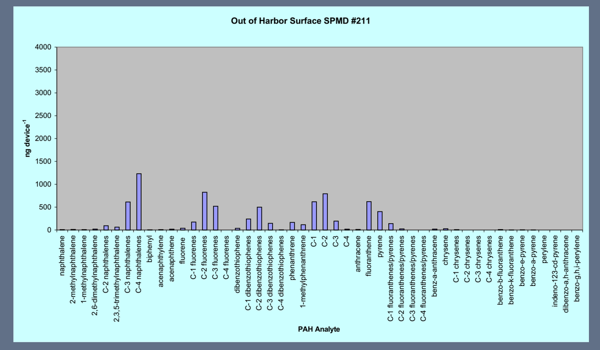

Figure 12. Analyte chart of a representative out of harbor surface SPMD

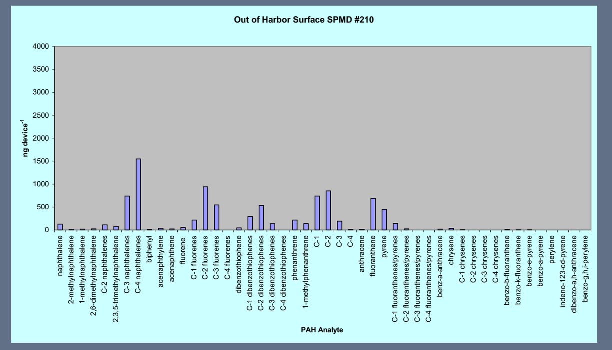

Figure 13. Analyte chart of a representative out of harbor surface SPMD (replicate of Figure 12).

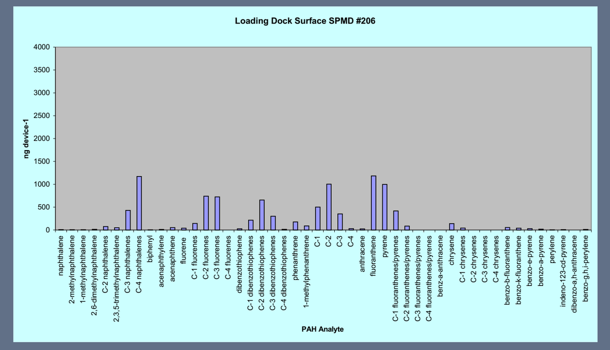

Figure 14. Analyte chart of the loading ramp sample

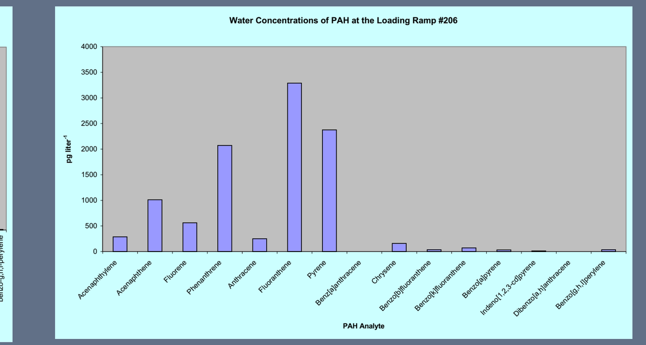

Figure 15. PRC-calculated water concentrations at the loading ramp. Note how total PAH concenrtrations exceed the fuel dock sample in Figure 15.

RESULTS

Objective 1. Cost, ease of use, and utility of data

Cost

LDPEs are less costly
- cheaper to make
- extraction process is not patented

Use

Both devices are similar to use
- patented process for SPMD cleanup and extraction extends analysis time

Data

SPMDs produce data with a wider range of utility than LDPEs
- allow quantification of analytes in the water column
- used in numerous published studies

LDPEs provide a "fingerprint" of organic contamination in the water column
- screening tool
- results are relative within a run
- less comparable to other studies

RESULTS

Objective 2. Source location and analytical fingerprint of contamination

Location

The highest concentrations were found in the surface sample at the fuel dock for SPMDs and LDPEs
- two times higher than any other sample location

No other locations were pinpointed as contaminant sources
- well-mixed harbor
- non-point-source contamination from spilled fuel

Analytical Fingerprint

The SPMDs and the LDPEs detected similar trends in PAHs
- Uncombusted diesel fuel was dominant chemical signature
- bell-shaped alkyl-PAH homologue distributions
- dominated by naphthalene homologues
- truncated at the 4-ring PAH

The cluster analysis with all devices grouped PSDs with similar analyte fingerprints (Figure 5)
- Separated field blank (Figure 6)
- Separated fuel dock surface SPMD (Figure 7)
- Grouped fuel dock LDPE with in-harbor SPMDs (Figure 8)
- Grouped other LDPEs into their own cluster (Figure 5)
- Grouped SPMDs into geographic areas (Figures 9 and 10)
- Distinctions not made between surface and bottom samples

ACKNOWLEDGEMENTS

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RESULTS

Objective 3. Water Concentration Calculations

Calculations

Concentrations for analytes with available calibration data (Table 1)
- In this study, 15 out of 48 measured analytes

Large differences in calculated water concentrations depending on PRC used
- Anthracene: most appropriate PRC in this study
  - had good recoveries
  - available calibration data are reliable
- Pyrene: overestimates water concentrations
  - did not equilibrate in calibration experiments (Huckins, pers. comm.)
  - generally less reliable than the other PRCs
- Phenanthrene: recoveries too low in this study
  - phenanthrene-based calculations followed anthracene-based results

SPMDs allow calculations of water concentrations from SPMDs

Huckins *et al* (2002) estimate that *the overall error in SPMD-derived water concentration estimates can be reduced to about 2-fold using PRCs*

Selected Analytes matter for PAH Concentration Calculations

Limited analytes available for water concentration calculations
- Can lead to erroneous inferences in terms of total PAH concentrations in water (Figures 14-16)
  - No calibration data for akylated homologues
  - Homologues comprise large fraction of total PAH in water column

Conclusions about total PAH concentrations in water should be made considering the available calibration data.

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RESULTS

Objective 4. Applicability of analytical data to future eider risk assessment

The applicability of different PSD data depends on the objectives and methods of the risk assessment process
- LDPEs provide a fingerprint of harbor contamination
- LDPEs most useful as low-cost screening tools

- SPMDs allow quantification of PAH concentrations
- SPMDs comparable to published literature

Please see poster PH07, tomorrow, for a discussion of the risk assessment process for Steller's eiders and harbor-related contamination.

CONCLUSIONS

SPMDs are precise sampling devices that allow the user to standardize methods, minimize sampling variability, and estimate water concentrations.

LDPEs are less expensive and provide a "fingerprint" of contamination, but are not as comparable across studies and do not allow calculation of water concentrations.

SPMDs spiked with PRCs can be used to calculate average water concentrations of certain PAHs in the water column; however some of the analytes "lost" during water calculation (eg. akylated homologues) may comprise a large fraction of the mass of PAH in the water column.

PSDs will be useful in the assessment of risk to Steller's eiders from harbor-related petroleum contamination. Please see poster PH07 tomorrow for a discussion of how PSD data will be used in the eider risk model.

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